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Flux growth at ambient pressure of millimeter-sized single crystals of LaFeAsO , $\text{LaFeAsO}_{1-x}\text{F}_x$, and $\text{LaFe}_{1-x}\text{Co}_x\text{AsO}$

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Flux growth at ambient pressure of millimeter-sized single crystals of LaFeAsO, LaFeAsO_{1-x}F_x, and LaFe_{1-x}Co_xAsO

Abstract

Millimeter-sized single crystals of LaFeAsO, LaFeAsO_{1-x}F_x, and LaFe_{1-x}Co_xAsO were grown in NaAs flux at ambient pressure. The detailed growth procedure and crystal characterizations are reported. The as-grown crystals have typical dimensions of 3×4×0.05–0.3 mm³ with the crystallographic *c*-axis perpendicular to the plane of the platelike single crystals. Various characterizations confirmed the high quality of our LaFeAsO crystals. Co and F were introduced into the lattice leading to superconducting LaFe_{1-x}Co_xAsO and LaFeAsO_{1-x}F_x single crystals, respectively. This growth protocol is expected to be broadly applicable to grow other RMAOs (*R* = rare earth, *M* = transition metal) compounds.

Keywords

Physics and Astronomy, Materials Science and Engineering, cobalt compounds, crystal growth from solution, electrical resistivity, high-temperature superconductors, iron compounds, lanthanum compounds, lattice constants, magnetic susceptibility, magnetisation

Disciplines

Condensed Matter Physics | Metallurgy

Comments

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Flux growth at ambient pressure of millimeter-sized single crystals of LaFeAsO, LaFeAsO_{1-x}F_x, and LaFe_{1-x}CoxAsO

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Flux growth at ambient pressure of millimeter-sized single crystals of LaFeAsO, LaFeAsO_{1-x}F_x, and LaFe_{1-x}Co_xAsO

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Millimeter-sized single crystals of LaFeAsO, LaFeAsO_{1-x}F_x, and LaFe_{1-x}Co_xAsO were grown in NaAs flux at ambient pressure. The detailed growth procedure and crystal characterizations are reported. The as-grown crystals have typical dimensions of 3×4×0.05–0.3 mm³ with the crystallographic *c*-axis perpendicular to the plane of the platelike single crystals. Various characterizations confirmed the high quality of our LaFeAsO crystals. Co and F were introduced into the lattice leading to superconducting LaFe_{1-x}Co_xAsO and LaFeAsO_{1-x}F_x single crystals, respectively. This growth protocol is expected to be broadly applicable to grow other *RMA*SO (*R*=rare earth, *M*=transition metal) compounds. © 2009 American Institute of Physics.

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After the initial report of superconductivity with $T_c \sim 26$ K in LaFeAsO_{1-x}F_x,¹ the maximum superconducting transition temperature for this class of materials was quickly raised to ~ 55 K by replacing La with other rare earth elements² or applying an external pressure.³ Shortly after, superconductivity with T_c up to 38 K was observed in doped AFe₂As₂ (*A*=Ca, Sr, Ba, and Eu, “122”) compounds,⁴ which share the same structural unit of FeAs layers with the *R*FeAsO (*R*=rare earth, “1111”) system. Although the 1111 system was discovered earlier and manifests a higher T_c , the focus of the scientific community has shifted toward the 122 systems because (1) sizeable high quality single crystals of the 122 system have been produced by many groups and both electron and hole doping can be systematically manipulated,^{5–12} and (2) the growth of large single crystals of the 1111 system has been proven to be difficult so that the largest crystals are still in submillimeter size despite extensive efforts.^{13–15} Under ambient pressure, platelike NdFeAsO_{1-x}F_x crystals with the lateral size ranging from 5 to 30 μm and thickness of 1–5 μm can be grown by the flux method using NaCl as the flux.¹⁵ High pressure growth has generally been more successful in growing larger crystals from the NaCl flux and typical crystals have dimensions of the order of 300 μm.^{13,14} A recent work reported the growth of CeFeAsO single crystals with the largest dimension reaching 600 μm in Sn flux.¹⁶ In this letter, we report the details of the flux growth at ambient pressure and characterizations of millimeter sized single crystals of both undoped and doped LaFeAsO.

