Electrical switching of some zinc oxide based ceramics

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Electrical switching of some zinc oxide based ceramics

by

Kwangsoo No

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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Department: Materials Science and Engineering
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INTRODUCTION

Zinc oxide ceramics with certain additives exhibit excellent nonohmic current-voltage characteristics \[1, 2\]. Devices, based on these ceramics and known as zinc oxide varistors, have been used to protect electric circuits from high voltage surges. It is believed that the observed nonohmic behavior of these ceramics is closely related to their microstructure. The ceramics consist of a dense aggregate of n-type doped zinc oxide grains with thin intergranular boundary phases.

Certain zinc oxide ceramics also exhibit current controlled negative differential resistance (CCNDR) behavior \[3\] or memory switching behavior \[4, 5\]. Recently, Hunter and Schaefer \[6\] found that ZnO-based ceramics can be made to exhibit CCNDR, memory switching, and/or threshold switching behaviors depending on the particular additive oxide compositions. According to their investigation, the predictability was poor as to which compositions would exhibit memory switching and which would exhibit threshold switching. It was even possible, by varying the sintering condition, to have the same composition give, in one case, memory switching and, in another, threshold switching. They identified the best compositions for threshold switching materials all of which contained numerous additive oxides. Because of the use of multicomponent additive oxides, the microstructures of their ceramics were so complicated that it was almost impossible to analyze them, even though the switching behavior was assumed by them to be closely related to the microstructure.
A model of switching behavior, especially threshold switching, was proposed by Hunter based on the assumption that their microstructures were similar to those of zinc oxide varistors, because the additive oxides used to make their threshold switching materials were similar to those used in making varistors [7]. Pure zinc oxide shows intrinsic n-type semiconducting properties, $\rho \approx 1 \, \Omega\cdot\text{cm}$, when it is prepared by normal ceramic fabrication techniques.

Zinc oxide ceramics with certain additive oxides show high resistivity, which is required for the ceramics to exhibit switching as well as varistor nonohmic behavior. The causes of the high resistivity can be attributed to three possible barriers to charged carrier movement: high resistance within the grains themselves, high resistance within the grain boundaries, and high resistance at the interfaces between electrodes and the ceramic. The high resistivity ohmic behavior and breakdown (nonohmic) behavior of zinc oxide varistors are both believed to be due to barriers formed in the outer region of doped zinc oxide grains.

The objectives of this study were:

1. To produce new threshold switching ceramics which have simpler compositions and microstructure than the multicomponent ceramics of Hunter and Schaefer [6].

2. To test Hunter's proposed switching model on the basis of the observed microstructure of the new threshold switching ceramics [7], and
3. If the Hunter model was not successful, to study the electrical characteristics of the individual phases in the microstructure to arrive at a better understanding of the switching behavior of these ceramics.
LITERATURE REVIEW

Electrical Conduction in Solids-Short Review

Electrical conduction in solids is comprehensively reviewed in reference [8]. Solids are classified into three categories on the basis of their electrical conductivities: metallic conductors, semiconductors, and insulators. Metallic conductors have free electrons which are already in the conduction band at low temperature and which move almost freely within the solid when a potential gradient is present. The electrons in semiconductors and insulators are so localized in the valence band or in discrete energy levels in the band gap at low temperature that their conductivities are much lower than for metallic conductors. The conductivities of semiconductors and insulators depend on the difference in energy levels between the highest energy occupied states and the lowest energy unoccupied states with thermal energy normally being the source for excitation of electrons to produce mobile charge carriers.

The above picture is adequate only for perfect crystals, but perfect crystals are not found in nature. Electron traps are always more or less present, even in carefully prepared crystals. These traps affect the movement of electrons and the overall electrical characteristics of the solid. Furthermore, most solids are used in polycrystalline forms which contain very defective regions called grain boundaries. The effect of grain boundaries on the electrical characteristics of particular solids has been studied [1, 2]. Potential
interfaces between dissimilar materials in solids also produce electrical effects. Integrated circuits consist of combinations of diodes and transistors in which junctions between different types of materials control the electrical characteristics of the devices. The sudden termination of the atom array of a crystal at its surface usually gives rise to distortions of the band structure near the surface, and creates surface states which affect the electrical characteristics of the solid.

To test the electrical characteristics of semiconductors or insulators and to use them in devices, contact electrodes, usually consisting of metals, are applied to the surface of the materials. There are two types of contacts possible for metal-semiconductor or metal-insulator interfaces: ohmic contacts and blocking contacts [9, 10]. An ohmic contact is defined as one which has a negligibly small impedance as compared with the series impedance of the bulk of the semiconductor or insulator. A blocking contact is defined as one which, due to a work function difference between the electrode material and the semiconductor or insulator, creates a depletion region extending into the bulk of the material from the interface with the electrode.

The terminology "ohmic" does not refer to Ohm's law, because the current-voltage characteristics of ohmic contacts may or may not be linear, depending on many factors. There are two ways of making ohmic contacts: (1) choose metals of low work function for contact with an n-type semiconductor such that $\Phi_m < \Phi_s$, where $\Phi_m$ and $\Phi_s$ are the work
functions of metal and semiconductor, respectively; or choose metals of high work function for contact with a p-type semiconductor such that $\phi_m > \phi_s$; and (2) dope the semiconductor surface heavily near the contact to make the potential barrier thin enough for efficient quantum mechanical tunneling [9]. The magnitude of the electrical conduction of a solid measured with ohmic contacts is controlled by the impedance of the bulk of the solid (bulk limited). If a voltage is applied between the two electrodes, free electrons and holes, generated in the solid by thermionic processes, flow to the external circuit. The conduction current carried by electrons is given by

$$J = qn_0 \mu V/d$$  \hspace{1cm} (1)

where

- $J$ = the current density,
- $q$ = electronic charge,
- $n_0$ = the concentration of free electrons,
- $\mu$ = the mobility of electrons,
- $V$ = applied voltage, and
- $d$ = the thickness of the specimen.

Equation (1) follows Ohm's law provided that $n_0$ and $\mu$ are independent of voltage gradient.

Charge carriers injected from a contact into a perfect crystal will produce a net space charge in the solid, and this net space charge
produces the so-called space-charge-limited (SCL) current. The SCL current for trap free solids is given by [11]:

\[ J = 9\varepsilon \mu V^2 / 8d^3 \]  

(2)

where \( \varepsilon \) is the permittivity (or dielectric constant) of the solid. The onset of departure from ohmic behavior (or the onset of SCL conduction) takes place when Eq. (2) becomes equal to Eq. (1). The applied voltage at which this condition occurs is

\[ V_o = 8q\mu_0 d^2 / 9\varepsilon, \]

(3)

which depends on the square of the thickness of specimen.

Perfect crystals are never encountered; traps and recombination centers are always more or less present. Injected carriers in the solids will either be temporarily captured at traps or be lost permanently at recombination centers. In single crystals, trap energy levels are generally discrete, while their energies are distributed in accordance with certain distribution functions in amorphous and polycrystalline materials [12]. Reference [9] discusses SCL conduction for solids having various trap distributions (see Appendix A). The square law given in Eq. (2) is observed for solids having traps only after all traps are filled (see Figure 1). The triangle of this plot is sometimes referred to as the Lampert triangle. The trap free limit (TFL) is the condition for the transition from trapped current-voltage
Figure 1. Schematic current-voltage characteristics of a solid having deep traps [9].

characteristics to trap-free current-voltage characteristics. The threshold voltage for this transition can be expressed as

\[ V_{TFL} = qN_t d^2/2\varepsilon \]  

(4)

where \( N_t \) is the trap density. The TFL voltage also depends on the square of the thickness of the specimen.

When the metal work function is larger than the work function of a n-type semiconductor, i.e., a nonohmic contact situation, electrons flow from the semiconductor to the metal, leaving a positive space.
charge region in the semiconductor as is shown in Figure 2; \( W \) is the width of the space charge region; and \( \phi_B \) is the height of the potential barrier which an electron in the metal has to surmount in order to pass into the semiconductor. The barrier height is the difference between the metal work function, \( \phi_m \), and the electron affinity of the semiconductor, \( \chi \). The analogous condition for a blocking contact for a p-type semiconductor is \( \phi_m < \phi_s \).

Figure 2 also shows four basic electrical transport processes through the blocking contact under forward bias [13]. The processes are (1) the emission of electrons from the semiconductor over the potential barrier into the metal, (2) quantum mechanical tunneling of...
electrons through the barrier into the metal, which is referred to as field emission, (3) electron-hole recombination in the space-charge region, and (4) minority carrier (hole) injection from the metal into the semiconductor, which is equivalent to the recombination in the neutral region. The value of electrical conduction measured for a solid with a blocking contact is electrode limited.

Current Controlled Negative Differential Resistance and Threshold Switching Characteristics

Figure 3 shows a schematic of the current-voltage characteristics of threshold switching behavior and current controlled negative differential resistance (CCNDNR) behavior. The switching material shows a high resistance 'off' state until voltage drop across the material reaches a certain critical voltage, $V_{TH}$. Just above the critical value, the material abruptly makes a transition from a normal high resistance 'off' state to a low resistance 'on' state (dashed lines in Figure 3(b)). A load resistor, $R_L$, is usually used to protect the material against an overpower situation after the transition. The current through the material after the transition depends on the value of the load resistor, as is shown in Figure 3(b) (see Appendix B). If the load resistance is changed to a higher value, the current through the material after transition will be decreased, because the larger load resistor offers a greater impedance to current flow. However, the current-voltage characteristic of the 'on' state is independent of the value of the load resistor, as is shown in Figure 3(b). As current
Figure 3. A schematic representation of a measuring circuit and dc current-voltage characteristics of threshold switching behavior and CCNDR behavior.
through the material is decreased in the 'on' state, the resistance of the material increases. The 'on' state is maintained until current through the material falls to a holding value, \(I_h\), below which the material returns to its original high resistance 'off' state. The only difference between a CCNDR characteristic and a threshold switching characteristic is the length of the transition time. One can measure discrete points between the 'off' state and the 'on' state in the dc current-voltage characteristics of CCNDR behavior, but it is almost impossible in threshold switching behavior to measure discrete points between the two states, because the transition from the 'off' state to the 'on' state occurs in a time on the order of nanoseconds.

Switching characteristics have been observed in various classes of materials, such as amorphous semiconductors [14]; crystalline solids such as \(\text{Nb}_2\text{O}_5\) [15], \(\text{SiO}_2\) [16], and \(\text{Al}_2\text{O}_3\) [17]; and organic films [18]. Such characteristics have also been observed in junction devices, such as metal-insulator-semiconductor (MIS) devices [19], heterojunctions [20], and \(p^+-n-n^+\) junctions [21].

Various models have been proposed to explain the switching process in amorphous semiconductors. The models are generally broken into two categories. The thermal model proposes that switching is entirely due to runaway local Joule heating through the formation of current filaments [22]. On the other hand, electronic models propose that the switching process is entirely due to alterations in the distribution of electron energies. One electronic model [23], known as the double injection model, describes the switching mechanism as follows (see
Figure 4). When an electric field is applied, electrons and holes are injected from the electrodes into the semiconductor where they are captured by positively and negatively charged states situated near the Fermi level. This causes the formation of negative and positive space charges near the cathode and anode, respectively, as is shown in Figure 4(a). The space charge regions limit the current flow in the vicinity of the electrodes, and the field will be redistributed - decreasing near the electrodes and increasing in the center, as is shown in Figure 4(b). Increasing the applied voltage increases the thickness of the space charge regions, until eventually they meet and overlap, as is shown in Figure 4(c). The overlap region becomes electrically neutral, causing the conductivity in this region to increase. The increased conductivity of the overlap region causes the field intensity there to decrease, while the field intensity near the

![Figure 4. A double injection model [23]. See text for explanation](image-url)
electrodes increases, as is shown in Figure 4(d). As more and more charge carriers are injected, the width of the space charge overlap region will increase, and the overall resistance will collapse, creating an 'on' state, as is shown in Figure 4(e). Here, the overlap region has spread completely across the semiconductor, and the bands are practically flat. Thin Schottky barriers are established near the electrodes, but electrons can easily tunnel through them from the Fermi level of the metal cathode into the conduction band of the semiconductor, and holes can tunnel from the anode into the valence band of the semiconductor. A minimum current density is required to maintain trap filling against recombination mechanisms. Below this minimum current density, the material returns to the high resistance 'off' state.

Defect Structure and Electrical Characteristics in Pure and Doped ZnO

Intrinsic defects in ZnO

Single crystal ZnO is always observed to exhibit a metal excess for oxygen deficiency under experimentally attainable zinc and oxygen partial pressures [24]. Figure 5 shows the energy band structure of ZnO. It has not been agreed whether the major intrinsic defects in ZnO are zinc interstitials, $Zn_i$ [24, 25], or oxygen vacancies, $V_o$ [26, 27]. Because these two possibilities would exhibit similar electrical characteristics, it has never been possible to experimentally distinguish which of them predominates. Both these types of intrinsic defects would act as donors, upon being ionized according to Eq. (5),
thereby producing mobile electrons, and giving rise to substantial n-type electrical conductivity.

\[ \text{Zn}^{\ast} = \text{Zn}^\ast + e^- \]

and

\[ \text{Zn}^{\ast} = \text{Zn}^{\ast} + e^- . \quad (5) \]

The other important type of intrinsic defects in ZnO are zinc vacancies, \( V_{\text{Zn}} \), which would act as acceptors upon ionization. Because the material is always metal excess, the concentration of zinc vacancies is always lower than that of the donor type intrinsic defects, \( \text{Zn} \) or \( V_0 \), so that zinc vacancies are believed to have little effect on the overall electrical properties of ZnO materials sintered at normal conditions.
The concentrations of intrinsic defects, which determine the n-type conductivity of ZnO, depend on ambient zinc and oxygen partial pressures. The conductivity of undoped ZnO is around $1 \Omega^{-1}\text{cm}^{-1}$, in spite of its fairly wide band gap ($\sim 3.34$ eV) [26]. The conductivity of undoped ZnO decreases on exposure to an oxygen atmosphere and increases in low oxygen partial pressures [28-30]. These observations have been explained as being due to a depression of the mobile electron concentration resulting from a depression of the intrinsic donor concentration as the material becomes less oxygen deficient in high oxygen partial pressure, and as being due to an increase in electron concentration resulting from an increase of the intrinsic donor concentration as the material becomes more oxygen deficient in low oxygen partial pressures. This depression model has been used to explain the abnormal electrical characteristics of doped ZnO materials, which will be discussed in the following section.

**Doped ZnO-defects and electrical characteristics**

Zinc oxide has a hexagonal wurtzite type crystal structure. The wurtzite structure consists of a hexagonal close packed array of oxygen ions with half the tetrahedral interstices filled with cations [31]. The structure has two kinds of vacant interstitial sites: tetrahedral sites (those not normally occupied by Zn ions) and octahedral sites, either of which may incorporate other cations with sizes similar to the size of the host cation.
Several sets of contradictory observations have been reported on resistivity changes of ZnO accompanying doping with various metal ions. Some dopants, such as Al$^{3+}$ [32, 33], Ga$^{3+}$ [33], and In$^{3+}$ [34], increase the free electron concentration in ZnO and decrease the resistivity of ZnO. Since the above three metals have a $s^2p^1$ outer electron configuration (IIIB group elements), a +3 ionic state is the most favored. The following three processes have been proposed as possibilities to explain the increase in electrical conductivity of ZnO doped with +3 state ions [33]:

\[
X_2O_3 = 2X_{zn}^\cdot + 20 + 1/2O_2 (g) + 2e' \quad (6a)
\]

\[
X_2O_3 = 2X_{zn}^\cdot + 3O + V_{zn}^\cdot + e' \quad (6b)
\]

or

\[
X_2O_3 = 2X_{zn}^\cdot + 20 + O_{i}^\cdot + e' \quad (6c)
\]

where $X$ stands for +3 state metal ion.

At the other extreme, some dopants, such as Li$^+$ [35, 36], Mn$^{4+}$ [26], and Mn$^{2+}$ [37], increase the resistivity of ZnO. Interstitial Li$^+$ ions are believed to suppress the electron concentration through the following proposed defect reactions [35]:

\[
Li_i^\cdot + Zn_{zn}^\cdot + e' = Li_{zn}^\cdot + Zn_i^\cdot
\]

or
depending on whether the predominant intrinsic defects in ZnO are zinc interstitials or oxygen vacancies, respectively.

Since transition metal ions readily exist in several ionization states, it is difficult to predict the final ionic state or the defect interaction process when these ions are used to dope ZnO. This may be the reason why literature on defect processes in ZnO doped with transition metal ions has not been found during this study. It also has never been fully established what type of position is occupied by transition metal ions in the ZnO structure. Usually, +2 state metal ions are located in tetrahedral sites, and +3 state ions are located in octahedral sites [38, 39]. The literature also shows discrepancies in the observed effects of some transition element dopants on the resistivity of ZnO. For example, an increase in the concentration of Co ions was found to produce an increase in conductivity of ZnO single crystals [40]. However, the conductivity of polycrystalline ZnO was found to decrease after doping with Co ions [41]. The latter observation will be discussed further in the following section.

**Electrical characteristics of doped ZnO varistors**

Varistors are two-terminal solid-state devices showing nonlinear current-voltage characteristics. Zinc oxide varistors are made from heavily doped multiphase ceramics composed of dense n-type semiconducting ZnO grains doped with transition metal ions with thin
insulating intergranular layers consisting of a mixture of additive oxides.

Zinc oxide varistors are characterized by nonohmic current-voltage behavior, as is shown in Figure 6. The current-voltage curve of a ZnO varistor can be divided into three regions. At low voltage, the varistor exhibits ohmic behavior with high resistance. At intermediate voltage, the current increases abruptly with voltage in what is described as the breakdown region. The breakdown region is characterized by a high nonohmic exponent, $\alpha$, for a wide current range. At even higher voltage, the current increases more slowly.

Although there is still not a generally-accepted theory to explain the current-voltage characteristics of varistors, there appears to be agreement that depletion layers near the grain boundaries of ZnO are major barriers to conduction.

