Noncentrosymmetric Tetrel Pnictides RuSi4P4 and IrSi3P3: Nonlinear Optical Materials with Outstanding Laser Damage Threshold

Shannon Lee  
*Iowa State University and Ames Laboratory,* shelee@iastate.edu

Scott L. Carnahan  
*Iowa State University and Ames Laboratory,* scottc@iastate.edu

Georgiy Akopov  
*Ames Laboratory,* gakopov@ameslab.gov

Philip Yox  
*Iowa State University and Ames Laboratory,* pyox@iastate.edu

Lin-Lin Wang  
*Ames Laboratory,* llw@ameslab.gov

*See next page for additional authors*

Follow this and additional works at: [https://lib.dr.iastate.edu/chem_pubs](https://lib.dr.iastate.edu/chem_pubs)

Part of the [Materials Chemistry Commons](https://lib.dr.iastate.edu/chem_pubs)

The complete bibliographic information for this item can be found at [https://lib.dr.iastate.edu/chem_pubs/1293](https://lib.dr.iastate.edu/chem_pubs/1293). For information on how to cite this item, please visit [http://lib.dr.iastate.edu/howtocite.html](http://lib.dr.iastate.edu/howtocite.html).

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Noncentrosymmetric Tetrel Pnictides RuSi4P4 and IrSi3P3: Nonlinear Optical Materials with Outstanding Laser Damage Threshold

Abstract
Noncentrosymmetric (NCS) tetrel pnictides have recently generated interest as nonlinear optical (NLO) materials due to their second harmonic generation (SHG) activity and large laser damage threshold (LDT). Herein nonmetal-rich silicon phosphides RuSi4P4 and IrSi3P3 are synthesized and characterized. Their crystal structures are reinvestigated using single crystal X-ray diffraction and 29Si and 31P magic angle spinning NMR. In agreement with previous report RuSi4P4 crystallizes in NCS space group $P_1$, while IrSi3P3 is found to crystallize in NCS space group $Cm$, in contrast with the previously reported space group $C2$. A combination of DFT calculations and diffuse reflectance measurements reveals RuSi4P4 and IrSi3P3 to be wide bandgap ($E_g$) semiconductors, $E_g = 1.9$ and $1.8$ eV, respectively. RuSi4P4 and IrSi3P3 outperform the current state-of-the-art infrared SHG material, AgGaS2, both in SHG activity and laser inducer damage threshold. Due to the combination of high thermal stabilities (up to 1373 K), wide bandgaps ($≈ 2$ eV), NCS crystal structures, strong SHG responses, and large LDT values, RuSi4P4 and IrSi3P3 are promising candidates for longer wavelength NLO materials.

Keywords
laser damage threshold, noncentrosymmetric crystal structures, second harmonic generation, tetrel pnictides

Disciplines
Materials Chemistry

Comments

Authors

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/chem_pubs/1293
Noncentrosymmetric Tetrel Pnictides RuSi₄P₄ and IrSi₃P₃: Nonlinear Optical Materials with Outstanding Laser Damage Threshold

Shannon Lee, Scott L. Carnahan, Georgiy Akopov, Philip Yox, Lin-Lin Wang, Aaron J. Rossini, Kui Wu, and Kirill Kovnir*

Noncentrosymmetric (NCS) tetrel pnictides have recently generated interest as nonlinear optical (NLO) materials due to their second harmonic generation (SHG) activity and large laser damage threshold (LDT). Herein nonmetal-rich silicon phosphides RuSi₄P₄ and IrSi₃P₃ are synthesized and characterized. Their crystal structures are reinvestigated using single crystal X-ray diffraction and ²⁹Si and ³¹P magic angle spinning NMR. In agreement with previous report RuSi₄P₄ crystallizes in NCS space group P₁, while IrSi₃P₃ is found to crystallize in NCS space group Cm, in contrast with the previously reported space group C₂. A combination of DFT calculations and diffuse reflectance measurements reveals RuSi₄P₄ and IrSi₃P₃ to be wide bandgap (Eₒ) semiconductors, Eₒ = 1.9 and 1.8 eV, respectively. RuSi₄P₄ and IrSi₃P₃ outperform the current state-of-the-art infrared SHG material, AgGaS₂, both in SHG activity and laser induce damage threshold. Due to the combination of high thermal stabilities (up to 1373 K), wide bandgaps (=2 eV), NCS crystal structures, strong SHG responses, and large LDT values, RuSi₄P₄ and IrSi₃P₃ are promising candidates for longer wavelength NLO materials.