Both pre-fired LaFeAsO and precursor mixture of LaAs, 1/3 Fe₂O₃, and 1/3 Fe were used as the charge in the growth. NaAs flux was prepared by reacting Na and As chunks in a sealed Ta tube. The Ta tube was sealed in a quartz ampoule and heated to 600 °C at the rate of 30 °C per hour and held at temperature for 12 h. The charge and NaAs flux with the molar ratio of 1:20 were mixed and sealed in a Ta tube under

$\sim 1/3$ atmosphere of argon gas. The Ta tube was then sealed in an evacuated quartz tube. To ensure safety, the quartz tube was then loaded into an Inconel tube. The entire assembly was then heated in a tube furnace, with a quartz retort under flowing nitrogen, to 1150 °C at a rate of 90 °C per hour. After holding at 1150 °C for 24 h, it was cooled to 600 °C at 3 °C per hour followed by a furnace quench to room temperature. As NaAs is highly hydrophilic, the separation of the crystals from flux is easily accomplished by rinsing them with deionized water in a closed fume hood.

The inset of Fig. 1(a) shows a picture of a single crystal of LaFeAsO against a millimeter scale. The as-grown crystals are platelike with typical dimensions of 3×4×0.05–0.3 mm³. Some crystals manifest linear dimensions as large as 4–5 mm. The crystallographic *c*-axis is perpendicular to the plane of the platelike single crystals. Figure 1(a) shows a rocking curve for the (1 1 7) reflection. The measured mosaicity of the crystal was 0.04° full width half maximum for the (1 1 7) reflection at room temperature, indicating the excellent quality of the single crystal. Room temperature powder x-ray diffraction on crushed crystals confirmed that the crystals are single phase [see Fig. 1(b)] with lattice parameters, $a=4.022(2)$ Å and $c=8.746(6)$ Å, consistent with previous reports.^{17–19} Elemental analysis performed using wavelength dispersive x-ray spectroscopy (WDS) in a JEOL JXA-8200 Superprobe electron probe microanalyzer confirmed the atomic ratio of 1:1:1:1 with no noticeable compositional variation of the atomic ratio across the crystal. In particular, we carefully sampled for evidence of Na on clean and cleaved surfaces of various pieces and none was found. The measured structural and magnetic transition temperatures, presented below, agree with previous reports on polycrystalline samples, ruling out the possible substitution of La by Na. Since the starting materials were also exposed to quartz or Ta tubes, we also searched for possible incorporation of Si and Ta. No sign of Si was found but we observed ~ 0.2 at. % Ta homogeneously distributed in the bulk.

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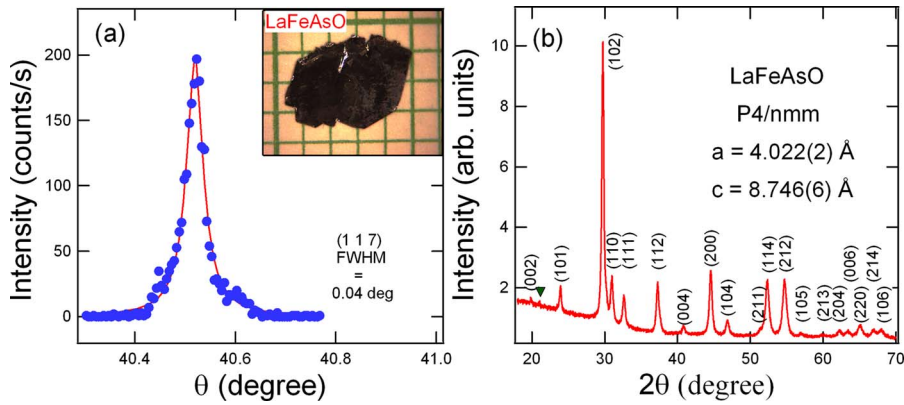


FIG. 1. (Color online) (a) Rocking curve through the (1 1 7) reflection of the LaFeAsO single crystal used for the x-ray diffraction study. Inset: picture of a LaFeAsO single crystal on millimeter grid paper. (b) Powder x-ray diffraction pattern of pulverized LaFeAsO single crystals. The weak extra diffraction peak (\blacktriangledown) at $2\theta \sim 21^\circ$ is from sodium arsenate hydrate.