Figure 6. Schematic current-voltage characteristics of ZnO varistors
Two different models have been proposed to explain the formation of electron depletion layers in polycrystalline ZnO. The earlier model, called the heterojunction model, requires the presence of an intergranular layer of insulating material between the ZnO grains. Electron traps in the insulating layer are said to absorb electrons from the doped ZnO grains, and depletion layers are formed in the ZnO grains on either side of the insulating intergranular layer, as is shown in Figure 7(a) [42]. However, recent studies on the microstructure of ZnO varistor ceramics [43, 44] were unable to detect continuous insulating intergranular phases for a large majority of the grain boundaries examined within the resolution of the measurements (several Å). Based on this fact and other observations, Einzinger [45] proposed a second model, the $n_{\text{ZnO}}^{-\text{i}}\text{ZnO} - n_{\text{ZnO}}$ homojunction model, which suggests that the formation of the depletion region is due to surface oxidation of the ZnO grains. This oxidation leads to a lowering of the concentration of intrinsic donor defects, $\text{Zn}_{1}$ or $\text{V}_{0}$, in the outer region of the ZnO grains compared to that in the grain cores, and, consequently, the energy band is depleted near the boundaries between the ZnO grains, as is shown in Figure 7(b). The major controlling defects for the homojunction model are singly-ionized deep donors which are substitutionally incorporated onto zinc sites. These deep donors suppress the concentration of the conduction electrons in ZnO [24].
Figure 7. Schematic representations of depletion layer models (a) with insulating intergranular layer (heterojunction) [42] and (b) without intergranular layer (homojunction) [45]
Rare Earth Perovskite Oxides—Lanthanum Cobaltates

Oxides with the perovskite structure constitute a large group of materials of great importance in solid state physics and chemistry. The electrical conductivities of perovskite oxides vary over many orders of magnitude. Some, such as BaTiO$_3$ and SrTiO$_3$, are noted for their high resistivity, which makes them useful as dielectric materials, while others, such as CaMoO$_3$ and LaTiO$_3$, are semiconductors with high conductivities.

Perovskite oxides basically have the chemical formula ABO$_3$, where A is a large cation and B a small cation. The structure consists of a cubic closed-packed arrangement of A cations and oxygen ions, with B cations located in octahedral interstices [31]. Whether an oxide will possess the perovskite structure or not depends mainly on the relationship between the ionic radii of the constituent ions. Goldschmidt [46] defined a tolerance factor, $t$, to determine the limits of stability of crystal structures:

$$t = \frac{(R_A + R_B)}{2(R_B + R_O)}$$  \hspace{1cm} (8)

where $R_A$, $R_B$, and $R_O$ are the ionic radii of A, B, and oxygen ions, respectively. The perovskite structure is stable within the range $0.75 < t < 1.00$. In rare earth perovskite oxides, the rare earth metal ion occupies the A type site. The tolerance factors of lanthanide cobaltates, LnCoO$_3$ (Ln=La, Pr, Nd, and Sm), are within the range of the values for a stable perovskite structure [47]. Praseodymium cobaltate,
PrCoO₃, is one of the major phases found in the two-phase threshold switching material of this study. Because literature pertaining to PrCoO₃ is rare, the following survey will be concerned with the more common lanthanum cobaltate, LaCoO₃, which is believed to have electrical properties similar to those of PrCoO₃.

Goodenough [48] succeeded in showing qualitatively that the electric and magnetic properties of perovskite oxides are determined mainly by the degree of interaction of the d-orbitals of the B cations with the p-orbitals of the neighboring oxygen anions. An energy band diagram was proposed on the basis of this model [49], as is shown in Figure 8. The orbitals of e₉ symmetry are located in the upper part of the band gap; those of t₂₉ symmetry are located in the lower part and are so localized that the electrons in these orbitals do not contribute to the conductivity. Lanthanide cobaltates are known to act as p-type semiconductors [50], so that the electric properties

![Energy band diagram for a perovskite oxide](image)

Figure 8. Energy band diagram for a perovskite oxide [49]
should be related to hole concentration instead of electron concentration. However, the above model is still valid if the \( t_{2g} \) and \( p_{\pi} \) energy levels in the band gap are close to the valence band. This allows electrons to be thermally excited from the valence band into the localized levels creating holes. According to this band model, lanthanide cobaltate should be a poor conductor at low temperature, because low spin Co\(^{III}\) \((t_{2g}^{6}e_{g}^{0})\) is more stable than high spin Co\(^{3+}\) \((t_{2g}^{4}e_{g}^{2})\). The resistivity of LaCoO\(_{3}\) has been reported to be higher than 1 x 10\(^{-5}\) \(\Omega\)-cm at 4.2\(^{\circ}\)K [51] in agreement with this prediction. As the temperature increases, the splitting energy between \( e_{g} \) and \( t_{2g} \) is lower, the concentration of high spin Co\(^{3+}\) increases, and the resistivity of the cobaltate decreases. The resistivity of LaCoO\(_{3}\) was reported to be around 1 \(\Omega\)-cm at room temperature, and at higher temperatures, 125 < \(T\) < 650\(^{\circ}\)C for LaCoO\(_{3}\), the resistivity decreases much more rapidly, and goes through a broad maximum at 650 < \(T\) < 937\(^{\circ}\)C, which indicates that most Co\(^{III}\) has been converted to Co\(^{3+}\) above 650\(^{\circ}\)C. Above 937\(^{\circ}\)C, where the material undergoes a transition from a rhombohedral structure to a pseudocubic structure, LaCoO\(_{3}\) shows metallic behavior \((\rho \sim 10^{-3}\ \Omega\)-cm\) [51]. The resistivity of the analogous material PrCoO\(_{3}\) has been reported to be around 10 \(\Omega\)-cm at room temperature, and the material has been observed to undergo a semiconductor-metal transition upon heating like that of LaCoO\(_{3}\) [52].

'B' cation vacancies in the \(ABO_{3}\) perovskite structure are not expected, because \(BO_{4}\) octahedra are essential for the occurrence of the perovskite structure [48]. Perovskite oxides usually contain more or
less either oxygen vacancies or 'A' cation vacancies, depending on the preparation atmosphere, and the former are by far more common than the latter [49]. In that case, the crystal structure is usually distorted.

A variety of perovskite oxides can be prepared by a partial substitution of the 'A' and/or 'B' ions with accompanying changes in the electric and magnetic properties of the materials. Introduction of Sr$^{2+}$ ions into La$^{3+}$ sites of LaCoO$_3$ to give La$_{1-x}$Sr$_x$CoO$_3$ creates a proportional number of Co$^{4+}$ ions ($t_{2g}^5e_g^0$ or $t_{2g}^4e_g^1$), and this causes the resistivity to decrease, because the unpaired electron concentration increases as Sr$^{2+}$ content increases. Metallic conductivity has been reported at room temperature for $x = 0.4$ in La$_{1-x}$Sr$_x$CoO$_3$ [47]. The introduction of various transition 'M' ions, such as Ti$^{4+}$, Mn$^{4+}$, Ni$^{3+}$, Fe$^{3+}$, Mg$^{2+}$, and Zn$^{2+}$, into the Co$^{3+}$ sites of LaCoO$_3$ to give LaCo$_{1-x}$M$_x$O$_3$ has been investigated [53, 54]. The conductivity change accompanying this partial substitution was explained by the differing conductivities of each end member, LaCoO$_3$ and LaMO$_3$, and/or by the spin configurations of 'M' ions and cobalt ions. However, the last explanation is not fully successful, because the transition 'M' ions are multivalent, so that the ionization states of these ions are hard to predict.
INITIAL MODEL FOR THRESHOLD SWITCHING

The proposed model [7] for ZnO based threshold switching materials to be tested in the initial stage of this study is based on a combination of the model for the electrical behavior of ZnO varistors [55] and the double injection model for the behavior of amorphous semiconductors [23]. In this composite model, switching ceramics must consist of n-type semiconducting ZnO grains separated by thin insulating intergranular layers of amorphous material. These thin layers are considered to act as a series of switches throughout the bulk of the material. Traps in the insulating layers capture electrons from the ZnO grains creating back-to-back depletion layers in adjoining grains, as is shown in Figure 9(a). However, for switching materials, the traps are not filled throughout the entire thickness of the intergranular layer. When a small voltage is applied, there is little gradient in potential in the bulk of the ZnO grain, but rather most of the potential gradient occurs near or in the insulating layer; this latter condition is contrary to the varistor model. As the applied voltage increases, the n-type ZnO on the left can readily inject holes into the insulating layer, but, since the depletion layer is becoming wider, the supply of holes for injection is limited. When the field is large enough so that the bottom of the conduction band for the ZnO grain on the right is below the top of the valence band of the ZnO grain on the left, as is shown in Figure 9(b), a supply of holes is created in the ZnO on the right near the insulating layer. These holes
Figure 9. Band structure threshold switching model proposed by Hunter [7]; (a) no field, (b) near threshold, (c) on state.
are then injected by the field into the insulating layer. At some critical voltage (the 'threshold' value), when the region containing the electrons injected into the insulating layer from the left overlaps the region containing the holes injected from the right, the field in the insulating layer collapses, as is shown in the double injection condition in Figure 9(c). This causes a rapid decrease in the resistance of the bulk of the material to produce the 'on' state. Since the fields in the two depletion layers are maintained, the injection of holes and electrons continues, permitting the material to be maintained in the 'on' state with a reduced overall field.
EXPERIMENTAL PROCEDURE

Materials Selection

Four different types of materials were chosen for study: multicomponent multiphase threshold switching materials, two-phase threshold switching materials, single-phase undoped and Co-doped ZnO, and single-phase undoped and Zn-doped PrCoO₃. The multicomponent threshold switching material studied initially had the composition which was claimed by Hunter and Schaefer [6] to be one of the best to exhibit reproducible threshold switching. This material consisted of ZnO with six additive oxides, Co₃O₄, Cr₂O₃, Sb₂O₃, MnO₄, Pr₆O₁₁ and La₂O₃, and had a complicated microstructure. One of the objectives of this study was to produce threshold switching materials with simplified microstructure. This simplification was successfully accomplished by producing two-phase threshold switching materials consisting of a Co-doped ZnO phase and a Zn-doped PrCoO₃ phase. The electrical characteristics of individual grains and of intergranular and interphase boundaries in the two-phase materials were studied. To confirm these observations and to broaden understanding of switching in two-phase materials, single-phase materials of undoped and Co-doped ZnO and undoped and Zn-doped PrCoO₃ were investigated.

Powder Preparation

Raw materials

The raw materials used to fabricate the threshold switching materials were ZnO, CoO, Co₃O₄, Cr₂O₃, Sb₂O₃, MnO₄, Pr₆O₁₁, and La₂O₃.
The powders were commercially acquired\(^1\) except for Pr\(_6\)O\(_{11}\) and La\(_2\)O\(_3\).

The purities of the powders were better than 99.9%, except for CoO and Co\(_3\)O\(_4\), which had purities better than 99.5%. La\(_2\)O\(_3\) and some Pr\(_6\)O\(_{11}\) powders were prepared in the Ames Laboratory\(^2\), and their purities were better than 99.9%. Most of the Pr\(_6\)O\(_{11}\) powder used was obtained from Molycorp\(^3\) and had a purity of 96.3%, but more than 99% of the impurities were other lanthanides. It is known that praseodymium oxide disproportionates into PrO\(_2\) and Pr(OH)\(_3\) with long exposure to laboratory air [56]. Therefore, the concentration of Pr in the praseodymium oxide from each source was determined using atomic absorption spectroscopy\(^4\) after decomposition of residual Pr(OH)\(_3\) by calcination at 800\(^\circ\)C for two hours. In all batches, calcined praseodymium oxide powder of known Pr content was weighed out for mixing with the other oxides.

**PrCoO\(_3\)**

Cobalt oxide, Co\(_3\)O\(_4\), and praseodymium oxide powders were mixed for four hours in a plastic vial with plastic balls using a SPEX mill\(^5\). The powder mixture was heated in an alumina crucible at 1200\(^\circ\)C for 40

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\(^1\)Fisher Scientific, Fair Lawn, NJ.

\(^2\)Ames Laboratory, Iowa State University, Ames, IA.

\(^3\)Molycorp, Inc., Louvier, CO.

\(^4\)VIDEO12 aa/ae spectrophotometer, Allied Analytical Systems, Waltham, MA.

\(^5\)SPEX Industries, Inc., Edison, NJ.
hours. It has been reported that PrCoO$_3$ starts to form at around 960°C from a 2:1 mole mixture of Co$_3$O$_4$ and Pr$_6$O$_{11}$ [57]. Repeated grinding and heating were used to complete the reaction. The alumina crucible was heavily contaminated with cobalt before use, which helped to minimize cobalt loss by diffusion into the alumina crucible during the heat treatment. The reacted powder was slightly sintered, and was ground for four hours in a SPEX mill using a plastic vial with plastic balls. The heating and grinding were repeated four times.

Since some cobalt was lost by vaporization during reaction and final sintering, attempts to prepare stoichiometric PrCoO$_3$ from an exact 2:1 mole ratio of Co$_3$O$_4$ and Pr$_6$O$_{11}$ were not successful. After the resulting material was chemically analyzed, a compensating cobalt excess powder mixture was used to prepare stoichiometric PrCoO$_3$ material.

**Zn-doped PrCoO$_3$**

Two different processes were used to prepare Zn-doped PrCoO$_3$ powders. In one process, mixtures of ZnO, Co$_3$O$_4$, and Pr$_6$O$_{11}$ were repeatedly heated and ground using the procedure described above for the preparation of PrCoO$_3$ powder. This process never produced satisfactory material, as will be described in the Results and Discussion Section, and was eventually discarded. In the second process, two-phase threshold switching materials were first produced which consisted of Co-doped ZnO and Zn-doped PrCoO$_3$ phases. The Co-doped ZnO phase was then leached out using strong base leaving behind grains of Zn-doped PrCoO$_3$. This process began with the Co-excess
PrCoO₃ powder prepared as described above. This powder was mixed with ZnO at various concentrations. The two-phase mixtures were reacted at 1300°C for 10 hours, which are the same conditions used for preparation of two-phase threshold switching materials. The reacted powders were sintered, so they were crushed in a porcelain mortar and ground in a plastic vial with plastic balls until large aggregates were eliminated. It has been reported [58], and has been observed by this investigator, that ZnO can be dissolved in a strong base. It has also been observed that PrCoO₃ does not dissolve in the same medium. The Co-doped ZnO phase was leached out of the ground two-phase powder using a 10 M NaOH solution at 100°C. The solution was heated in a boiling water bath using a Nalgene beaker. The undissolved portion of the powder was filtered and washed with distilled water using a Buchner funnel. Aggregates were observed in the remaining powder; it was ground in a porcelain mortar prior to the next leaching treatment. The powder was repeatedly ground and leached until the solution was not blue after filtration. This was taken to indicate that no further Co-doped ZnO was being dissolved. The remaining powder was filtered and washed with hot distilled water to reduce sodium ion contamination. Sodium contamination was checked using a procedure described in Reference [59]. Approximately 10 ml of the solution were evaporated to approximately 1 ml. A platinum wire was cleaned until it gave no color in a Bunsen flame. The end of the wire was dipped in the solution and returned to the flame. The presence of sodium ion imparts an intense yellow color to the flame. The washing process was continued beyond the point when
yellow flame disappeared, which generally required four or five
washings. In all cases, the washing was repeated at least fifteen
times. The leached and washed powder was dried in a 110°C oven
overnight.

Specimen Preparation

Oxide powders to be sintered into specimens were mixed in three
different ways: hand mixing in a vinyl bag, ball milling in a high
alumina ball mill with alcohol medium, and SPEX milling in a plastic
vial with plastic balls. The ball milling was used only to prepare
multicomponent threshold switching materials. Because of possible
contamination by Al₂O₃, which has been reported to affect the electrical
characteristics of ZnO materials [60], the ball milling process was
discarded for preparation of the two-phase threshold switching
materials and single-phase materials primarily studied in the present
work. The hand mixing process prevents contamination, but is tedious
and time-consuming. SPEX milling was used to prepare most mixtures of
powders in this study.

The mixtures were pressed in a 1.27 cm diameter steel die to form
cylindrical tablets having thicknesses between 0.3 and 1 cm. The
tables were isostatically pressed at 30,000 psi. Polyvinyl alcohol
was sometimes used as a forming aid for reacted PrCoO₃ powders. In
this case, the tablets were dried in a 110°C oven overnight and
calcined at 700°C to vaporize the polyvinyl alcohol before the tablets
were sintered.
The tablets were sintered in air at 1200°C to 1300°C for 10 hours to 200 hours. The tablets were contained in an open-ended alumina tube inside a SiC furnace\(^1\) equipped with a type S thermocouple and powered by a SCR unit\(^2\) with a programmable controller\(^3\). Heating and cooling rates were 3°C/min. Single-phase Co-doped ZnO tablets were held at 1000°C for 10 hours before being taken to the sintering temperature in order to complete the conversion of Co\(_3\)O\(_4\) to CoO; otherwise, the tablets bloated during sintering. The tablets were supported on a platinum sheet during sintering to prevent possible reaction between the materials and the alumina furnace setter. The platinum sheet was cleaned using HCl before being used to sinter a different material. The furnace tube and thermocouple protection tube were changed before being used to sinter a different material to prevent contamination from the tubes. Because sintering temperature and soaking time can affect the dopant concentration and distribution, the sintering temperature and soak time were fixed at 1300°C and 10 hours for all specimens used to study the effects of additive oxides on electrical characteristics. To acquire single-phase materials with different average grain sizes, tablets were sintered at 1300°C for 10 to 200 hours. Because the cobalt oxide vapor pressure is high compared to that of praseodymium oxide at the sintering temperature, the tablets were

\(^1\) Lindberg, Watertown, WI.

\(^2\) Model 931, Eurotherm, Reston, VA.

\(^3\) Model 812, Eurotherm, Reston, VA.
surrounded by cobalt oxide powder when single-phase PrCoO₃ specimens were heated for longer than 10 hours. The vapor pressures of zinc and cobalt oxides are similar, so that the tablets containing only these oxides were heated without protection.

After sintering, the tablets were cut using a diamond saw¹ to obtain cylindrical specimens with different thicknesses. The faces of these specimens were ground on a 600 mesh SiC grinding disc and were polished with 0.3 μm Al₂O₃ powder using a polisher/grinder¹. Co-doped ZnO materials were fragile with the edges of the specimens tending to break during cutting and grinding. To avoid this problem, the tablets were embedded in an air-setting resin before being cut, and the resin was later removed by heating. After polishing, all specimens were washed in acetone, alcohol, and deionized water using an ultrasonic cleaner, and were dried in a 110°C oven overnight.

Seed grain ZnO

Because it was desirable to test the electrical characteristics of individual grains and grain boundaries in two-phase materials, it was necessary to prepare specimens with an array of microelectrodes on the surface. The grain size of ordinary two-phase threshold switching materials was too small to avoid grain overlap even with microelectrodes, so it was necessary to prepare large particle size ZnO

¹Buehler, Ltd., Lake Bluff, IL.
using a technique known as the seed grain method [61]. Zinc oxide with 0.5 mole percent BaCO₃ was hand mixed in a vinyl bag for two hours. The mixture was calcined at 800°C for two hours. The calcined powder was crushed in a vinyl bag, pressed into tablets, and sintered in air at 1400°C for 10 hours. During sintering, the tablets were supported on pure ZnO tablets to prevent possible contamination. The sintered specimens consist of large ZnO grains, of average grain size around 100 μm, surrounded by an intergranular phase. The BaO locates in the boundary layer and will react with water to form soluble Ba(OH)₂. The tablets were put into boiling water to leach out the intergranular phase and separate into individual ZnO grains which are called 'seed grains'. The grains were washed in distilled water and sieved into size groups. Grains larger than 105 μm were used in the fabrication of large grain size threshold switching materials suitable for application of microelectrodes.