1. Introduction

Noncentrosymmetric (NCS) intermetallics exhibit a plethora of emergent properties, such as unconventional superconductivity, topologically non-trivial quantum properties over large energy windows, piezoelectricity, and nonlinear optical properties.[¹–⁴] The fundamental driving force for the formation of these NCS structures is not yet well understood. For ionic compounds, the use of NCS building blocks, such as IO⁻ or a combination of mixed anions (O/F) was proven to be effective to realize NCS structures.[⁴–⁷] However, for intermetallics with small differences in electronegativities of all constituent elements, there is no clear concept how to produce NCS structures. Among binary transition metal (M) phosphides and silicides the total number of NCS phases is relatively low. To avoid substantial metal–metal bonding, we consider only materials where the metal content is <50%. For hundreds of known binary transition metal silicides and phosphides with M/Si or M/P < 1, less than 10% have been reported to crystallize in NCS structures.

In turn, for ternary transition metal silicon phosphides, M–Si–P, with M/(Si+P) < 1, the number of NCS is drastically higher at ~95%.[⁸] The Si and P form NCS local coordination around the transition metal, made possible by the high structural flexibility demonstrated by the Si-P framework. Additionally, SiP₄ tetrahedra are capable of forming networks by sharing corners and edges, similar to SiO₄ tetrahedra seen in silicates.[⁹–¹²] Distinct from silicates, the formation of Si–Si and P–P bonds are also possible, as is exhibited in A-Si-P systems, A = alkali or alkaline-earth metals.[¹²–¹⁸] Unlike large electropositive cations, transition metals may form strong covalent bonds with Si and P, thus higher chemical, thermal, and radiation stability is expected.

Recent discoveries of NCS ternary tetrel pnictides (Ba₃Si₃P₆, MgSiAs₂, and MnSiP₃)[¹¹,¹³,¹⁹] demonstrate promise in nonlinear optical (NLO) applications in the infrared region of the electromagnetic spectra due to strong second harmonic generation (SHG) activity and exceptional laser damage threshold (LDT). NLO materials can upconvert incoming frequencies of light. The infrared region is important for applications in optoelectronic devices, remote detection of explosive materials, biomolecular sensing, and long-distance laser communications.[²⁰–²³] NLO materials should combine several important properties that include: 1) noncentrosymmetrical crystal structure; 2) a suitable hand gap for good transmission at the required spectrum region; 3) large second harmonic generating coefficients; and...
4) high laser damage threshold—where these four properties are only some of the criteria needed for a good NLO candidate.\cite{24–26}

The landscape of ternary transition metal tetrel pnictides remain understudied for NLO applications, regardless of the many reported NCS structures in this family of M-Si-P compounds and despite the promising properties recently reported for MnSiP\textsubscript{2}.\cite{27} For example, while multiple phases and crystal structures were reported for late 4d and 5d transition metal silicon phosphides where M = Ru, Rh, Os, Ir, Ag, Pt, Au,\cite{28–31} single phase syntheses were not developed and properties were not characterized. Among this group of silicon phosphides, RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3} are particularly promising due to their red-

glish color, indicating a relatively large bandgap (about 2 eV). With these two compounds, some headway can be made investigating the fundamental structure-property relationships that may lead to future endeavors with metal tetrel pnictides. In this work we synthesize single phase samples, redetermine NCS crystal structures, and characterize optical properties of RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3}.

2. Results and Discussion

2.1. Synthesis

The original reported synthesis of RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3} included extremely slow cooling rates to obtain \( \sim 0.2 \) mm crystals using a Sn flux with long reaction times at high temperatures.\cite{29,31} Our synthetic method instead used metal silicide precursors (reacted from elements via arc-melting) to obtain phase-pure single phase syntheses were not developed and properties were not characterized. Among this group of silicon phosphides, RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3} are particularly promising due to their red-

glish color, indicating a relatively large bandgap (about 2 eV).