Single crystals of comparable quality could be obtained by starting with either pre-fired polycrystalline LaFeAsO or precursor mixture ($\text{LaAs} + 1/3 \text{Fe}_2\text{O}_3 + 1/3 \text{Fe}$). The former generally leads to crystals with smaller lateral size. Also, depending on the purity of starting materials, needle like FeAs crystals were sometimes observed.

Figure 2(a) shows the temperature dependence of magnetic susceptibility $\chi = M(T)/H$ measured with a quantum design magnetic property measurement system. There is a clear anisotropy with $\chi_{ab} > \chi_c$ over the entire temperature range of 2–300 K. While cooling, both χ_{ab} and χ_c show a steplike anomaly starting at $T_s \sim 153$ K. The starting temperature and the Curie–Weiss-type tail at low temperatures agree well with previous reports on magnetic properties of polycrystalline samples.^{19,20} Specific heat and in-plane electrical resistivity measurements²¹ were also performed on LaFeAsO single crystals and observed anomalies at ~ 153 K.

Temperature dependent, single crystal x-ray and neutron diffraction experiments provided direct evidence for the structural and magnetic transitions in our crystals. Single crystal x-ray diffraction measurements were performed using high energy x rays at the station 6-ID-D in the MU-CAT sector of the Advanced Photon Source, Argonne National Laboratory. The evolution of orthorhombic distortion as a function of temperature was extracted from the splitting of the (2 2 0) diffraction spots using the program FIT2D (Ref. 22) and shown in Fig. 2(b). The sharp increase in the orthorhombic distortion below $T_s \sim 154.5$ K confirms the structural transition from tetragonal $P4/nmm$ to orthorhombic $Cmma$ in our LaFeAsO crystals.

Single crystal neutron diffraction measurement was performed using the Ames Laboratory HB1A fixed-incident-

energy triple-axis spectrometer at the High Flux Isotope Reactor of Oak Ridge National Laboratory. The order parameter was measured by sitting on the (1/2 1/2 3/2) magnetic peak position and slowly ramping the temperature from 10 to 180 K while counting in ~ 3 minutes time intervals. The temperature dependence of the intensity of the magnetic reflection (1/2 1/2 3/2) clearly shows the onset of magnetic order at $T_{SDW} \sim 140$ K, [see Fig. 2(b)] which is about 14 K below T_s . The transition temperatures agree with those determined by anisotropic magnetization, in-plane electrical resistivity and specific heat measurements and are consistent with previous reports on polycrystalline samples.^{1,18–20}

Having demonstrated that NaAs is a suitable flux for the growth of the parent compound LaFeAsO, we extended the growth to the doped $\text{LaFe}_{1-x}\text{Co}_x\text{AsO}$ and $\text{LaFeAsO}_{1-x}\text{F}_x$ series by partially replacing Fe with Co and NaAs with NaF, respectively. A number of single crystals with various doping contents have been grown. WDS analysis of cleaved surfaces confirms that the doping element entered into the lattice [see Figs. 3(a) and 3(b)] for both series. As with the parent compound, WDS analysis found no sign of Na but ~ 0.2 at. % of Ta in all of our doped crystals. Figures 3(c) and 3(d) show the low-field magnetization and in-plane resistivity of two superconducting compositions. While the content of Co doping could be accurately determined by WDS analysis, WDS has difficulty in accurately determining the ratio of O:F at these levels. For the crystal shown in Fig. 3(a), a tentative composition suggested by WDS is $\text{LaFeAsO}_{0.91}\text{F}_{0.09}$, while superconductivity was observed at $T_c \sim 11$ K from magnetization and electrical resistivity measurements. According to the phase diagram of $\text{LaFeAsO}_{1-x}\text{F}_x$,¹ a $T_c \sim 11$ K suggests a