**Electrode Fabrication**

For the multicomponent threshold switching materials and some of the two-phase threshold switching materials investigated early in this study, five small Ag electrodes were sputter deposited on one surface of the specimen, and the other surface was painted with In-Ga metal. Because the effective area for current flow was not known for these multielectrode specimens, this procedure was abandoned in favor of using In-Ga metal painted onto both surfaces. In-Ga metal was used
because it is easy to apply and has been widely used as an electrode for ZnO varistors in the study of their electrical characteristics [1-3]. To test for evidence of blocking contacts between the ceramic and the electrodes, other metals, such as vacuum evaporated Al and sputtered Au, were applied to both sides of some specimens. For two-phase seed grain specimens, photolithographic techniques were used to deposit arrays of Al microelectrodes on one surface.

Electrical Measurements

Dc characteristics

Dc current-voltage characteristics were measured using the circuits shown in Figure 10. The data were acquired and manipulated using a microcomputer and peripherals interfaced using a general purpose interface bus (GPIB). A curve tracer was used as a power supply. The curve tracer had built-in current-limiting resistors to protect against overpower situation in the test specimen. For specimens having resistance higher than 1 MΩ, the current-voltage data obtained using the circuit in Figure 10(a) did not represent the characteristics only of the specimen, but rather a parallel combination of the input impedance of the digital multimeter measuring voltage and the resistance of the specimen. Two modifications were used to measure the dc characteristics of high resistance specimens. First, the data were acquired using the circuit shown in Figure 10(a), and the current through the specimen was calculated by treating the DMM and specimen as parallel impedances. Second, measurements were made with the
Figure 10. Circuits for measuring dc characteristics. 1 = DM5010 programmable digital multimeter, Tektronix, Inc., Beaverton, OR; 2 = 177 microvolt DMM, Keithley, Inc., Cleveland, OH; 3 = PET 8032, Commodore, Inc., Santa Clara, CA; 4 = 2031 disk drive, Commodore, Inc., Santa Clara, CA; 5 = MX80 printer, Epson America, Inc., Torrance, CA; 6 = 7225A plotter, Hewlett Packard, San Diego, CA; 7 = type 576 curve tracer, Tektronix, Inc., Beaverton, OR
circuit shown in Figure 10(b). Because the shunt resistances of the digital multimeter measuring current were not high compared to the resistance of the specimen, the current data represented directly the characteristics of the specimen. Both the compensated data calculated from measurements using the circuit shown in Figure 10(a) and the direct data from the circuit shown in Figure 10(b) matched well.

**Ac characteristics**

The grain and interfacial (electrode and intergranular) contributions to total specimen resistance were separated by complex impedance spectroscopy [62, 63]. This method was originally developed to study the various microscopic contributions to the resistance of ionic conductors. The method has also been used to study electronic conductors [64], especially ZnO varistors [29]. An ideal complex impedance spectrum and equivalent circuit are shown in Figure 11. \( R_b \) is the resistance from the grains; \( C_g \) is the geometric capacitance; and \( R_{gb}, C_{gb}, R_e, \) and \( C_e \) are the lumped resistances and capacitances associated with the grain boundaries (gb) and electrodes (e), respectively. The three semicircular arcs represent dispersions at low, medium, and high frequencies caused by electrode interfacial polarization, grain boundary polarization, and the grain polarization (which is often referred to as 'bulk polarization'), respectively. Frequency \( 'f' \) increases in the direction indicated. The center of each dispersion arc is depressed by an angle \( '\alpha' \) which is taken as being related to the distribution of relaxation times associated with each
$$R_s = \text{Re}[Z]$$

$$X_s = 1 / (R_s C_{\text{series}}) = \text{Im}[Z]$$

Figure 11. Idealized complex impedance diagram and corresponding equivalent circuit model (inset)
polarization.

In order to apply this technique of analysis, it is necessary to measure ac equivalent series resistance and capacitance of the specimen. This was done using the circuit shown in Figure 12. A microcomputer controlled data acquisition by the microprocessor-based bridge at numerous frequencies between 230 Hz and 20 kHz, and by the LCR meter at high frequencies, ranging from 10 kHz to 10 MHz. The specimen jig was designed based on ASTM standard D150-81 [65] to provide effective shielding and grounding. After the data were acquired as a function of frequency, they were fitted to corresponding arcs using a regression program.

**Other measurements**

The dc resistivities of some specimens were measured using a four-point probe method [66] using the circuit shown in Figure 13. Four spring loaded probes were pressed against a flat surface of the specimen, and a voltage was impressed on the two outside probes while the floating potential, V, was measured across the inside probes. The current, I, passing through the outside probes was also determined by measuring the potential drop across the 1 kΩ resistor. The resistivity was calculated as

\[ \rho = 4.532t \frac{(V/I)F(t/S)}{} \] (9)

where t and S are specimen thickness and probe spacing, respectively,
Figure 12. Instrumentation block diagram for ac conductivity measurements. 1 = 1688 precision LC digibridge, GenRad, Concord, MA; 2 = 4275A multi-frequency LCR meter, Hewlett Packard, San Diego, CA; 3 = 2031 disk drive, Commodore, Inc., Santa Clara, CA; 4 = PET 8032, Commodore, Inc., Santa Clara, CA; 5 = 7225A plotter, Hewlett Packard, San Diego, CA; 6 = MX80 printer, Epson America, Inc., Torrance, CA. (Note: 4 on specimen loads indicates four terminals (high and low terminals for current and potential terminals))
and $F(t/S)$ is a thickness correction factor [67]. Data were measured at different polarities and impressed voltages to check that the specimen exhibited a linear relationship between voltage and resistivity.

The type of majority carriers in the materials was determined using a hot probe technique [68] employing the circuit shown in Figure 14. This method uses the polarity of a thermal emf generated between two metal probes to determine the type of majority carriers. One probe was heated using a heater coil to give a temperature gradient across the thickness of the specimen. The warmer probe will be positive with respect to the cold probe when the specimen has n-type conductivity.
and negative when the specimen has p-type conductivity. The polarity was observed with a null detector.

Electrical Characteristics of Individual Grains and Interphase Boundaries in Two-Phase Threshold Switching Materials

To study the electrical characteristics of individual grains and interphase boundaries in two-phase threshold switching materials, an array of microelectrodes was fabricated onto the surface using a photolithographic technique. Because the average grain size of normal threshold switching materials was smaller than the size of microelectrodes that could be conveniently deposited onto them, large
grain size threshold switching materials were prepared using seed grain ZnO.

One surface of the specimen was ground, polished, and mounted onto a slide glass with air-setting resin. Then, the specimen was ground to thin it to several tens of microns thickness and polished. During thinning, the section was observed through a transmission optical microscope to confirm that the specimen thickness encompassed only one grain for ZnO grains. For PrCoO$_3$ grains, this observation could not be made, because this phase is not transparent at these specimen thicknesses. The thin section was etched with a dilute HClO$_4$ solution to better reveal the microstructure.

An Al microelectrode array was deposited onto the thin section using photolithography [69] and sputtering [70] techniques. After the average grain size of the thin section of the specimen had been measured, a layout for the microelectrode array was made on graph paper so that the side length of the square electrodes would be around one quarter of the average grain size, and the distance between electrodes would be about equal to the average grain size. The size of the electrode layout on the graph paper was 50 times larger than actual microelectrode array size. After the pattern was cut on a mylar sheet using a coordinatograph$^1$, the pattern was reduced by 50 onto a glass photoplate. Then, a positive photomask was made for the electrode array. A negative mask was made from the positive using photoduplication.

$^1$Model PP12-12LTLA, Mutoh Industry LTD, Tokyo, Japan.
With this negative mask on an alignment machine\textsuperscript{1}, the pattern was exposed onto the thin section coated with a photoresist sensitive to ultraviolet light. The photoresist was then treated to open the pattern of the microelectrode array for deposition of sputtered aluminum metal. To check the opening, some thin sections were etched after the pattern was open to the surface. Etched (roughened) surfaces were observed in each opening, which indicated that there was no thin layer of photoresist remaining across the opening. The same patterning process was repeated with the positive mask to provide protection to the deposited electrodes while unnecessary aluminum metal was being etched away.

When, by chance, electrode pairs were located on interesting grains or on either side of grain and interphase boundaries, two ultra sharp measurement probes were located on the pair using a micromanipulator\textsuperscript{2}. Traces of the dc current-voltage characteristics were made on the screen of a storage curve tracer\textsuperscript{3}.

Microstructure Study

The switching action of ceramics is believed to be closely related to their microstructure. The microstructures of the ceramics being

\textsuperscript{1}Model System 3, Hybrid Technology, Santa Clara, CA.

\textsuperscript{2}Model 6000, Micromanipulator, Inc., Carson City, NV.

\textsuperscript{3}Tektronix 577, Tektronix Company, Beaverton, OR.
studied were observed using an optical microscope$^1$ and a scanning electron microscope$^2$ with energy dispersive X-ray spectroscopy capability.

Thin sections of undoped and Co-doped ZnO materials are transparent so that the doping profile in this material could be observed based on the transmitted color difference between undoped ZnO (pale yellow) and Co-doped ZnO (green). The doping profile within a grain was also observed using energy dispersive X-ray spectroscopy. This latter method was used for both ZnO grains and PrCoO$_3$ grains.

Other Studies

Powder X-ray diffraction patterns were produced using a diffractometer$^3$ to determine phase(s) present in the materials. The weight losses and the shrinkage of the specimens during sintering were measured. The weight loss and the sign of the enthalpy of reactions in powder mixtures during heating were measured using a combined thermogravimetric (TG) and differential thermal analyzer (DTA)$^4$. The bulk densities of sintered specimens were measured using a water immersion technique [71]. The particle size distributions of powders

$^1$Ultraphot II, Zeiss, West Germany.
$^2$JEOL-JSM-U3, JEOL, Japan.
$^3$Siemens, West Germany.
$^4$Rigaku, Japan.
were analyzed using a sedimentation method\textsuperscript{1}. The chemical compositions of the materials were determined using an atomic absorption spectroscope.

\textsuperscript{1}Sedigraph 5000ET, Micromeritics, Norcross, GA.
RESULTS AND DISCUSSION

Multicomponent Threshold Switching Materials

The multicomponent threshold switching material chosen to begin this study was claimed by Hunter and Schaefer [6] to be one of the best to exhibit reproducible threshold switching. The material consisted of 3 mole percent each of $\text{Co}_3\text{O}_4$, $\text{Cr}_2\text{O}_3$, $\text{Sb}_2\text{O}_3$, $\text{MnO}_4$, $\text{Pr}_6\text{O}_{11}$, and $\text{La}_2\text{O}_3$ added to $\text{ZnO}$, and was sintered at $1300^\circ\text{C}$ for 10 hours. The fabrication technique used in this study was different from that described in Reference [6] in two ways. First, the powder mixtures were ball milled in this study to encourage homogeneous phase distribution in the materials. Second, prior to sintering, the tablets were isostatically pressed in this study to improve the bulk density of the materials.

Dc current-voltage characteristics

Figure 15 shows the dc current-voltage characteristics of a multicomponent threshold switching material. The maximum peak power (MPP) setting protected the specimen from degradation due to excessive currents after switching. The material shows high resistance 'off' state conduction until a certain threshold voltage drop is reached. Just above that threshold voltage drop, the material rapidly transforms to a lower resistance 'on' state. As the current is reduced, the 'on' state is maintained until the current through the material falls to a holding value below which the material returns to its original high resistance 'off' state. The figure shows three consecutive sweeps.
Figure 15. Dc current-voltage drop characteristics of a multicomponent threshold switching material. (a) First sweep; (b) second and third sweeps
The threshold voltage drop for the 1st sweep was higher than those for the subsequent sweeps. The time interval between consecutive sweeps was always at least one day to reduce any effects of remnant heat generated by joule heating in the 'on' state of the preceding sweep. The lowering of threshold voltage drop after the initial sweep is thus not due to any remnant heat effect, but rather is due to permanent specimen damage which occurred during the high current 'on' state of the initial sweep. All threshold switching materials tested in this study showed a lowering of threshold voltage drop after the first sweep, with the amount of reduction depending on the current level of the 'on' state for the preceding sweep. Consequently, only first sweep threshold voltage drops were used in this study to compare electrical characteristics between switching materials.

The maximum peak power setting for the second sweep (Figure 15) was lower than that for the first or third sweeps. During the second sweep, when the maximum peak power was set at only 2.2 W, the material exhibited current controlled negative differential resistance (CCNDR) behavior rather than threshold switching behavior. This kind of power dependency of the dc current-voltage characteristics was always observed in threshold switching materials in this study. Consequently, the maximum peak power setting was always fixed at the same value whenever electrical characteristics were compared between materials in this study.
When the switching materials were sintered at 1400°C, they were partially melted, lost their threshold switching characteristics, and exhibited slightly nonlinear dc current-voltage characteristics, as is shown in Figure 16. A sudden melting of the materials was usually observed just above the normal sintering temperatures, between 1200 and 1350°C, in this study; melting always destroyed switching behavior.

Microstructure

Figure 17 shows the microstructures of the multicomponent threshold switching material sintered at two different temperatures. The microstructures of multicomponent material sintered at lower temperatures were similar to the microstructure of the material sintered at 1350°C. Large pores were observed in the microstructure of the material sintered at 1350°C, as is shown in Figure 17(a). The refractory nature of the additive oxides may have affected the ability of the mixture to sinter. The normal sintering temperature for ZnO varistor materials and for pure ZnO is around 1300°C, which is generally sufficient to produce a dense microstructure [1, 2]. Figure 17(b) shows the microstructure of the material sintered at 1400°C. The material was partially melted at that sintering temperature. One can observe a significant density increase in the material sintered at 1400°C compared to that sintered at 1350°C.

Continuous thin intergranular layers, which are a characteristic of ZnO varistor materials, were not observed in the microstructures of the multicomponent materials studied here; instead, at least two
Figure 16. Dc current-voltage drop characteristics of a partially-melted multicomponent material sintered at 1400°C. Threshold switching behavior is not observed.
Figure 17. Microstructures of multicomponent threshold switching materials (BSE images). Sintered (a) at 1350°C and (b) at 1400°C
distinctive discontinuous phases were observed in the backscattered electron (BSE) images of the materials, regardless of the sintering temperatures. When electrons interact with the specimen in a scanning electron microscope (SEM), the number of backscattered electrons produced depends on the atomic number of the elements in the specimen [72]. When contrast is observed between two phases in a BSE image, such as Figure 17, the phase having atoms of higher atomic number generates more backscattered electrons and is brighter than the phase having atoms of lower atomic number. To analyze the elements present in each phase, X-ray spectra were collected at each spot noted on Figure 17 using energy dispersive X-ray spectroscopy (EDXS); these spectra are shown in Figure 18. The characteristic X-rays were generated inside the specimen within a depth of around 2 μm (at the operating conditions of the SEM), and the average grain size of the specimen was around 4 μm; therefore, it was possible that some X-rays were generated from grains hidden beneath those indicated by the spots, even though large size grains were selected for analysis. Based on the contrast in the BSE images and on the X-ray spectra, it is believed that the white phase contains mainly heavier elements, such as Pr, La, and Sb, and that the dark phase contains Zn and the transition metal elements.

Figure 19 shows X-ray powder diffraction patterns of the multicomponent threshold switching material. No significant difference was observed between the patterns of the materials sintered at 1350°C and 1400°C. Two phases, ZnO and LaCrO₃, were identified by matching
Figure 18. X-ray spectra emitted from the spots on Figure 17(a)
Figure 19. Powder X-ray diffraction patterns of multicomponent threshold switching materials sintered at (a) 1350°C and (b) 1400°C
the pattern with the published diffraction patterns [73]. It was impossible to assign the remaining peaks to any particular phase, indicating that more than two phases are present in these multicomponent materials.

The switching behavior of ZnO based multicomponent switching materials has been assumed to be closely related to the microstructure of the ceramics [7]. However, attempts were not successful in this study to completely characterize the complex microstructure of multicomponent threshold switching materials. The observations in this initial study can be summarized as:

1. Continuous thin intergranular layers which are characteristic of ZnO varistor materials were not observed.
2. The multicomponent threshold switching materials contain a rare earth perovskite phase, LaCrO₃, which has not been observed in the microstructure of ZnO varistors [41, 74] with compositions similar to the switching materials.
3. Probably because of the presence of refractory oxide additives in the original powder, the multicomponent threshold switching materials did not sinter well below 1400°C, and, at that temperature, they partially melted. The presence of large amounts of porosity probably affected the mechanical and, possibly, the electrical properties of the material.
4. The multiphase microstructures of multicomponent threshold switching materials proved to be too complex to be adequately characterized by the methods available to this investigator, and
consequently, correlation of electrical characteristics with microstructure could not be accomplished.

Preliminary Attempts to Simplify the Composition and Microstructure of Threshold Switching Materials

One of the objectives of this dissertation study was to explore materials which have simpler compositions and microstructures than the multicomponent materials discussed in the preceding section without giving up their threshold switching characteristics. Hunter and Schaefer [6] studied the electrical characteristics of ZnO based switching materials of various compositions produced by various fabrication techniques. They observed that materials containing equal mole fractions each of the additives, Co$_3$O$_4$ and Pr$_6$O$_{11}$, exhibited reproducible threshold switching behavior. This discovery is the basis for the production of the simplified switching materials described in this section.

Figure 20 shows the dc current-voltage drop traces of a material consisting of 5 mole percent each of Co$_3$O$_4$ and Pr$_6$O$_{11}$ in ZnO as reported by Hunter and Schaefer [7]. As was observed for multicomponent threshold switching materials, the threshold voltage drop for the first sweep was higher than for the second and subsequent sweeps. This simplified material exhibited reproducible threshold switching, even when the material was tested at a higher current 'on' state, than could be supported by multicomponent threshold switching materials. The multicomponent threshold switching materials were usually degraded at
Figure 20. Dc current-voltage drop traces of ZnO based threshold switching material having 5 mole percent each of Co$_3$O$_4$ and Pr$_6$O$_{11}$ [7].
(a) First sweep; (b) second sweep
currents below 100 mA, losing their threshold switching behavior, and exhibiting either current controlled negative differential resistance behavior (with a lower threshold voltage drop) or a nearly linear dc current-voltage drop behavior with low resistance. However, the simplified material exhibited reproducible threshold switching behavior even at currents above 1 A [7].

In the present study, equal molar amounts of Co$_3$O$_4$ and Pr$_6$O$_{11}$ were added to ZnO at various concentrations. Figure 21 shows the dc current-voltage drop characteristics of materials prepared in the early stages of this study consisting of different concentrations of additive oxides: 1 mole percent, 2.5 mole percent, and 5 mole percent each of Co$_3$O$_4$ and Pr$_6$O$_{11}$. The material with 1 mole percent additives exhibited varistor behavior with a nonlinear coefficient, $\alpha$, around 15. The material with 2.5 mole percent additives exhibited switching at relatively high current, 40 to 60 mA, and CCNDR behavior as the current was decreased down to zero. Hunter and Schaefer [7] observed that materials with both of these compositions exhibited reproducible threshold switching. The material with 5 mole percent additives exhibited reproducible threshold switching behavior, with the dc characteristics of the material fabricated in this study being similar to those of the material observed in reference [7]. However, the materials fabricated in this study lost their switching characteristics at fairly low 'on' state currents.

The fabrication techniques used in both studies were nearly the same, except that the powder mixtures in this study were ball milled
Figure 21. Dc current-voltage drop characteristics of ZnO based threshold switching materials having same mole percent each of Co$_3$O$_4$ and Pr$_6$O$_{11}$.
in a high alumina ball mill to provide homogeneous phase distribution and those described in reference [7] were not. A second phase in the form of aggregated grains within the ZnO matrix was observed in the materials described in reference [7], while this second phase was uniformly distributed in the ZnO matrix for the ball milled materials of the present study. Two possible causes of the differences in tolerance to 'on' state currents between the materials in the two studies may be considered. First, the particle size and shape of the starting powders and the distribution of phases in the sintered structure are probably important, and these factors were different in the two studies. Second, aluminum contamination from the ball milling may affect electrical characteristics. It has been observed that aluminum ions behave as donors in ZnO varistors, controlling carrier density and decreasing the resistance of the varistors by a small amount, on the order of 100 ppm [60]. To prevent Al contamination, SPEX milling with a plastic vial and plastic balls was used to blend most of the powders prepared in subsequent stages of this study.

**Precautions necessary in fabricating materials containing Pr$_6$O$_{11}$**

The new switching materials were initially fabricated using mixtures of ZnO, Pr$_6$O$_{11}$, and Co$_3$O$_4$ powders. After sintering, the tablets generally had low porosity and good mechanical strength. However, the sintered tablets disintegrated into powder after standing in laboratory air for several days to several months, depending on composition and fabrication technique. As the additive oxide content increased, the tablets disintegrated faster. When the powder mixture
was calcined before the tablets were formed, the disintegration was delayed, but the tablets eventually turned to powder after a long period of time. It has been reported that Pr$_{6}O_{11}$ disproportionates into PrO$_2$ and Pr(OH)$_3$ with long exposure to laboratory air [56]. During the disproportionation, the volume of the original praseodymium oxide phase will be changed, and internal stresses will be developed which will crack the tablets if unreacted Pr$_{6}O_{11}$ is present. However, pure Pr$_{6}O_{11}$ tablets were observed in this study to be stable for over a year, so the presence of another Pr-rich oxide phase may be necessary to produce the problem. No evidence of unreacted praseodymium oxide can be identified in the X-ray diffraction pattern of the simplified switching material shown in Figure 22(a). The pattern matches well with the published patterns of ZnO and PrCoO$_3$ [73]; however, there are several unidentified peaks of low intensity. Figure 22 also includes the X-ray diffraction patterns of the praseodymium oxide used in this study before calcination (b) and after calcination (c). Extra peaks were observed in the pattern of praseodymium oxide before calcination, which may indicate that some disproportionation had occurred.

Some light rare earth sesquioxides are hygroscopic [75], which presumably would lead to stability problems in air if such unreacted oxides are present in a specimen. However, in a rare earth oxide varistor of similar composition to the simplified threshold switching materials, the investigators observed thin intergranular layers of Pr$_2$O$_3$ after the ZnO grains were leached out in acid, but no unstability
Figure 22. X-ray diffraction patterns of (a) ZnO-Pr$_6$O$_{11}$-Co$_3$O$_4$ switching material and praseodymium oxide (b) before being calcined and (c) after being calcined.
in air was reported [74].

It was observed in the present study that the interior of the tablet always started to disintegrate first. This observation suggests that the problem was not due to disproportionation, because the reaction requires moisture and would be expected to start at the surface of the tablet.

Whatever the cause of tablet disintegration, a solution was suggested by the X-ray diffraction pattern in Figure 22(a), which shows that the simplified threshold switching material consists of two major phases: ZnO and PrCoO$_3$. Since a praseodymium oxide phase is not needed for switching and seems to be responsible for tablet disintegration, this phase was eliminated by prereacting Pr$_6$O$_{11}$ and Co$_3$O$_4$ to prepare PrCoO$_3$ powder prior to its being added to the ZnO powder. The PrCoO$_3$ powder was found to require some excess Co, because some Co will diffuse into the ZnO grains during sintering, resulting in residual unreacted praseodymium oxide being present in the materials, causing the tablets to eventually disintegrate into powder. Tablets fabricated using prereacted Co-excess PrCoO$_3$ powder were found to be stable for at least several years.

**Study of Simplified Two-Phase Threshold Switching Materials**

Two-phase threshold switching materials were fabricated with mixtures of prereacted Co-excess PrCoO$_3$ and ZnO powders. In this study, praseodymium oxide powders from two different sources were
used, and two different powder preparation techniques were used. Consequently, the reproducibility of switching behavior was tested using the different combinations of praseodymium oxide powder sources and powder preparation techniques listed in Table 1. For all specimens tested, the amount of PrCoO$_3$ was 30 weight percent of the original powder mixture, which corresponded to approximately 5 mole percent Co$_3$O$_4$, 2.5 mole percent Pr$_6$O$_{11}$, and 92.5 mole percent ZnO.

**Microstructure**

Figure 23 shows the microstructure of a two-phase threshold switching material (TTSM). The continuous intergranular layer typical of the structure of ZnO-based varistor materials was not observed within the resolution of the imaging techniques; instead, the material consisted of a dispersion of two major phases. Figure 23(c) shows traces of the relative intensities of X-rays generated by the electron beam at points along the line indicated in Figure 23(d). The trace of Zn X-ray intensities indicates that Zn is located mainly in the grey phase with minor amounts in the white phase. The trace of Co X-ray intensities shows that Co is present in both the white phase and the grey phase; however, Co content in the white phase is higher than in the grey phase. The trace of Pr X-ray intensities shows that Pr is located only in the white phase. Figure 24 shows a X-ray diffraction pattern of the material. The pattern was matched to the published patterns of ZnO and PrCoO$_3$ phases. The combination of X-ray diffraction and elemental distribution analyses identifies the grey
Table 1. Sources of powders and fabrication techniques for various two-phase threshold switching materials

<table>
<thead>
<tr>
<th>Group Id.</th>
<th>Prereaction of Pr&lt;sub&gt;2&lt;/sub&gt;CoO&lt;sub&gt;3&lt;/sub&gt; Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Co&lt;sub&gt;Co+Pr&lt;/sub&gt; in Pr&lt;sub&gt;2&lt;/sub&gt;CoO&lt;sub&gt;3&lt;/sub&gt; (atomic %)</th>
<th>Sources</th>
<th>Grinding method</th>
<th>Mixing method</th>
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<tr>
<td>TTSB</td>
<td>1300</td>
<td>10</td>
<td>1.156</td>
<td>Ames Lab</td>
<td>Porcelain mortar</td>
<td>Ball milling</td>
</tr>
<tr>
<td>TTSM</td>
<td>1200</td>
<td>50</td>
<td>1.358</td>
<td>Molycorp</td>
<td>SPEX mill</td>
<td>SPEX mill</td>
</tr>
</tbody>
</table>
Figure 23. Microstructure of a two-phase threshold switching material. (a) Etched-optical image, (b) polished-BSE image
Figure 23 (continued). (c) X-ray spectra generated from points along the line in (d) the microstructure of a two-phase threshold switching material.
Figure 24. X-ray diffraction patterns of (a) normal two-phase threshold switching material and (b) large grain size threshold switching material.
phase as ZnO doped with Co that has diffused in from the surrounding PrCoO$_3$ grains, and the white phase as PrCoO$_3$ doped with Zn that has diffused in from the adjacent ZnO grains.

Gradual slopes in elemental concentration profiles were observed near the boundary region between Co-doped ZnO grains and Zn-doped PrCoO$_3$ grains. As has been noted before, because X-rays are generated in a sizable volume around the point of beam incidence, there is always a chance that grains in the microstructure below those visible on the surface contributed to the intensities. Thus, it is almost impossible to precisely determine the elemental distribution within a small region of microstructure using energy dispersive X-ray spectroscopy; an instrument with better resolution, such as a Scanning Auger Microscope (SAM), would be better to this task.

**Dc characteristics**

It was observed that most of these two-phase materials exhibited reproducible threshold switching regardless of the sources of the praseodymium oxide powder or the powder preparation techniques; however, the specimen switching characteristics, such as threshold voltage drop and 'off' state resistance, depended on the powder preparation technique. It was usually observed that the material switched at a higher current as the particle size of prereacted PrCoO$_3$ powder decreased.

Figure 25 shows dc current-voltage drop characteristics of materials sintered at different temperatures. The materials were
Figure 25. Dc current-voltage drop characteristics of two-phase threshold switching materials (TTSB) sintered at different temperatures.
fabricated using ball milled PrCoO$_3$ powder (TTSB group). No clear-cut relationship was found between sintering temperature and the electrical characteristics. When the materials were sintered at 1350°C, they partially melted, lost their threshold switching behavior, and exhibited varistor behavior. All threshold switching materials studied also lost their switching capability after being partially melted.

Mixtures of ZnO, Co$_3$O$_4$, and Pr$_{6}O_{11}$ did not melt at 1350°C, even though the overall material had similar composition to two-phase ZnO-PrCoO$_3$ threshold switching material. The individual oxides of Co and Pr and pure PrCoO$_3$ phase all have melting points well above any sintering temperature used in this study. Co and Pr oxides were reacted to form PrCoO$_3$ before being mixed with ZnO to make two-phase threshold switching material. This prereaction either decreased the temperature at which a low-melting phase forms between PrCoO$_3$ and ZnO or increased the reaction rate between PrCoO$_3$ and ZnO leading to the formation of the low-melting phase. When single-phase PrCoO$_3$ specimens were doped with ZnO, there was evidence of the formation of a low-melting phase. This will be discussed further in the section on single-phase materials.

Figure 26 shows a typical log-log plot of the dc current-voltage drop characteristics of a two-phase threshold switching material (TTSM group). At low voltage drops, the material exhibited high resistance ohmic ($\alpha = 1$) behavior. Above a certain voltage drop, $V_{\text{NONOHMIC}}$, the materials changed to nonohmic behavior. The nonlinear exponent, $\alpha$, was around 4. Above the threshold voltage drop, $V_{\text{TH}}$, the
Figure 25. Dc characteristics of a two-phase threshold switching material (TTSM)
material switched to the 'on' state. In this state, the material exhibited negative differential resistance behavior with 'α' around -2 as the current through the material increased within the current range capable of being tested in this study.

When making dc measurements, one must be very careful in the interpretation of apparent resistivities. The true dc ohmic (α = 1) resistivities of specimens must be independent of specimen thickness. However, the apparent ohmic resistivity was found to depend on specimen thickness, with the apparent ohmic resistivity decreasing approximately exponentially as specimen thickness increased. This suggests that the apparent ohmic resistance of the specimen represents not only the bulk characteristic of the material, but also the influence of other sources of impedance, such as partially-blocking contacts between the electrodes and the bulk material. To compensate for electrode effects on measured resistance, the following scheme was used (see Figure 27). Let A equal the resistance at zero specimen thickness, i.e., the impedance of blocking contacts between the bulk material and the electrodes. Then, the apparent ohmic resistance, \( R_{\text{OHMIC}} \), should be given by \( R_{\text{OHMIC}} = A + Bd \), where B is the true bulk resistivity of the material divided by electrode area, and d is specimen thickness. Plotting \( R_{\text{OHMIC}} \) vs d allows determination of A by extrapolating \( R_{\text{OHMIC}} \) to zero thickness, as is shown in Figure 27. By subtracting A from each \( R_{\text{OHMIC}} \) value, a true or compensated value for ohmic resistance results. Calculation of the true of compensated bulk ohmic resistivity of each specimen in Figure 27 gives a
Figure 27. A relationship between ohmic resistance and specimen thickness of a two-phase threshold switching material (TTSM)

\[ R_{\text{OHMIC}} = A + Bd \]

A = 52.894 MΩ
B = 108.712 MΩ/cm
thickness-independent value for ohmic resistivity of about 100 MΩ-cm.

The nonohmic current-voltage drop behavior in the high voltage drop region of Figure 26 appears to follow an $\alpha = 4$ relationship, which has been interpreted [9] to indicate that the current is space charge limited (SCL) due to the presence of traps and recombination centers (see Appendix A). The value of $V_{NONOHMIC}$ is defined as the voltage drop at the transition from the ohmic region to the SCL region, and is determined by the intersection of lines extended from the ohmic and nonohmic regions, as is shown in Figure 26. Both the nonohmic voltage drop, $V_{NONOHMIC}$, and the threshold voltage drop, $V_{TH}$, depend on square of specimen thickness, as is shown in Figure 28. These relationships between the voltage drop and the specimen thickness fit the predicted relationship proposed in SCL theory (Eqs. 3 and 4).

**Ac complex impedance spectra**

To attempt to identify the sources of ohmic resistance in two-phase threshold switching materials, ac complex impedance spectra were studied from specimens having various thicknesses. Figure 29 shows typical complex impedance spectrum for a specimen having a relatively large thickness of 0.79 cm. Clearly-defined arcs were not observed for any two-phase threshold switching specimen tested; instead, the spectra appeared to consist of several overlapping arcs which were distorted from the idealized semicircles shown in Figure 11. For this reason, impedance spectrum analysis was not a fruitful technique.
Figure 28. A relationship between nonohmic voltage drop, $V_{\text{NONOHMIC}}$, and threshold voltage drop, $V_{\text{TH}}$, and the square of specimen thickness ($TTSM$).
Figure 29. Ac complex impedance spectrum of a two-phase threshold switching material.
There are several possible explanations for the type of spectrum shown in Figure 29. Macdonald [76] theoretically analyzed complex impedance spectra for various idealized equivalent circuits. He defined a physical parameter, \( M \), as \( d/Z_0 \), where \( d \) and \( L_0 \) are the distance of separation of plane parallel electrodes and the Debye length, respectively. His analysis showed that the arcs should merge together as \( M \) decreases toward zero. Since \( L_0 \) is a material property which is independent of the geometry of the specimen, Macdonald's analysis suggests that the arcs should overlap as \( d \) decreases. In this study, the thickness of the specimen was usually less than one cm because of difficulties in fabrication. If Macdonald's analysis is correct, a one-cm thickness may correspond to be too small a \( M \) value for this material to allow for arc separation in the complex impedance spectrum.

Brailsford and Hohnke [77] suggest another possible cause for spectrum distortion. They claim that arc overlap may be caused by the conductivities of grains varying from grain to grain as a result of grain size differences. Every discrete impedance source produces its own arc. They are added sequentially and with equal weight over a finite range of total conductivity. Because of variations in grain size, dopant concentration profiles generated by interdiffusion between grains are not the same in all grains. This nonuniformity of doping has been verified in the Co doping of ZnO grains, as will be discussed later. This leads to a variety of dopant levels in grains which, presumably, provides a wide variety of conductivity levels
leading to arc overlap in the impedance spectrum. If this is the reason for arc overlap, it will be impossible to produce useful complex impedance spectra of two-phase threshold switching materials fabricated using present fabrication techniques.

A Study of the Electrical Characteristics of Individual Grains and Interphase Boundaries in Two-Phase Threshold Switching Materials

The roles of individual grains and interphase boundaries in two-phase threshold switching materials were studied using microelectrode pairs sputtered onto the surface of thinned specimens. A similar study for ZnO varistors can be found in reference [78].

Because the grain sizes of 'normal' threshold switching materials (as shown in Figure 28) are too small to conveniently deposit an array of microelectrodes that will be isolated on individual grains, seed grain ZnO was prepared, mixed, and sintered with prereacted Co-excess PrCoO$_3$ to make large grain size threshold switching materials. Figure 30 shows the microstructure of this material. In addition to grey Co-doped ZnO grains and white Zn-doped PrCoO$_3$ grains, their intergranular phases are observed between some of the ZnO grains. The tablet of this material disintegrated into powder after being left in laboratory air for several months. Cracks were observed in the ZnO grains and at intergranular boundaries after the specimen being left. This kind of problem was also observed for switching materials fabricated using mixtures of Co$_3$O$_4$, Pr$_6$O$_{11}$, and ZnO powders. Figure 30 also shows X-ray scans for Zn, Co, and Pr along the same line in the
Figure 30. Microstructure and x-ray scan across a line of a large grain size threshold switching material. (a) Microstructure, (b) Zn Kα, (c) Co Kα, (d) Pr Lα
microstructure. Two points should be made regarding the Co X-ray line scan. First, the Co distribution across the large ZnO grain was not uniform. Instead, the outer region of the grain was doped more heavily than the center of the grain. Second, the Co content in the intergranular phase was far lower than in the PrCoO$_3$ grains and even lower than in the ZnO grains. These observations led to the conclusion that the intergranular phase formed because the ZnO absorbed most of the Co from surrounding PrCoO$_3$ grains, leaving a residual Pr-rich phase, possibly low melting, that occupied the intergranular spaces.

The X-ray diffraction pattern of a large grain size threshold switching material is shown in Figure 29(b). Most of the peaks were matched to the published patterns of ZnO and PrCoO$_3$. Compared with the pattern of a normal threshold switching material shown in Figure 29(a), several weak unidentified peaks were observed, as are indicated in Figure 29(b). It was assumed that the unidentified peaks were generated from the Pr-rich intergranular phase. The unidentified peaks were compared to the published patterns for various forms of praseodymium oxide. The fit was best for PrO$_2$. The microstructure of this large grain size threshold switching material is similar to that of a rare earth ZnO varistor [74]. The investigators in reference [74] identified the intergranular layer as being a solid solution of ZnO and Pr$_2$O$_3$ using X-ray diffraction and X-ray fluorescence analysis of isolated intergranular materials remaining after ZnO grains were removed by leaching with an HF-HNO$_3$-HCl-H$_2$O solution. Solid solution of ZnO and praseodymium oxide was observed to be important to form
the continuous intergranular phase [74]. These observations will be discussed further when single-phase PrCoO$_3$ materials are discussed.