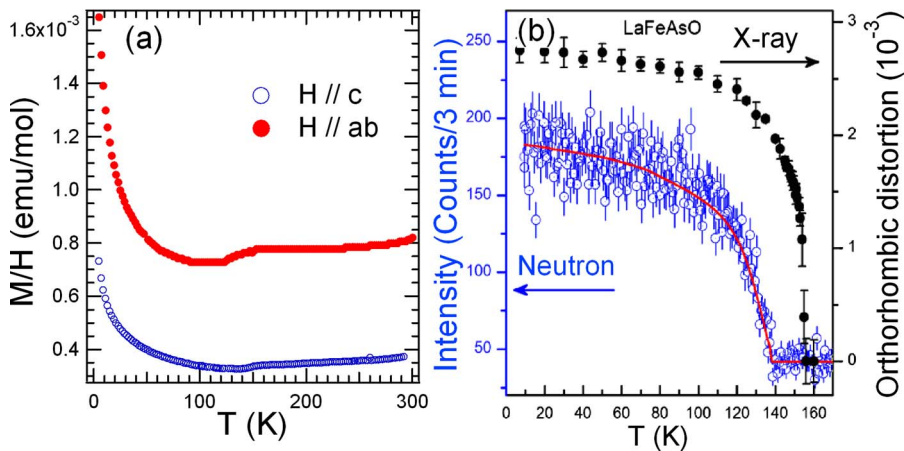


FIG. 2. (Color online) (a) The temperature dependence of magnetization of a LaFeAsO crystal measured under a magnetic field of 30 kOe. (b) The temperature dependence of orthorhombic distortion (x ray) and intensity of the magnetic reflection (1/2 1/2 3/2) (Neutron) of a LaFeAsO crystal.

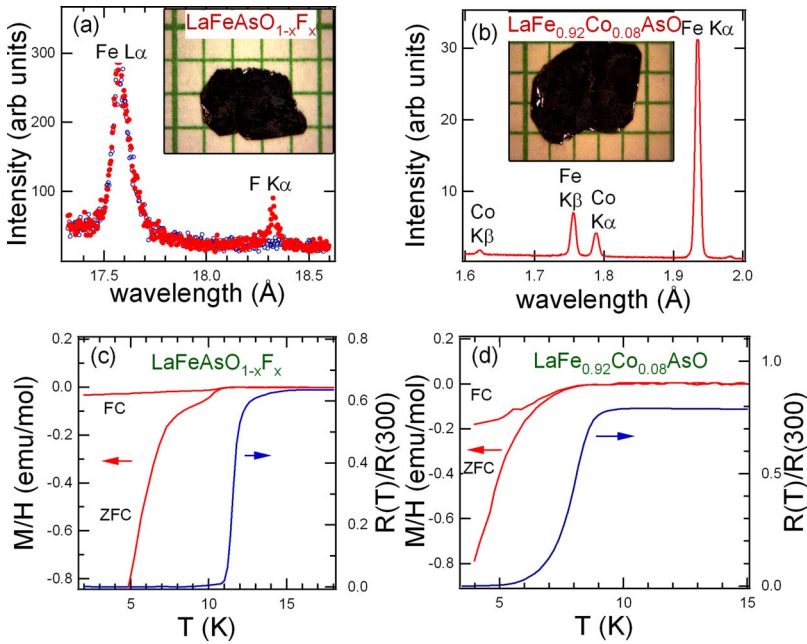


FIG. 3. (Color online) Electron microprobe spectrum of x-ray intensity vs wavelength for (a) the F-doped sample (●) compared to a F-free sample (○) and (b) Co-doped LaFeAsO. Insets show pictures of crystals on millimeter grid paper. Low-field M/H data measured under a field of 35 Oe perpendicular to c -axis and in-plane electrical resistivity for (c) a F-doped crystal and (d) LaFe_{0.92}Co_{0.08}AsO.

composition of LaFeAsO_{0.97}F_{0.03} with the F-content lower than our estimate. Whether this discrepancy arises from the uncertainty of our elemental analysis, or the suppression of superconductivity by 0.2 at. % Ta, remains to be resolved.

In summary, we have grown LaFeAsO, LaFe_{1-x}Co_xAsO, and LaFeAsO_{1-x}F_x crystals with sizes up to 4–5 mm from a NaAs flux at ambient pressure. Proof of concept growths of doped and undoped NdFeAsO crystals have been performed and we therefore expect that NaAs flux can be applied to crystal growth of other RMA_sO (M =transition metal) members. The availability of these sizeable single crystals will enable comparisons to be made with AFe_2As_2 systems and cuprate superconductors using a variety of techniques, hopefully leading to a complete understanding of the iron pnictide superconductors.

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