After thinning and before microelectrodes were applied, an optical microscope was used to confirm that, for ZnO grains, the specimen was only one grain thick. This could not be confirmed for PrCoO$_3$ grains, because they were not transparent to light at the specimen thickness used. It was realized that, during testing with a specific pair of microelectrodes, it was possible that part of the current path may have passed through surrounding grains. This uncertainty was partially overcome by examining the microstructure after testing for evidences of damage generated by current passage.

The kinds of microstructural features tested between pairs of microelectrodes were a) a group of several undoped ZnO grains in polycrystalline pure ZnO, b) individual Co-doped ZnO grains and groups or clusters of Zn-doped PrCoO$_3$ grains in large grain size threshold switching materials, and c) a combination of several Co-doped ZnO and Zn-doped PrCoO$_3$ grains in normal two-phase threshold switching materials.

Tests of undoped ZnO grains

An electrode array deposited on a thin section of undoped polycrystalline ZnO is shown in Figure 31. In this case, it is obvious that each electrode covers several ZnO grains so that measurements between pairs of electrodes will also constitute a test of a number of grains and grain boundaries. A linear low resistance (~200 Ω) dc
Figure 31. Microelectrode array deposited on undoped ZnO thin section and a dc current-voltage drop trace for several undoped ZnO grains. (a) Microelectrode array, (b) dc current-voltage drop trace (2.3 W MPP setting)
current-voltage drop trace was observed for groups of several undoped ZnO grains; a typical trace is shown in Figure 31. As has been discussed in the Literature Review Section, pure ZnO exhibits n-type semiconductivity due to its intrinsic defects.

Tests of individual Co-doped ZnO grains

Tests with pairs of electrodes on the same Co-doped ZnO grain in large grain size switching material showed a high resistance 'off' state, followed by switching at a high threshold voltage drop (~ 700 V) on the first sweep, as is shown in Figure 32(a). When the current was decreased, the grain did not return to its original high resistance 'off' state, but rather showed unstable conduction all the way back to zero voltage. For subsequent sweeps, e.g., Figure 32(b), the grain did not show any switching, but behaved like the 'on' state of the first sweep, showing unstable conduction.

Careful microstructural examination showed a 'damaged trace' due to a 'breakdown' through the Co-doped ZnO grain after the initial sweep, as is shown in Figure 32(c) and (d). The word 'breakdown'\(^1\) is used because the transition to a low resistance 'on' state was not reversible, i.e., the specimen never returned to the high resistance 'off' state. As was shown in the Co X-ray line scan in Figure 30(c), Co distribution across some ZnO grains, especially large grains, was not uniform, being more concentrated in the outer portion than in the

\(^1\)It is important to realize that the difference between switching followed by 'breakdown' and reversible switching is just a matter of the magnitude of the current flow permitted in the 'on' state.
Figure 32. Dc current-voltage drop traces for the same single Co-doped ZnO grain in large grain size threshold switching material (2.3 W MPP setting). (a) First sweep and (b) second sweep.
Figure 32 (continued). Microstructure near a Co-doped ZnO grain after the first sweep. (c) Reflected light image and (d) transmitted light image
ZnO GRAIN

DAMAGED TRACE
interior. The ZnO grain shown in the photomicrographs of Figure 32 appears to have an undoped region in the center, as is shown in the reflected light, Figure 32(c), and transmitted light, Figure 32(d), images. The electrodes were so located as to include both Co-doped and undoped portions of the grain between them. The 'damaged trace' is observed only in the outer Co-doped region of the ZnO grain, but not in the central undoped region. These observations are consistent with the initial high resistance of the Co-doped ZnO grain being due to the highly-resistive Co-doped region, which undergoes 'breakdown' during the first sweep to produce a 'damaged trace' which remains permanently conductive. No such 'breakdown' is needed for conduction to take place through the semiconducting undoped region of the ZnO grain. Scanning electron microscopic examination showed that the 'damaged trace' was actually a crack.

The square in the upper left of Figure 32(c) shows a pristine microelectrode as deposited on the thin section. Both of the electrodes used for testing were 'burned' during the initial sweep due to high current density following 'breakdown'.

Tests of clusters of Zn-doped PrCoO₃ grains

Individual Zn-doped PrCoO₃ grains were too small to be tested singly using pairs of microelectrodes. Consequently, only the electrical characteristics of clusters of these grains were tested. Clusters of Zn-doped PrCoO₃ grains showed stable and reproducible threshold switching, as is shown in Figure 33. The threshold voltage drop of the first sweep was much lower than the first sweep threshold
Figure 33. Dc current-voltage drop traces (2.3 W MPP setting) of clusters of Zn-doped PrCoO$_3$ grains (a) for the first sweep and (b) after several consecutive sweeps. (c) Microstructure near the cluster of grains tested.
or 'breakdown' voltage drop of Co-doped ZnO grains. The threshold voltage drops of subsequent sweeps were similar to those of the first sweep. Figure 33(c) shows the microstructure in the vicinity of the grains tested. A 'damaged trace' was not observed in the cluster of grains between the microelectrode pair. Because of high current flows through the material after switching to the 'on' state, a blocking electrode will be easily damaged; in Figure 33(c), the burned electrode was the cathode during the sweep. This observation is consistent with PrCoO₃ exhibiting p-type conductivity. A barrier between the metal electrode and a p-type semiconductor blocks hole movement, so that the hole-injecting electrode, the cathode, contributes most of the impedance, while the electron-injecting electrode, the anode, contributes little impedance.

**Tests of combinations of Co-doped ZnO and Zn-doped PrCoO₃ grains**

These combination test paths showed high first sweep threshold voltage drops, as is shown in Figure 34(a). For subsequent sweeps, these test paths exhibited reproducible threshold switching with a lowered threshold voltage drop, as is shown in Figures 34(b) and (c). The threshold voltage drops of these combination test paths for subsequent sweeps were similar in magnitude to those observed for clusters of Zn-doped PrCoO₃ grains, which were discussed in the preceding section. These observations are well matched to the dc current-voltage characteristics observed for bulk two-phase threshold switching materials, which always exhibit a higher threshold voltage for the first sweep, but a lower threshold voltage for subsequent sweeps.
Figure 34. Dc current-voltage drop traces of a combination of Co-doped ZnO and Zn-doped PrCoO$_3$ grains (a) for the first sweep, (b) four consecutive sweeps, and (c) the sixth sweep. (d) Microstructure of combinations of Co-doped ZnO and Zn-doped PrCoO$_3$ grains after tested.

<table>
<thead>
<tr>
<th>MPP set (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) First sweep</td>
</tr>
<tr>
<td>(b) Four consecutive sweeps</td>
</tr>
<tr>
<td>(c) Sixth sweep</td>
</tr>
</tbody>
</table>
sweeps. 'Damaged traces' were observed primarily on ZnO grains along the combination test paths, as is shown in Figure 34(d). The 'damaged traces' did not follow straight line paths between the electrodes, but usually branched into two or three paths. Therefore, the effective area of the current path through the specimen in the 'on' state is probably much smaller than the geometric area of the specimen and is indeterminant.

The observations of the dc current-voltage characteristics of the two major phases of two-phase threshold switching materials as determined using microelectrodes can be summarized as:

1. Pristine Co-doped ZnO grains showed a high resistance 'off' state with a high 'breakdown' voltage on the first sweep. The first sweep produced a 'damaged trace' in the Co-doped portion of the ZnO grains which provided a low resistance path for all subsequent sweeps, i.e., Co-doped ZnO grains do not exhibit normal threshold switching behavior, but an irreversible change to a significantly lower resistance after 'breakdown'.

2. Zn-doped PrCoO₃ grains showed a low threshold voltage for the first and all subsequent sweeps, and exhibited stable and reproducible threshold switching behavior.
Studies on Single-Phase Polycrystalline Materials

To further understand the observed switching behavior in two-phase materials, the electrical characteristics were studied for single-phase polycrystalline Co-doped ZnO and Zn-doped PrCoO$_3$ which constitute the individual phases of two-phase threshold switching materials.

Undoped and Co-doped ZnO materials

The effect of Co doping on the electrical characteristics of ZnO materials was studied. Pepe et al. [79] reported that, based on lattice parameter measurements, ZnO dissolved up to 10 atom percent Co. Consequently, the maximum Co dopant concentration in this study was set at 10 atom percent in order to prevent formation of second phase.

Three different cobalt oxide powders were blended with ZnO and sintered in order to fabricate Co-doped ZnO materials. Table 2 lists the chemical formulas and mean particle sizes of the starting powders. The purpose of using different forms of cobalt oxide was to determine whether the oxidation state of the Co in the starting powder had any effect on the electrical characteristics of the Co-doped ZnO produced.

Microstructure

Achievement of a uniform distribution of Co throughout the ZnO was an important goal in the fabrication of single-phase polycrystalline samples. Undoped ZnO grains are pale yellow in transmitted light, but doping with Co turns the grains green. Consequently, the distribution of Co dopant in ZnO grains can be judged by color differences in transmitted light. Figure 35 shows transmitted
### Table 2. Chemical formulas and mean particle sizes of cobalt oxide and ZnO powders used to fabricate Co-doped ZnO materials

<table>
<thead>
<tr>
<th>Group Name</th>
<th>Form of oxide</th>
<th>Treatment</th>
<th>Mean particle size&lt;sup&gt;a&lt;/sup&gt; (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ</td>
<td>Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Untreated</td>
<td>14.5</td>
</tr>
<tr>
<td>CZJ</td>
<td>Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Jet milled</td>
<td>4.4</td>
</tr>
<tr>
<td>COZ</td>
<td>CoO</td>
<td>Untreated</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>Untreated</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Analyzed using sedimentation method.

Light images of Co-doped ZnO materials which were fabricated with untreated (CZ) Co<sub>3</sub>O<sub>4</sub> powder (a) and with jet milled (CZJ) Co<sub>3</sub>O<sub>4</sub> powder (b). The Co distribution was not uniform in Co-doped ZnO materials fabricated with untreated large mean particle size Co<sub>3</sub>O<sub>4</sub> powder, as is shown in Figure 35(a). It is believed that localized saturation of ZnO with dopant resulted when small particle size ZnO powder was doped with large particle size (CZ) Co<sub>3</sub>O<sub>4</sub>. Clearly, there was a need to improve Co uniformity over that achieved by reacting untreated powders. Ball milling is usually used to assure a uniform microstructure in the manufacture of ZnO varistors, but this process tends to contaminate the material with other dopants derived from the milling media which may affect the electrical characteristics. As is shown in Figure 35(b), jet milling the Co<sub>3</sub>O<sub>4</sub> powder before mixing it with the ZnO powder improved the uniformity of distribution of Co in the material, with
Figure 35. Transmitted light images of Co-doped ZnO materials: (a) CZ, 10.20 atom % Co/[Co + Zn] and (b) CZJ, 9.71 atom % Co/[Co + Zn]
little risk of contamination. In addition to observations based on color, the distribution of Co across a ZnO grain from a CZJ specimen was also determined using energy dispersive X-ray spectroscopy. As Figure 36 shows, the Co concentration was observed to be uniform across the grain. Cobalt doping across ZnO grains has also been observed [41] to be uniform for a ZnO varistor material of a composition similar to that for two-phase threshold switching material.

Only the single ZnO phase was detected on X-ray diffraction patterns of Co-doped ZnO materials regardless of Co concentration.

Figure 37 shows the microstructures of Co-doped ZnO materials fabricated with two different forms of cobalt oxides: (a) jet milled (CZJ) Co$_3$O$_4$ and (b) untreated (COZ) CoO. The total Co concentrations for both materials are similar. It was observed that most of the pores in Co$_3$O$_4$-ZnO materials were located on the intergranular boundaries, but that most of the pores in CoO-ZnO materials were located within the grains. The reason for these microstructural differences is not known. It was also observed that the tablets of CoO-ZnO materials were weak and broke easily during cutting and grinding.

**Electrical characteristics** Figure 38(a) shows the dc characteristics of single-phase polycrystalline undoped and Co-doped ZnO materials prepared with jet milled (CZJ) Co$_3$O$_4$ powder. Undoped and slightly doped ZnO materials exhibited ohmic behavior over the entire current density range tested in this study. As Co content increased, the materials showed nonohmic behavior at successively lower current densities. It was impossible to determine a nonohmic
Figure 36. Co X-ray intensities at points within a CZJ Co-doped ZnO grain
Figure 37. Microstructures of (a) CZJ material (SE and BSE image) and (b) COZ material (BSE only image)
Figure 38(a). Dc characteristics of CZJ materials
voltage drop for the heavily doped materials, because the nonlinear coefficient was continuously changing. The materials having higher doping concentrations exhibited current controlled negative differential resistance behavior before the materials switched to their 'on' states. It was expected that these materials would show switching on the initial sweep followed by a permanent conductive state for subsequent sweeps, as was observed in the study of the electrical characteristics of individual Co-doped ZnO grains in two-phase threshold switching material described in the section entitled Tests of Individual Co-Doped ZnO Grains. However, the CZJ heavily Co-doped ZnO single-phase samples tested in this study showed threshold switching (with lowered threshold voltage drops) even for subsequent sweeps.

Figure 38(b) shows the dc characteristics of Co-doped ZnO materials prepared with untreated (CZ) Co₃O₄ powder. Like the CZJ-based materials, these CZ-based materials also showed ohmic behavior at low current densities. Two differences were observed in the characteristics of CZ materials compared to those of CZJ materials. First, CZ materials exhibited nonohmic conduction within the current density range tested in this study, even at low Co concentrations, whereas purely ohmic behavior was observed at these dopant levels in CZJ materials. Second, nonlinear coefficients did not change in the nonohmic region for a given CZ specimen as they did for the corresponding CZJ specimen, although the coefficient varied between 2 and 4 for different CZ specimens cut from the same tablet. In both
Figure 38(b). Dc characteristics of CZ materials
cases, the materials having higher doping concentration exhibited threshold switching behavior.

Figure 39 shows the relationship between dc ohmic resistivity and Co concentration for Co-doped ZnO single-phase materials prepared with the two different Co$_3$O$_4$ powders. Undoped ZnO material had a resistivity of around 1 Ω-cm when it was sintered in air at 1300°C. As Co content increased, the measured ohmic resistivity increased for both groups of materials. The resistivity of CZ material was higher than CZJ material by about a factor of $10^3$ at similar Co concentrations. A resistivity increase accompanying additions of Co$_3$O$_4$ has also been observed for rare-earth ZnO varistor materials [43]. Table 3 lists the resistivity data of these varistor materials with various additives. Contrary to the observations in this study and for the varistor materials just cited, it has also been observed by other investigators that the resistivity of single crystal ZnO decreases upon being doped with Co [42]; however, the experimental procedure and the Co doping concentration were not specified.

In analyzing the measured ohmic resistance of these materials, it is important to realize that there are three possible sources of resistance in a polycrystalline material: due to possible blocking contacts between the bulk and the electrode, due to grain boundary effects, and due to the grains themselves. A series of experiments was performed to attempt to clarify which of these sources of resistance might be contributing to the overall ohmic resistance measured for these single-phase materials. These will be described in
Figure 39. Relationship between dc ohmic resistivity and Co concentration.
Table 3. Ohmic resistivities of rare earth oxide-ZnO varistors [43]

<table>
<thead>
<tr>
<th>Additives (atm %)</th>
<th>Sintering temperature (°C)</th>
<th>Resistivity (Ω-cm)</th>
<th>AGS(^a) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Pr</td>
<td>Co</td>
<td>1300</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>1350</td>
</tr>
<tr>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>1300</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
<td>1350</td>
</tr>
</tbody>
</table>

\(^a\)AGS stands for average grain size.

the following paragraphs, starting with experiments designed to detect the presence of blocking electrodes. One possible indication of a contribution from blocking contacts to measured resistance would be the observation of an increase in apparent resistivity with decreasing specimen thickness. Such an increase would arise because the thinning of the specimen would not result in a commensurate reduction in overall resistance because of the relatively constant resistance due to the blocking electrodes. Figure 40 shows relationships between measured dc ohmic resistivity and specimen thickness for Co-doped ZnO materials fabricated with jet milled \(\text{Co}_3\text{O}_4\) powder. The Co concentrations are indicated on the figure. The resistivity data are scattered at small specimen thicknesses, but are essentially constant independent of the specimen thickness for the overall range of specimen thickness. This constant resistivity is an indication that the observed high ohmic resistivity of Co-doped ZnO material was probably not due to blocking
Figure 40. Relationship between dc ohmic resistivity and specimen thickness.
contacts formed between the bulk and the electrode, but rather was probably a bulk material effect.

Ac complex impedance spectroscopy is another method which is useful to separate the sources of measured resistance of polycrystalline specimens. (This method has been described in the section entitled Ac Characteristics.) Figure 41 shows ac complex impedance spectra of CZJ Co-doped ZnO materials having various Co concentrations. Within the frequency range of the instrumentation available for this study, 230 Hz to 10 MHz, a single arc was observed for each material. The size of the arc increased as Co content increased, which indicates that Co doping increased the particular impedance source in the material responsible for this arc. It is not known prior whether the 'complete' impedance spectrum of these specimens consists of one, two, or three arcs. This depends on whether or not there are measurable grain boundary and/or electrode contributions to the specimen impedance. However, it is possible to make educated guesses as to how many arcs the specimen contains, and which are actually being observed in the frequency range of this study. Extrapolation of the single observed arc to its right-hand intersection with the horizontal axis gives a resistance value very close to the resistance measured by dc methods. This comparison is shown in the last two columns of Table 4. While the values are fairly scattered between specimens cut from the same tablet, this close agreement for each specific specimen suggests that the single arc observed in the ac spectrum is, in fact, the lowest frequency arc in the spectrum.
Figure 41. Ac complex impedance spectrums of Co-doped ZnO materials
Table 4. Extrapolated ac resistivities and dc ohmic resistivities for the specimens of which ac complex impedance spectra are shown in Figure 42

<table>
<thead>
<tr>
<th>Specimen resistivity name</th>
<th>Extrapolated ac resistivity to the left (KΩ-cm)</th>
<th>Extrapolated ac resistivity to the right (KΩ-cm)</th>
<th>Dc ohmic (KΩ-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.44</td>
<td>101</td>
<td>102</td>
</tr>
<tr>
<td>B</td>
<td>1.27</td>
<td>145</td>
<td>140</td>
</tr>
<tr>
<td>C</td>
<td>0.39</td>
<td>298</td>
<td>284</td>
</tr>
<tr>
<td>D</td>
<td>0.04</td>
<td>265</td>
<td>262</td>
</tr>
<tr>
<td>E</td>
<td>1.71</td>
<td>166</td>
<td>165</td>
</tr>
</tbody>
</table>

(i.e., there most probably is no additional arcs in the right of the observed arc). It is expected that the left-hand intersection of the highest frequency arc in a spectrum will occur at zero resistance which would correspond to infinite frequency. Presumably, this highest frequency arc should be attributable to the impedance of the grains themselves. The observed single arc is most probably not the highest frequency arc in the spectrum, because its left-hand intersection does not occur at zero resistance (see Figure 42 and Table 4). Therefore, there is indirect evidence that there is probably one or possibly two small arcs at higher frequencies (to the left) of the single observed arc. If there are actually three arcs in the total spectrum, then the observed single (lowest frequency) arc should be attributed to electrode impedance (i.e., there is an electrode blocking
Figure 42. Ac complex impedance spectra of Co-doped ZnO specimens cut from a single tablet. (A-D) In-Ga electrodes deposited, (E) Au electrode deposited, (F) magnified spectrum for high frequency region of (A). Numbers and characters represent the data and solid lines are regressed arcs.
Figure 42. Continued
contribution to dc specimen resistance). If there are only two arcs in the total spectrum, then the single observed (lowest frequency) arc is due to grain boundary impedance, and there are no measurable electrode effects in the dc measurements. One way to discriminate between these two possibilities would be to compare the lowest frequency arcs of spectra determined with two different electrode metals of differing work function, one with greater blocking tendency than the other. If no significant differences in these lowest frequency arcs are observed with these two different metals, then there probably are no electrode effects, there are only two arcs in the total spectrum, and the observed arc is due to impedance associated with the grain boundaries. On the other hand, if the lowest frequency arc is enlarged with the more blocking type of metal electrode, the lowest frequency arc is associated with electrode impedance, i.e., blocking contact effects are present in dc measurements.

The spectra of Figure 41 were determined using In-Ga electrodes. Since ZnO is a n-type semiconductor (as was demonstrated by hot probe measurements), a metal with a higher work function than In-Ga would have a greater blocking tendency in contact with ZnO. Gold is such a higher work function metal [80]. Impedance spectra measured with Au electrodes (e.g., Figure 42(e)) also give a single arc in the accessible frequency range, with the extrapolated low frequency end agreeing well with dc resistivity (as measured also with Au electrodes), indicating that the observed arc is the lowest frequency arc. The extrapolated right-hand intersection of this arc gives
resistance values about the same as was observed with In-Ga electrodes. Thus, no significant differences in lowest frequency arcs are observed with the two different electrode materials, and this is an indication that no measurable blocking contact effects were present with either electrode metal.

To further test for the presence of a blocking contact, the dc resistances were measured at sections along the length of a tablet of CZJ Co-doped ZnO materials with the following procedure. A tablet was imbedded into air setting polymer. After removing the excess polymer covering the tablet and polishing both surfaces, an Au electrode was deposited so as to cover one surface of the tablet, and this surface was covered again with the polymer to provide protection for the electrode during further cutting and grinding. Three small Au electrodes were deposited on the other surface of the tablet using a metal mask, as is shown in Figure 43, and dc resistances were measured between two of the top electrodes at three different voltages in the range where the material showed ohmic behavior. Then, part of the thickness of the tablet was cut away, the new surface was polished, three new Au electrodes were deposited using the same mask, and the dc resistance measurements were again made. This thinning and testing procedure was continued until the remaining portion of the tablet was too thin to be conveniently cut. If a blocking contact was contributing to the high resistance measured for Co-doped ZnO materials, the resistance measured between two electrodes deposited on the same surface would remain the same or become higher as the specimen
Figure 43. A relationship between resistance and thickness for a Co-doped ZnO material. Each symbol represents each data from a set of two small electrodes.
thickness decreased to near zero because the volume of the conduction path, which is related to the specimen thickness as well as the separation between the two electrodes, decreased. Figure 43 shows the observed relationship between measured resistance and thickness. The resistance values were found to be independent of the thickness when the tablet was thicker than about 0.2 cm. Below about 0.2 cm, the measured resistance decreased as the tablet thickness decreased. This decrease may be explained by assuming that part of the current was shunted through the thin specimen to the high conductivity electrode deposited on the back surface, and only part of the current path passed directly through the high-resistance ZnO material between the two top electrodes.

Based on the results described above, it is concluded that the high observed resistance of Co-doped ZnO material was not due to a blocking contact between the bulk material and metal electrode, but rather was due to the bulk characteristics of the material itself.

The CZJ specimens used to measure the dc ohmic resistivities shown in Figure 40 were all cut from the same tablet; they showed considerable scatter in resistivity values. To test whether density differences at different positions along the length of the original tablets might be affecting the measured resistivity, specimens having similar thicknesses were cut from a single tablet, and the densities of the specimens were measured using a water immersion technique. Even though isostatic pressure has been applied to the unfired tablets after they had been formed with biaxial pressure, a density variation was observed along the length, with the top and bottom of the tablets...
being denser than the center. Figure 44 shows a plot of resistivity as a function of bulk density for these specimens. The numbers above each data point represent the position of the specimen along the length of the original tablet; position 1 was the top end of the tablet as it was oriented during sintering. Figure 44 also includes ac resistivities extrapolated by regression to the right (low frequency) ends of the arcs. The extrapolated ac resistivity was slightly lower than the dc ohmic resistivity in each case. Since pores have infinite resistivity, it might be expected that resistivity would increase as density decreased. However, the resistivity did not show any consistent relationship with bulk density. Rather, the higher-density top and bottom portions of the tablet had slightly higher resistivity than the lower-density interior portions.

A possible source of impedance in a polycrystalline specimen is high resistive material in the region around the grain boundaries. For example, there is general agreement [1, 2] that, in ZnO varistors, depletion layers formed near the boundary of ZnO grains are major barriers to conduction. In the present work, as explained above, extrapolation to the left ends of the large arcs in the impedance spectra of Co-doped ZnO materials did not lead to a zero impedance, which indicates that the observed arcs do not represent the impedance contributed by the grains themselves. Since it has also been shown above that the observed arc does not appear to be associated with electrode effects, it seems most likely that the observed arc is due to the impedance of conduction barriers associated with or near the
Figure 44. Relationship between resistivity and bulk density for CZJ Co-doped ZnO material

RESISTIVITY (Mohm-cm)

BULK DENSITY (g/cm³)

- DCohmic region
- AC extrapolated to right
- AC extrapolated to left

Numbers represent the position of the specimen along the length of the original tablet.
grain boundaries. If the observed arc represented the impedance from grain boundary depletion layers, it would be expected that the size of the arc would decrease as average grain size increased, because the relative fraction of material adjacent to grain boundaries decreases as grain size increases. To test this possibility, the average grain size of a Co-doped material was varied by annealing at 1300°C for up to 200 hours. Table 5 lists average grain size, Co concentration, and resistivity of the annealed materials measured with In-Ga electrodes. The data were so scattered that no relationship could be determined between resistivity and average grain size. Co concentration was

Table 5. Average grain size, Co concentration, and resistivity of Co-doped materials annealed for various time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>AGS^a (µm)</th>
<th>Co conc.^b (atom %)</th>
<th>Extrapolated ac resistivity To the left (Ω-cm)</th>
<th>Extrapolated ac resistivity To the right (Ω-cm)</th>
<th>Dc ohmic (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20.89</td>
<td>3.10</td>
<td>8.56</td>
<td>142</td>
<td>139</td>
</tr>
<tr>
<td>20</td>
<td>28.29</td>
<td>3.08</td>
<td>107.10</td>
<td>4.5 x 10^3</td>
<td>4.5 x 10^3</td>
</tr>
<tr>
<td>50</td>
<td>34.96</td>
<td>3.25</td>
<td>146.44</td>
<td>10.4 x 10^3</td>
<td>9.6 x 10^3</td>
</tr>
<tr>
<td>104</td>
<td>39.18</td>
<td>3.40</td>
<td>-^c</td>
<td>181</td>
<td>176</td>
</tr>
<tr>
<td>204</td>
<td>40.36</td>
<td>4.50</td>
<td>20.85</td>
<td>1.3 x 10^3</td>
<td>1.2 x 10^3</td>
</tr>
</tbody>
</table>

^aAGS stands for average grain size.

^bCo/[Co + Zn].

^cNegative value.
observed to increase as the material was annealed for longer times, which probably indicates that the vapor pressure of ZnO is higher than that of CoO at 1300°C. No relationship was observed between resistivity and Co concentration. Values of resistivity were also measured on the same specimens with Au electrodes replacing In-Ga electrodes to check whether data scattering might be due to blocking contacts. The data were similar for both electrode materials.

Since Co exists in several oxidation states, it may be that one oxidation state has a more powerful effect on ZnO conductivity than another. To test whether the oxide form of cobalt dopant used in the starting powder affected the electrical characteristics of Co-doped ZnO materials, some Co-doped ZnO materials were fabricated by blending ZnO powders with CoO rather than Co3O4; these materials constitute the COZ group. The fabrication technique for COZ materials was exactly the same as that for the materials fabricated using Co3O4 and ZnO powders (CZ and CZJ groups). The dc current-voltage characteristics of COZ materials were similar to those of CZ and CZJ materials.

Figure 45 shows relationships between apparent resistivity and specimen thickness for several Co concentrations. As Co content increased, the resistivity at a given thickness increased, as was also observed for Co3O4-ZnO materials (Figure 39). At a given Co concentration, the resistivity decreased as thickness increased, which is a positive indication that impedance due to blocking contacts contributes to the measured dc ohmic resistance of the COZ materials. The figure also includes extrapolated ac resistivities of the materials. The shapes
Figure 45. Relationship between apparent resistivity and specimen thickness for COZ materials.
of the ac complex impedance spectra for COZ materials were similar to those for CZ or CZJ materials, which showed a single large arc within the frequency range tested in this study. The extrapolated (low frequency) ac resistivity was lower than the measured dc ohmic resistivity. This probably indicates that another arc (associated with electrode effects) would be present at very low frequencies; however, the bridges used in this study had a lower frequency limit of 0.23 KHz, so that it was impossible to test this hypothesis.

To further test whether blocking contacts formed between COZ materials and the electrodes, a tablet was imbedded in air-setting polymer, and the repeated measurements were made of the dc resistance between two small electrodes as the specimen was gradually thinned. A schematic of the specimen configuration is shown in Figure 43. Figure 46 shows the relationship between measured resistance and specimen thickness. As thickness decreased, the resistance increased. If blocking contacts were present, the resistance should be independent of thickness at large thicknesses and should increase near zero thickness due to a restricted current path. Neither of these effects was observed, and so the evidence for possible blocking contact problems from ac measurements could not be either supported or refuted by these data.

A continuously increasing resistance for large thickness may indicate nonuniformity of true resistivity at different locations in the tablet. To test for nonuniformity of resistivity, a tablet was
Figure 46. A relationship between resistance and thickness for a COZ material
imbedded in air-setting polymer, and the repeated measurements of the resistance between two small electrodes were made while thinning along its diameter, as is shown in Figure 47. In this case, no electrode was applied on the bottom of the specimen. If the resistivity of the bulk material is uniform, the resistance will be independent of the depth from the top of the specimen until the specimen thickness approaches zero, near which the measured resistance is expected to increase due to a restricted current path. Figure 47 shows the relationship between measured resistance and the depth from the top of the specimen. The resistance at the center was higher than that at the top of specimen, which indicates that the resistivity of the bulk material was not uniform across the diameter of the tablet. As the depth approached the specimen diameter (i.e., the specimen became very thin), the resistance increased again. After a slice was cut from the tablet, the resistance between the two top electrodes was also measured with and without an In-Ga electrode painted onto the bottom of the slice. The squares in Figure 47 represent the data taken from slices with a bottom In-Ga electrode. The resistances of the slices without the bottom electrode were slightly higher than those measured before the slices were removed from the tablet, but the resistances of the slices with a bottom electrode were much lower than those measured before the slices were removed from the tablet. These results indicate that the increasing resistance for the thinnest slices (without bottom electrodes) was due to restriction of the current path, and not due to a high electrode impedance. The addition of a
Figure 47. Relationship between resistance and depth for a COZ material
bottom electrode to the thin specimen provided a low resistance current path which included very little oxide material, which is further indication that blocking electrode contacts were not present with COZ materials, in disagreement with the ac resistance results.

The observations of the electrical characteristics of single-phase polycrystalline Co-doped ZnO materials can be summarized as follows:

1. Co-doped ZnO materials exhibited threshold switching. Complete breakdown producing damage traces, which was observed in individual Co-doped ZnO grains in two-phase threshold switching materials, was not observed for single-phase Co-doped ZnO materials.

2. As Co content increased, the resistivity of ZnO material increased. The high resistivity was observed to be independent of the form of cobalt oxide (Co$_3$O$_4$ vs CoO) in the starting powder mixture. The resistivity of the materials fabricated with large particle size Co$_3$O$_4$ powder was higher than that of the materials fabricated with small particle size powder.

3. No observation consistent with the formation of a blocking contact between bulk Co$_3$O$_4$-ZnO material and either Au or In-Ga electrodes was seen. Ambiguous evidence of the possibility of a blocking contact contribution to measured resistance was observed in CoO-ZnO materials.

4. The resistivity of the material was not uniform across the thickness and diameter of a tablet.
5. No evidence was observed of the formation of a depletion or other conduction barrier layer near grain boundaries of polycrystalline Co-doped ZnO materials.

Possible role of cobalt in conduction in ZnO. The nonohmic current-voltage behavior and high resistivity of doped ZnO varistor materials have been found to be closely related to an intergranular layer between ZnO grains [42]. Such an intergranular layer was not found in the microstructure of single-phase polycrystalline Co-doped ZnO materials in this study. Consequently, the barrier model for the nonohmic behavior of ZnO varistor materials is not satisfactory to explain the large increase in resistivity observed when single-phase ZnO is doped with Co.

The homojunction model proposed for ZnO varistors does not require the presence of intergranular layers [45]. Rather, the model proposes the formation of a depletion layer in the ZnO grains near the grain boundaries due to the local suppression of intrinsic defects. Transition metal ions, such as Mn, dissolve into ZnO to produce donor levels which are located deep in the band gap. These deep donors suppress the concentrations of native shallow donors, such as Zn\(_i\) or V\(_O\), which are the usual sources of the conduction electrons for undoped ZnO [64]. It seems logical that Co may play a similar role.

Cobalt oxide reduces from Co\(_3\)O\(_4\) to CoO at around 900°C in an air atmosphere [81]. This reduction produces extra oxygen which may combine with and eliminate intrinsic defects in ZnO, leading to the suppression of the concentration of conduction electrons. To test
whether this reduction was taking place in blended Co₃O₄-ZnO powders during sintering, weight changes during sintering were measured and compared to the predicted weight losses due to the reduction. Two causes of weight loss may occur: a loss due to vaporization on ZnO and CoO; and a somewhat larger loss as Co₃O₄ reduces to CoO prior, during, or after incorporation into the ZnO. Figure 48 shows weight losses that occurred during sintering of tablets of jet milled Co₃O₄-ZnO mixtures. The line in Figure 48 represents the sum of the predicted weight losses due to both of these processes, assuming that all Co₃O₄ converts to CoO. The magnitude of the weight losses due to ZnO and CoO vaporization were estimated from observed weight losses during the sintering of pure ZnO tablets. The fit between the observed and the predicted values was very good, indicating that most of the Co₃O₄ reduced to CoO during sintering. Figure 49 shows weight changes for three different powder mixtures of cobalt oxides and ZnO all having Co concentrations around 10 atom %. The heating schedule for these thermogravimetric (G) runs was exactly the same as that used for sintering the tablets. Continuous weight gains at lower temperatures were observed for all three powder mixtures. These gains were assumed to be due to oxidation of some Co²⁺ to Co³⁺ in the cobalt oxides during heating. Sudden weight losses starting around 840°C were observed for all powder mixtures. During these weight losses, endothermic reaction peaks were observed by Differential Thermal Analysis (DTA), as is shown by the practical trace at the top of the figure. The reduction of Co₃O₄ to CoO absorbs heat (endothermic reaction) [82].
Figure 48. Relationship between weight loss during sinter and Co concentration for CZJ materials

\[ \Delta W/W = 1599.94X/(24433.82-3.34X) + 0.338 \]

\( X \) ATOM % Co
Figure 49. TGA and DTA curves of blends of cobalt oxides and ZnO
It is expected that these sudden losses, therefore, represent a reduction of Co\(^{3+}\) to Co\(^{2+}\). After the sudden weight loss, the weight decreased gradually and continuously up to the final temperature, around 1000°C. Similar continuous weight gains followed by sudden weight losses were also observed for pure CoO and Co\(_3\)O\(_4\) powders at similar temperatures.

It is generally accepted [38, 39] that Co\(^{2+}\) ions are located substitutionally in tetrahedral Zn\(^{2+}\) sites in ZnO. Since the ionic state of Co\(^{2+}\) is the same as the host ion for which it substitutes, simply replacing Zn\(^{2+}\) with Co\(^{2+}\) would not be expected to produce changes in the concentration of conduction electrons, and therefore, would not be expected to produce large changes in resistivity. This study has shown beyond doubt that the resistivity of ZnO single-phase material increases drastically as Co-dopant concentration increases. In order to rationalize this effect, it is necessary to consider how the process of Co incorporation could lead to a reduction in conduction electron concentration. It has been shown that, during sintering of blended cobalt oxide-zinc oxide powders, Co\(^{3+}\) reduces to Co\(^{2+}\) at around 900°C. This process releases oxygen. It is well-documented that exposure of undoped ZnO to an oxidizing atmosphere produces an increase in resistivity due to depletion of intrinsic donor defects [28-30].

Depending on whether the change in oxidation state occurs before incorporation or after incorporation of the Co, two different modes of conductivity suppression may be hypothesized. If it is assumed that reduction of Co\(^{3+}\) to Co\(^{2+}\) occurs before the Co diffuses into the
ZnO grains, then one may hypothesize that reduction of cobalt oxide at the surface of a ZnO grain releases oxygen that will produce an 'oxidized' outer zone in the ZnO grain. The oxygen either may diffuse inward to suppress such intrinsic donors as Zn\textsubscript{i} or V\textsubscript{O}, or the intrinsic donors may diffuse outward to meet the source of the oxygen. The reactions responsible for donor destruction may be conceptualized as

\[ O_i + Zn_i \overset{\leftrightarrow}{=} Zn_{Zn} + O_o \]

or

\[ O_i + V_o \overset{\leftrightarrow}{=} O_o \]  \hspace{1cm} (10)

In either case, the 'oxidized' outer zone of the ZnO grain would be depleted in its source of conduction electrons and would be a high resistivity region. If the Co enters ZnO as Co\textsuperscript{3+} (accompanied by extra oxygen) and later reduces to Co\textsuperscript{2+}, releasing the oxygen to combine with intrinsic donors like Zn\textsubscript{i} or V\textsubscript{O}, the effect would be to produce higher resistivity material in the Co-doped regions of the ZnO grains. The reactions responsible for donor destruction may be conceptualized as

\[ Co_3O_4 + Zn_i \overset{\leftrightarrow}{=} 3Co_{Zn} + Zn_{Zn} + 4O_o \]

or

\[ Co_3O_4 + V_o \overset{\leftrightarrow}{=} 3Co_{Zn} + 4O_o \]  \hspace{1cm} (11)
It seems likely, therefore, that the processes responsible for the large increase in resistivity of ZnO accompanying doping with cobalt oxide are linked to the oxygen released during reduction of Co^{3+} to Co^{2+}, rather than to the inherent effect of substitutional Co^{2+} on the resistivity of ZnO. These processes may convert entire ZnO grains to high resistivity material if the grain size is small enough for uniform doping to occur during sintering or will produce a higher resistivity region near the grain boundaries of ZnO grains that are too large to have been uniformly doped during the limited time at the sintering temperature.

Undoped and Zn-doped PrCoO\textsubscript{3} materials

A reproducible and stable threshold switching behavior was observed when microelectrodes were used to determine the dc current-voltage characteristics of several Zn-doped PrCoO\textsubscript{3} grains in two-phase threshold switching material. To further understand this observed behavior, electrical characteristics were studied for single-phase polycrystalline undoped and Zn-doped PrCoO\textsubscript{3} materials.

Table 6 lists the fabrication techniques, chemical compositions, and the conditions of sintered tablets for (a) Pr-Co oxide materials, (b) Pr-Co-Zn oxide materials fabricated by blending the three oxide powders, and (c) Pr-Co-Zn materials fabricated with the residue produced by leaching out the Co-doped ZnO grains from two-phase threshold switching materials. It was observed that the Co contents of sintered Pr-Co oxide materials were lower than those of the starting
Table 6a. Fabrication techniques, compositions, and conditions of the tablets of Pr-Co oxide materials

<table>
<thead>
<tr>
<th>Group name</th>
<th>Composition as blended (atom percent)</th>
<th>Condition of tablets after sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Pr</td>
</tr>
<tr>
<td>Pr excess</td>
<td>50 (49.03)</td>
<td>50 (50.97)</td>
</tr>
<tr>
<td></td>
<td>45 (42.38)</td>
<td>55 (57.62)</td>
</tr>
<tr>
<td></td>
<td>40 (37.95)</td>
<td>60 (62.05)</td>
</tr>
<tr>
<td>Co excess</td>
<td>60 (57.59)</td>
<td>40 (42.41)</td>
</tr>
<tr>
<td></td>
<td>51 (50.03)</td>
<td>49 (49.97)</td>
</tr>
</tbody>
</table>

\(^a\)Powder mixtures were reacted at 1200°C for 40 hours before the tablets were sintered at 1300°C for 10 hours.

\(^b\)Values in parentheses were measured using atomic absorption spectroscopy.

Table 6b. Fabrication techniques, compositions, and conditions of the tablets of Pr-Co-Zn oxide materials

<table>
<thead>
<tr>
<th>Composition as blended (atom fraction)</th>
<th>Condition of tablets after sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Co</td>
</tr>
<tr>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>1</td>
<td>0.96</td>
</tr>
<tr>
<td>1</td>
<td>0.61</td>
</tr>
</tbody>
</table>

\(^a\)The powder mixtures were reacted at 1200°C for 40 hours before the tablets were sintered at 1300°C for 10 hours.
Table 6c. Fabrication techniques, compositions, and conditions of the tablets of Pr-Co-Zn oxide materials

<table>
<thead>
<tr>
<th>Composition as blended (wt %)</th>
<th>Condition of tablets after sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-excess PrCoO₃</td>
<td>ZnO</td>
</tr>
<tr>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>56.6</td>
<td>43.4</td>
</tr>
<tr>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>43.2</td>
<td>56.8</td>
</tr>
<tr>
<td>25.3</td>
<td>74.7</td>
</tr>
</tbody>
</table>

a The powder mixtures were reacted at 1300°C for 10 hours, Co-doped ZnO grains were leached out using strong basic solution, and the residue was used to fabricate the materials sintered at 1300°C for 10 hours.

b Co-excess PrCoO₃ had 57.6 atom % Co and 42.4 atom % Pr.
powder mixtures, because the vapor pressure of Co oxide at the sintering temperature was higher than that of Pr oxide.

As noted in Table 6a, the tablets having excess Pr turned to powder after storage in laboratory air, which is similar to the behavior of simplified threshold switching materials. Dense tablets were produced at a sintering temperature of 1300°C. As is noted in Tables 6b and 6c, some tablets, especially those with higher Zn concentration, were melted at this temperature, indicating that Zn is involved in the formation of a low-melting phase or combination of phases. This observation will be discussed further in the following section.

Microstructure Figure 50 shows microstructures of undoped PrCoO₃ materials with slight excess quantities of Pr oxide and Co oxide. Co-excess PrCoO₃ materials contained inclusions which were darker than the matrix phase in a backscattered electron image. Such inclusions were not observed for Pr-excess (Co-deficient) materials. As is shown by scans of Co and Pr X-ray spectra across an inclusion, the inclusion is rich in Co, but contains very little Pr, so the inclusions are most probably unreacted cobalt oxide grains.

Figure 51 shows the microstructures of two Pr-Co-Zn oxide materials made by reacting blends of three oxides. Neither microstructure showed a homogeneous Pr-Co-Zn oxide phase, but rather two phases were always observed in the backscattered electron images. The material fabricated with a 0.1 Zn-0.9 Pr-1 Co oxide powder mixture contained inclusions similar to those shown in Zn-free Co-excess
Figure 50. Microstructures of Zn-free PrCoO$_3$ materials: (a) Pr-excess and (b) Co-excess
Figure 51. Microstructures produced by sintering mixed oxide powders: (a) 0.1 Zn-0.9 Pr-1 Co oxide and (b) 0.1 Zn-1 Pr-0.9 Co oxide
PrCoO₃ materials (Figure 50(b)). Figure 52 shows X-ray spectra generated at the spots indicated in Figure 51(a). The inclusions contained mainly Co and Zn, which probably means that the inclusions are Co-Zn oxide grains formed by reaction of the Zn oxide with the excess Co oxide remaining after PrCoO₃ was formed during sintering.

The material fabricated with a 0.1 Zn-1 Pr-0.9 Co oxide powder mixture contained an intergranular phase (Figure 51(b)). The tablets of this material disintegrated after storage in laboratory air. Although the specimen had not yet disintegrated when the photomicrograph of Figure 51(b) was taken, the grains had already started to separate. The grain size of the Pr-excess material (Figure 51(b)) was much larger than that of the Co-excess material (Figure 51(a)) even though the fabrication techniques were exactly the same for both materials. As is noted in Table 6b, the tablets of the Pr-excess materials were partially melted. Pr-excess materials without Zn did not melt at the sintering temperature, but those materials in which the Co deficiencies were compensated with Zn did melt. The degree of melting was observed to increase as the Zn content increased. The microstructure of partially-melted material always contained the intergranular phase shown in Figure 51(b). The X-ray spectrum generated from the intergranular phase, Figure 52(d), shows that the intergranular phase contained more Zn than the grains, Figure 52(c). It should be pointed out that the intergranular layers are so thin that X-ray spectra generated from a spot in the layer undoubtedly contains contributions from underlying grains. Based on
Figure 52. X-ray spectra from the spots indicated on Figure 51
the backscattered electron image brightness comparisons between the grains and the intergranular layer, it can be concluded that the layers are richer in higher atomic number elements (e.g., Pr) than the grains. These results seem to indicate that the intergranular layer, which presumably results from formation of a low-melting material, consists mainly of Pr oxide with small amounts of Co and Zn oxides also being present.

After leaching out most of the Co-doped ZnO grains from a reacted powder mixture of Co-excess PrCoO₃ and ZnO, and sintering the residue, inclusions were observed in the microstructures, as are shown in Figure 53. Figure 54 shows X-ray spectra generated from the spots indicated in Figure 53. The gray inclusions contained mainly Co with a small amount of Zn, which probably indicates that the inclusions are Zn-doped Co oxide grains which did not dissolve in the strong basic leaching solution.

Because it proved impossible to prepare single-phase polycrystalline Zn-doped PrCoO₃ material either from Pr-excess or Co-excess materials, the electrical characteristics were tested for the materials prepared by the leaching method which contained small amounts of the Zn-doped Co oxide inclusions.

**Electrical characteristics** Figure 55 shows the dc characteristics of single-phase undoped PrCoO₃ materials using three different types of electrodes: painted In-Ga, vacuum evaporated Al, and sputtered Au. The three specimens showed different characteristics even though they were all cut from the same tablet. All specimens
Figure 53. Microstructures of Pr-Co-Zn oxide materials fabricated with powders remaining after Co-doped ZnO grains were leached out. (a) 50 w/o ZnO, (b) 45 w/o ZnO, (c) 40 w/o ZnO, and (d) 30 w/o ZnO
Figure 54. X-ray spectra generated from the spots indicated in Figure 53(a)
Figure 55. Dc current-voltage drop characteristics of undoped single-phase PrCoO$_3$ material
showed ohmic behavior in the low voltage drop region, but the apparent ohmic resistivities for the three were quite different, as is indicated in Figure 55. At higher voltage drops, the specimens with In-Ga and Al electrodes showed nonohmic behavior with nonlinear coefficients around 3. The specimen with Au electrodes also showed an abbreviated region of nonohmic behavior at relatively higher current density. All specimens exhibited switching at similar current density values. After the specimens switched, their resistance dropped sufficiently so that high current densities resulted, and they broke into several pieces. Even though the specimens were broken after the initial switching, reproducible switching was subsequently observed for the pieces of the original specimens. The current-voltage drop characteristics of the 'on' state of the specimens could not be determined because of instrument limitations.

The differences in apparent resistivities of specimens having different electrode materials may be an indication that blocking contacts between the bulk and the electrode contribute to the resistances of some specimens. Three different methods were used to test for the presence of blocking contacts. Several of these methods also allowed determination of the bulk resistivity of undoped PrCoO$_3$ material.

Ac complex impedance spectroscopy is a good method to separate the sources of resistance of polycrystalline material. This method was described in the Ac Characteristics Section. Figure 56 shows ac complex impedance spectra obtained for the above three specimens.
Figure 56. Ac complex impedance spectra of undoped PrCoO$_3$ material. (a) In-Ga electrodes, (b) Al electrodes, (c) a magnified plot at high frequencies, and (d) with various applied ac voltages.
Figure 56. Continued
Figure 56. Continued
The specimens with In-Ga and Al electrodes showed single large arcs in the frequency range 230 Hz to 20 MHz (Figures 56(a) and (b), respectively). Figure 56(c) shows a magnified plot of the spectra of Figure 56(a) and (b) in the 20 Ω range. The left ends of the arcs for the specimens with In-Ga or Al electrodes did not approach zero impedance, indicating that there is at least one additional higher frequency arc in the total spectra of these specimens. Figure 56(c) also includes the impedance spectrum observed for the specimen with Au electrodes. The impedance data acquired for this specimen over a wide frequency range, 1 to 200 KHz, delineated only a small portion of an arc. The resistivity derived by extrapolating the arc for the Au electrode specimen to its right and was similar to the values derived by extrapolating the arcs of the In-Ga and Al electrode specimens to their left ends. During impedance measurements in PrCoO$_3$ materials at frequencies higher than 100 KHz, the instrument sometimes suddenly indicated a 'data overflow' condition, even though the expected impedance was not in the overflow range. The frequencies at which the instrument indicated overflow varied among different thicknesses and materials without showing any trend. For specimens with In-Ga electrodes, the impedance reading jumped at a particular frequency, as is indicated in Figure 56(a). Upon further testing, it was discovered that the frequency at which a specimen showed the impedance jump varied among different specimen thicknesses, test voltages, and materials. For example, Figure 56(d) shows ac complex impedance spectra for a specimen with In-Ga electrodes with two different ac
voltages applied. A jump in the data was observed with both applied voltages, but at different frequencies.

The measured value of bulk resistivity of any material should be independent of the specimen thickness. Any deviation from this rule in measured values of resistivity is a possible indication that electrode effects may be influencing the measurements. To test whether a blocking contact between the bulk and electrode contributes to the observed high resistivity of the specimens with In-Ga electrodes and to determine the true value of the bulk resistivity of single-phase polycrystalline undoped PrCoO$_3$ material, the apparent resistivities measured using different methods were related to specimen thickness. Figure 57 shows the summary of the resistivity-thickness observations. As thickness increased, the apparent dc resistivity of the specimens with In-Ga electrodes decreased, which may be an indication that the measured value of resistance used to calculate resistivity includes a contribution due to a blocking contact between the bulk and the In-Ga electrode. The values for resistivity derived from extrapolating to the left end of the ac impedance arc are constant independent of specimen thickness. This end of the arc represents either grain boundary or grain resistivity. The figure also includes resistivities calculated from resistance values measured using a four-point probe and a dc resistivity value for a specimen with Au electrodes. These latter resistivity values were similar to those derived from extrapolated ac resistance. All of these give the same value as that for the ac impedance method, and therefore, are free of any blocking
Figure 57. Relationship between resistivity and specimen thickness for undoped PrCoO$_3$ material.
contact effects; these values should, thus, be the true bulk resistivity of the material. The true values were around 100 Ω-cm, which is 10 times higher than the reported value of about 10 Ω-cm for PrCoO$_3$ at room temperature [52]. The difference between the measured values in this study and the reported value in reference [52] is probably due to differences in specimen preparation techniques.

To further establish the presence of blocking contacts, tablets imbedded in air-setting polymer were sectioned using the procedure described for Co-doped ZnO materials. A schematic figure for the specimen configuration is shown in Figure 43. Two tablets were tested, one with an In-Ga bottom electrode and the other with an Au bottom electrode. If a blocking contact was contributing to the high resistance observed for the specimen with an In-Ga bottom electrode, the resistance measured between two electrodes deposited on the same surface should become higher as the specimen thickness decreased to near zero, because the volume of the conduction path, which relates to the specimen thickness as well as to the separation between the two electrodes, would be decreased. However, it was expected for the specimen with an Au bottom electrode that the resistance measured between the two electrodes would become lower as the specimen thickness decreased to near zero, because of the formation of an additional current path shunted through the thickness to the high conductivity bottom Au electrode. Figure 58 shows the relationship observed between the measured resistance and specimen thickness for the two different bottom electrodes. The resistances for large thicknesses were
Figure 58. Relationship between measured resistance and thickness for undoped PrCoO$_3$. 
independent of the specimen thickness and of bottom electrode metal. But below 0.1 cm thickness, two different relationships between measured resistance and thickness were observed, as was predicted above. For the specimen having an Au bottom electrode, the measured resistance decreased as thickness decreased, probably indicating that a shunting current path was formed through the thickness and the bottom electrode. However, the measured resistance increased as thickness decreased for the specimen having an In-Ga bottom electrode, probably indicating that the effective area of current path decreased as the thickness decreased, because the In-Ga electrode blocked the hole movement.

Based on the above three tests, it can be concluded that In-Ga does indeed form a blocking contact on PrCoO₃. Using a hot probe test, it was observed that undoped and Zn-doped PrCoO₃ materials behaved as p-type semiconductors. As was discussed in the Literature Review Section, an ohmic contact between a p-type semiconductor and a metal electrode is provided by choosing an electrode metal having a higher work function than the semiconductor. The work function of Au is higher than those of either In-Ga or Al [80]. Also, based on the above three tests, it can be concluded that Au does indeed provide an ohmic contact on PrCoO₃.

To test for the presence of grain boundary effects in the measured resistivity of undoped PrCoO₃, the materials were annealed for up to 100 hours to provide for grain growth. During annealing, the tablets were covered with cobalt oxide powder to suppress the loss
of Co by vaporization at the annealing temperature. Because an increase in grain size reduces the relative amount of grain boundary material in a specimen, it would be expected that the resistivity would decrease as the grain size increased if the grain boundaries impede hole movement. Figure 59 shows the relationship observed between bulk resistivity and average grain size. As average grain size increased, bulk resistivity increased. This observation was contrary to the expected behavior, and it may indicate that the resistivity near grain boundary was lower than the grain core for undoped PrCoO$_3$ material.

To test the effect of Zn doping on the electrical characteristics of PrCoO$_3$, measurements were made on sintered Pr-Co-Zn oxide materials fabricated from the residue powders remaining after Co-doped ZnO grains were leached out of two-phase materials. Figure 60 shows the dc characteristics of specimens with three different electrode metals. These specimens were cut from the same sintered tablet. The dc characteristics of the material are similar to those for undoped PrCoO$_3$ material (Figure 55). Blocking contacts were also observed for the specimens with In-Ga or Al electrodes, as was discussed above for undoped PrCoO$_3$ material. Figure 61 shows ac complex impedance spectra of the specimens with the three different electrode metals. The specimens with electrode metals having lower work function, In-Ga or Al, showed similar spectra to those for undoped PrCoO$_3$ material with these same electrodes (see Figure 56(c)). For the specimen with Au electrodes, a difference was observed in the spectra of Zn-doped and
Figure 59. Relationship between resistivity and average grain size for undoped PrCoO$_3$ material.
Figure 60. Dc current-voltage drop characteristics of a Zn-doped PrCoO$_3$ material
Figure 61. Ac complex impedance spectra of a Zn-doped PrCoO$_3$ material
undoped PrCoO$_3$ specimens, in which a second arc was observed for the Zn-doped material.

Figure 62 shows ac complex impedance spectra of Pr-Co-Zn oxide materials fabricated from leached residues of powders having different ratios of Co-excess PrCoO$_3$ and ZnO. Au electrodes were used in all cases. Two arcs were observed for most materials. The arcs were extrapolated using a regression procedure to determine whether the left ends of the arcs approached zero impedance. All materials showed nonzero impedance at the left ends of the observed arcs, probably indicating the presence of additional small arcs at frequencies above those available with the instruments used in this study. Table 7 shows the extrapolated resistances assuming the ideal circuit model shown in Figure 11. The table also includes data on porosity measured using a water immersion technique. Brailsford and Hohnke [77] analyzed the contribution to ac impedance spectra due to intergranular porosity and claimed that the major effect of the infinite impedance of porosity is to enlarge $R_{gb}$, the resistance from grain boundaries. Figure 63 shows the relationship observed between the resistance due to grain boundary polarizations, $R_{gb}$, and total porosity for the materials. The resistance increased as the porosity increased.

Figure 64 shows the relationship between the resistivity derived from the extrapolated resistance for grains, $R_p$, and weight percent of ZnO powder in starting powder mixture. Resistivity was found to decrease as the content of ZnO in the original powder increased. If it is assumed that increased amounts of ZnO in the unreacted powders
Figure 62. Ac complex impedance spectra of Zn-doped PrCoO$_3$ materials
Table 7. Extrapolated resistance data for Pr-Co-Zn oxide materials

<table>
<thead>
<tr>
<th>Weight % of ZnO in starting powder mixture</th>
<th>$R_T^b$ (Ω)</th>
<th>$R_e^c$ (Ω)</th>
<th>$R_{b+gb}$ (Ω)</th>
<th>$R_{gb}^c$ (Ω)</th>
<th>$R_b^c$ (Ω)</th>
<th>Porosity $^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>23.5</td>
<td>12.74</td>
<td>10.76</td>
<td>9.53</td>
<td>1.23</td>
<td>7.66</td>
</tr>
<tr>
<td>45</td>
<td>108</td>
<td>14.69</td>
<td>93.31</td>
<td>90.72</td>
<td>2.59</td>
<td>14.52</td>
</tr>
<tr>
<td>40</td>
<td>244</td>
<td>-$^e$</td>
<td>244</td>
<td>238.55</td>
<td>5.45</td>
<td>20.73</td>
</tr>
<tr>
<td>35</td>
<td>76.6</td>
<td>7.97</td>
<td>68.63</td>
<td>62.64</td>
<td>5.99</td>
<td>12.50</td>
</tr>
</tbody>
</table>

$^a$ Amount of ZnO in starting powder mixture relates to amount of Zn in the Zn-doped PrCoO$_3$.

$^b$ $R_T = R_b + R_{gb} + R_e$.

$^c$ $R_b$, $R_{gb}$, and $R_e$ are the resistances from the grains (b), the grain boundaries (gb), and electrodes (e), respectively.

$^d$ Theoretical density of PrCoO$_3$ takes as 7.575 g/cm$^3$ [83].

$^e$ Only one arc was observed for this material.
SPECIMENS HAVE SIMILAR THICKNESSES AND ELECTRODE AREAS

Figure 63. Relationship between R_{gb} and total porosity of Zn-doped PrCoO_{3}
Figure 64. Relationship between grain resistivity and ZnO concentration in starting powder for Zn-doped PrCoO$_3$
before leaching translate into higher levels of Zn dissolved in the PrCoO$_3$ material remaining after leaching, then Figure 64 indicates the grain or bulk resistivity of PrCoO$_3$ decreases as Zn content increases. This is consistent with previous reports [53] that Zn behaves as an acceptor in PrCoO$_3$ and thereby, enhances its inherent p-type conductivity.

The observations of electrical characteristics of undoped and Zn-doped PrCoO$_3$ materials can be summarized as follows:

1. Undoped PrCoO$_3$ showed p-type semiconducting behavior, with a bulk resistivity around 100 $\Omega$-cm.

2. The materials showed blocking contacts with electrode metals having low work function, such as In-Ga and Al. However, ohmic contact was observed with Au electrodes.

3. Undoped and Zn-doped PrCoO$_3$ showed switching at high current density with damage being produced by high current flow in the 'on' state.

4. As grain size increased, the resistivity of the material increased.

5. As the level of Zn doping in PrCoO$_3$ increased, the resistivity of the material decreased.

Comparison Between Observations and the Hunter Model for Two-Phase Threshold Switching Materials: Proposal for a Better Model

The Hunter model for ZnO-based threshold switching materials proposed for testing in the initial stage of this study was based on
the assumption that the materials consist of n-type semiconducting ZnO grains separated by thin intergranular layers of amorphous material. However, this study has shown that very satisfactory switching materials can be produced with no observable intergranular layers in the microstructure. It is true that, for some seed grain threshold switching materials and some Pr-excess Pr-Co-Zn oxide materials, continuous intergranular layers were observed; however, the formation of such layers always resulted in the structure of the ceramic being unstable, with the tablets turning to powder after storing in laboratory air. It was observed that these layers consisted of a low-melting oxide phase containing Pr, Co, and some Zn. The exact chemical or crystalline nature of the layer could not be identified. Obviously, such layers should be avoided when attempting to fabricate stable structures of these types of threshold switching materials.

Schottky barriers in ZnO grains near the grain boundaries were proposed in the Hunter model, with an intergranular phase being required to form the barriers. However, measurements of electrical characteristics with microelectrodes showed a high resistance 'off' state within the interior of individual Co-doped ZnO grains. This may be due either to bulk behavior or to a blocking contact, but cannot be due to a near-grain-boundary barrier, because no grain boundary was present inside the grains. Further exploration of the electrical characteristics of single-phase polycrystalline Co-doped ZnO materials showed that the high resistivity was not due to a blocking contact between the bulk and the electrode metal. Also, no measurable grain
boundary contribution to the high resistivity of Co-doped ZnO was observed in single-phase material. Consequently, it is concluded that the Hunter model for threshold switching behavior of ZnO based materials is not satisfactory to explain the observations on microstructure and the electrical characteristics of the materials in this study.

Based on the observed microstructure of two-phase material and on the studies of the electrical characteristics of individual grains and interphase boundaries in the two-phase material as well as of single-phase polycrystalline materials which have compositions similar to the individual phases of the two-phase material, a general understanding of switching in the two-phase material is possible. Upon sintering of powder mixture of PrCoO$_3$ and ZnO, Co ions from PrCoO$_3$ diffuse into surrounding ZnO grains, and Zn ions from ZnO diffuse in neighboring PrCoO$_3$ grains; consequently, the two-phase material consists of Co-doped ZnO and Zn-doped PrCoO$_3$ phases. Using quantitative microstructural analysis technique [31], it was determined that the volume fraction of Zn-doped PrCoO$_3$ phase in the two-phase material studied was around 25 percent. This value, along with the microstructure shown in Figures 28(a) and (b), indicates that Zn-doped PrCoO$_3$ grains are fairly isolated from one another by surrounding Co-doped ZnO grains.

Figure 65 compares the current-voltage drop characteristics of the two-phase material, a single-phase polycrystalline Co-doped ZnO material (around 10 atom percent CZ material), and a single-phase
Figure 65. Dc current-voltage drop characteristics of a two-phase threshold switching material, a Co-doped ZnO material, and a Zn-doped PrCoO₃ material.
polycrystalline Zn-doped PrCoO$_3$ material. The particular Co-doped ZnO material was chosen to compare its characteristics to those of the two-phase material, because the relative intensity of Co X-ray from an energy dispersive analysis of this material was similar to that of Co-doped ZnO grains of the two-phase material and also because the particle size of prereacted PrCoO$_3$ in the starting powder mixture of the two-phase material was similar to that of untreated Co$_3$O$_4$ powder in the starting powder mixture of CZ Co-doped ZnO material. The particular Zn-doped PrCoO$_3$ material was arbitrarily chosen, since the electrical characteristics of PrCoO$_3$ did not differ much with doping concentration and distribution. On the other hand, the electrical characteristics of PrCoO$_3$ material did change with different electrode metals. Therefore, the electrical characteristics of Figure 65 were all determined using the same electrode metal, In-Ga. The three materials showed ohmic behavior at low electric fields. At different electric fields, these three materials changed to nonohmic characteristics with nonlinear coefficients, $\alpha$, around 4. Each of these three materials exhibited switching to a low-resistance 'on' state. In the 'off' state, the ohmic resistivity of the two-phase material was similar to that of the Co-doped ZnO material, but was much higher than that of the Zn-doped PrCoO$_3$ material. Because the Zn-doped PrCoO$_3$ grains are isolated by surrounding Co-doped ZnO grains in the two-phase material, the low resistive Zn-doped PrCoO$_3$ grains do not contribute significantly to the ohmic resistivity of the two-phase material. Instead, the high observed ohmic resistivity of the two-phase
material is mainly due to the high resistive Co-doped ZnO grains. The increase in bulk ohmic resistivity produced by doping ZnO with Co is discussed in the section entitled Studies on Single-Phase Polycrystalline Materials. The threshold field, $V_{TH}/d$, of the Zn-doped PrCoO$_3$ material is much lower than those of the two-phase material and the Co-doped ZnO material. If the Zn-doped PrCoO$_3$ grains contributed strongly to the electrical characteristics of the two-phase material, its characteristics would show some indication as the PrCoO$_3$ grains switched at their characteristic field value. No such indication was observed. Based on these comparisons, it can be concluded that the Zn-doped PrCoO$_3$ grains do not make significant contribution to the overall observed 'off' state electrical characteristics of the two-phase material. Instead, the Co-doped ZnO grains are principally responsible for the 'off' state electrical characteristics of the two-phase material.

The studies of the electrical characteristics of individual Co-doped ZnO grains using microelectrodes showed 'damaged traces' in the outer Co-doped region of the grains. This observation suggests that the observed 'on' state of the two-phase material is due to filamentary conduction, which has often been observed in other switching materials [84, 85]. As was discussed in the section entitled Tests of Combinations of Co-Doped ZnO and Zn-Doped PrCoO$_3$ Grains, the filament, 'damaged trace', did not follow a straight line path between the electrodes, but usually branched into two or three paths. Therefore, the effective area of the current path through the specimen in the 'on' state is indeterminant.
Two-phase threshold switching materials showed a permanent reduction in threshold voltage drop, $V_{TH}$, after the first sweep. As was shown in the studies of the electrical characteristics of individual Co-doped ZnO grains using microelectrodes, the Co-doped ZnO grains were conductive after being damaged by excess current in the 'on' state. Even though single-phase polycrystalline Co-doped ZnO specimens did not show microscopic evidence of permanent breakdown at the initial switching, these specimens showed a permanent reduction in threshold voltage drop for subsequent sweeps. If a portion of the Co-doped ZnO phase is permanently damaged during the initial sweep by high current in the 'on' state, this may have the effect of reducing the effective thickness of high resistance material for subsequent sweeps, and would be expected to result in a reduction in the threshold voltage drop necessary for switching in subsequent sweeps. In support of this argument, Figure 28 shows that initial sweep threshold voltage drop for the two-phase material decreases as thickness of the undamaged specimen decreases. It was also observed that the magnitude of the permanent reduction in threshold voltage drop depended on the 'on' state current flowing after the specimen switched (the current was controlled by adjusting a current limiting resistor in the measuring circuit, Figure 3).
CONCLUSIONS

1. The multiphase microstructures of multicomponent threshold switching materials were too complex to be adequately characterized by the methods available to this investigator, and, consequently, correlation of electrical characteristics with microstructure could not be accomplished for these materials. It is nevertheless likely that the switching action would be closely related to the microstructure of these materials.

2. A simplified two-phase threshold switching material was identified. The material, produced by sintering mixtures of ZnO and prereacted PrCoO$_3$ powders, consisted of two major phases: Co-doped ZnO and Zn-doped PrCoO$_3$. The switching characteristics of the material depended on the fabrication technique and the measuring parameters during the test. The high ohmic resistance probably included a contribution from a blocking contact between the bulk and the In-Ga electrode.

3. The roles of individual grains in the switching behavior of the two-phase material were identified. Pristine individual Co-doped ZnO grains in the two-phase material showed high resistance. However, electrical breakdown occurred at a relatively high voltage drop during the initial sweep, and the switched grain became permanently conductive for subsequent sweeps. The Zn-doped PrCoO$_3$ grains in the two-phase material exhibited stable and reproducible threshold switching at relatively low threshold voltage drops.
4. Undoped ZnO showed n-type semiconducting behavior with a resistivity around \( 1 \, \Omega \cdot \text{cm} \). Upon being doped with Co, the resistivity of ZnO increased, and Co-doped ZnO materials exhibited threshold switching behavior instead of the breakdown which was observed for individual Co-doped ZnO grains in two-phase threshold switching material. It is important to realize that the difference between switching followed by 'breakdown' and reversible switching is just a matter of the magnitude of the current flow permitted in the 'on' state. The high resistivity was shown not to be due to a blocking contact between the bulk material and electrode metal, but rather was a bulk property.

5. A model was proposed to explain the resistivity increase of ZnO produced by doping with Co. The model proposed the suppression of intrinsic donor defects through oxidation by oxygen freed when Co\(^{3+}\) ions reduced to Co\(^{2+}\) during the sintering process.

6. Undoped and Zn-doped PrCoO\(_3\) showed p-type semiconducting behavior. A blocking contact was observed between the bulk material and electrode metals having low work function. Reproducible threshold switching behavior was observed for undoped and Zn-doped PrCoO\(_3\) materials at relatively high current levels.

7. The resistivity of undoped PrCoO\(_3\) was around 100 \( \Omega \cdot \text{cm} \). Upon being doped with Zn, the resistivity of PrCoO\(_3\) decreased. This observation was explained by assuming that Zn in PrCoO\(_3\) behaves as an acceptor due to the ionic state difference between the dopant and the host ion.
8. The Zn-doped PrCoO$_3$ grains do not appear to contribute to the overall observed 'off' state electrical characteristics of the two-phase switching material. Instead, the Co-doped ZnO grains solely determine the 'off' state electrical characteristics of the two-phase material.

9. The permanent reduction in threshold voltage drop of threshold switching materials for consecutive sweeps was due to permanent damage in some of the Co-doped ZnO grains during the high current 'on' state of the preceding sweep.
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Finally, I would like to acknowledge the patience, encouragement, and understanding of my wife, Kyungok, my parents, and my two daughters, Hannah and Jane Lee, throughout this work.
APPENDIX A: 'SPACE-CHARGE-LIMITED' (SCL) CONDUCTION FOR SOLIDS HAVING TRAPS
The 'space-charge-limited' (SCL) current density for trap free solids is given by [11]:

\[ J = 9e\mu V^2/8d^3 \]  

But, perfect crystals are never encountered; traps and recombination centers are always more or less present. The voltage square law given in Eq. (2) is observed for solids containing traps only after all traps are filled. The energies of traps are distributed in accordance with certain distribution functions in polycrystalline materials [12]. The general scaling rule [86, 87] for solids with any trap distributions can be expressed in the form of

\[ \frac{J}{d_{\text{eff}}} = f\left[\left(\frac{V}{d_{\text{eff}}^2}\right)^n\right] \]  

where \( d_{\text{eff}} \) is effective specimen thickness, taking into account the effect of nonuniform spatial distribution of traps [9]. This equation is universally valid provided that the carrier mobility is field independent, and that the effect of carrier diffusion is ignored [9]. The magnitude of \( n \) reflects the type of trap distribution. As an example, for the solids having deep traps distributed Gaussianly within the forbidden energy gap [88],

\[ n = m + 1 \]

and
where $\sigma_t$ is the standard deviation of the Gaussian function, $k$ is the Boltzmann constant, and $T$ is absolute temperature. For some solids, $m$ has been observed to be 4 [89], which provides a higher slope of nonohmic current-voltage characteristics than the predicted slope, 2, for trap free solids using Eq. (2) ($m=1$). This higher slope will be maintained until all traps are filled (see Figure 1).
APPENDIX B: EFFECT OF THE LOAD RESISTANCE ON THE MEASURED CURRENT-VOLTAGE DROP CHARACTERISTICS OF THRESHOLD SWITCHING MATERIALS
When the current-voltage characteristics of a material are tested, a load resistor is usually used to protect the material against an overpower situation. Some series resistances exist in any measuring circuit even without an identified load resistor. The following discussion concerns the effect of the load resistor on the measured current-voltage drop characteristics of threshold switching materials.

Figure 66 shows a schematic representation of the measuring circuit which was used in this study. The current through the circuit and the voltage drop across the specimen can be expressed as

\[ I = \frac{V_a}{R_s + R_L} \]

and

\[ V_D = I R_s = V_a \frac{R_s}{R_s + R_L} \]

Figure 66. A schematic representation of a measuring circuit
respectively, where $V_a$ is the dc applied voltage, and $R_s$ and $R_L$ are the resistances of the specimen and the load resistor. If there is no load resistor, $R_L = 0$, then, the voltage drop across the specimen will be the same as the applied voltage, independent of the specimen resistance, as is calculated in the example in Table 8(a). Because the applied voltage remains fixed at 1000 V which the specimen abruptly makes a high resistance (10 MΩ) 'off' state to a low resistance (10 kΩ) 'on' state, the transition will follow trace (a) in Figure 67. This situation is only possible for an ideal circuit, which has no resistance except the specimen resistance. If there is a 10 kΩ load resistor in the measuring circuit, then the current and the voltage drop across the specimen are calculated using Eq. (11), as is shown in Table 8(b). Even though the applied voltage remains fixed at 1000 V, $V_D$, the voltage drop across the specimen, changes to a lower value after the specimen switches. In this case, the transition will follow the trace (b) in Figure 67. The assumed values in this example are close to the values which were used and observed in this study.

The current-voltage drop characteristics of the specimen in the 'on' state depend on how much resistance changes in the specimen per increment of applied voltage. Table 9 shows two different calculations based on two different resistances at the same applied voltage of 1500 V. Figure 68 shows the trace for these two cases. Slopes of either sign can be observed. Case (b) (negative slope) was always observed in the current-voltage drop characteristics of the threshold switching materials in this study.
Table 8. Example calculations of the current and the voltage drop across the specimen based on the resistance of the specimen changing from 10 MΩ to 10 kΩ at 1000 V applied voltage

<table>
<thead>
<tr>
<th>State</th>
<th>$R_L$ (KΩ)</th>
<th>$V_a$ (V)</th>
<th>$R_s$ (KΩ)</th>
<th>$I$ (mA)</th>
<th>$V_D$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFF</td>
<td>0</td>
<td>1000</td>
<td>$1 \times 10^4$</td>
<td>0.1</td>
<td>1000</td>
</tr>
<tr>
<td>ON</td>
<td>0</td>
<td>1000</td>
<td>10</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>(a) $R_L = 0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OFF</td>
<td>10</td>
<td>1000</td>
<td>$1 \times 10^4$</td>
<td>0.1</td>
<td>1000</td>
</tr>
<tr>
<td>ON</td>
<td>10</td>
<td>1000</td>
<td>10</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>(b) $R_L = 10$ kΩ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Example calculations of the current and voltage drop across the specimen based on two different 'on' state resistances at 1500 V applied voltage

<table>
<thead>
<tr>
<th>Case</th>
<th>$R_L$ (KΩ)</th>
<th>$V_a$ (V)</th>
<th>$R_s$ (KΩ)</th>
<th>$I$ (mA)</th>
<th>$V_D$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ON</td>
<td>10</td>
<td>1000</td>
<td>10</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>(a)</td>
<td>10</td>
<td>1500</td>
<td>8</td>
<td>83</td>
<td>664</td>
</tr>
<tr>
<td>(b)</td>
<td>10</td>
<td>1500</td>
<td>4</td>
<td>107</td>
<td>428</td>
</tr>
</tbody>
</table>
Figure 67. Current-voltage drop traces for the example calculated in Table 8

Figure 68. Current-voltage drop traces for the example calculated in Table 9