2.2. Crystal Structures

Energy dispersive X-ray spectroscopy (EDS) was used to confirm the composition of the studied compounds. EDS resulted in the average compositions of RuSi\textsubscript{4.1(2)}P\textsubscript{4.1(2)} and IrSi\textsubscript{2.6(1)}P\textsubscript{2.6(1)}. An underestimation of the light element contents (Si and P) in the presence of heavy elements (such as Ir) is a common issue for EDS. Additionally, characteristic X-ray EDS signals of Ir (\( M_\alpha \) line at 1.98 keV) and P (\( K_\alpha \) line at 2.01 keV) overlap, which could affect the overestimation of Ir relative to Si and P.

The crystal structures of RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3} were originally reported in 1995 by Madar et. al.\cite{29,31} RuSi\textsubscript{4}P\textsubscript{4} was reported to crystallize in the triclinic space group \( P1 \) (No. 1), while IrSi\textsubscript{3}P\textsubscript{3} was reported in the monoclinic space group \( C2 \) (No. 5) with details outlined in Table 1. Both phases attracted our interest due to their NCS structures and potential as nonlinear optical materials.

### Table 1. Crystallographic details for RuSi\textsubscript{4}P\textsubscript{4} and IrSi\textsubscript{3}P\textsubscript{3} phases as compared to the original reported structures.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Space group</th>
<th>Current work</th>
<th>Reported\textsuperscript{[29]}</th>
<th>Current work</th>
<th>Reported\textsuperscript{[31]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuSi\textsubscript{4}P\textsubscript{4}</td>
<td>( P1 ) (No. 1)</td>
<td>( 0.41354 ) (synchrotron)</td>
<td>( 0.71073 ) (Mo ( K_\alpha ))</td>
<td>( 100(2) )</td>
<td>( 373 )</td>
</tr>
<tr>
<td>IrSi\textsubscript{3}P\textsubscript{3}</td>
<td>( Cm ) (No. 8)</td>
<td>( 0.71073 ) (Mo ( K_\alpha ))</td>
<td>( 0.71073 ) (Mo ( K_\alpha ))</td>
<td>( 100(2) )</td>
<td>( 373 )</td>
</tr>
<tr>
<td>( Z )</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, ( \rho )( \text{[g cm}^{-3}\text{]} )</td>
<td>3.732</td>
<td>3.74</td>
<td>5.293</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>( a ) [( \text{Å} )]</td>
<td>4.9362(2)</td>
<td>4.9363</td>
<td>6.5895(3)</td>
<td>6.577</td>
<td></td>
</tr>
<tr>
<td>( b ) [( \text{Å} )]</td>
<td>5.6326(2)</td>
<td>5.6341</td>
<td>7.2470(3)</td>
<td>7.229</td>
<td></td>
</tr>
<tr>
<td>( c ) [( \text{Å} )]</td>
<td>6.1649(2)</td>
<td>6.1624</td>
<td>5.4916(3)</td>
<td>5.484</td>
<td></td>
</tr>
<tr>
<td>( \alpha ) [( ^\circ )]</td>
<td>85.5073(8)</td>
<td>85.51</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>( \beta ) [( ^\circ )]</td>
<td>70.6990(8)</td>
<td>70.69</td>
<td>117.892(1)</td>
<td>117.91</td>
<td></td>
</tr>
<tr>
<td>( \gamma ) [( ^\circ )]</td>
<td>70.6990(8)</td>
<td>70.69</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Volume [( \text{Å}^3 )]</td>
<td>150.072(9)</td>
<td>150.05</td>
<td>232.78(2)</td>
<td>230.41</td>
<td></td>
</tr>
<tr>
<td>Final R indices</td>
<td>( R_1 = 0.024 )</td>
<td>( R_1 = 0.029 )</td>
<td>( R_1 = 0.013 )</td>
<td>( R_1 = 0.043 )</td>
<td></td>
</tr>
<tr>
<td>(all data)</td>
<td>( wR_2 = 0.054 )</td>
<td>( wR_2 = 0.032 )</td>
<td>( wR_2 = 0.028 )</td>
<td>( wR_2 = 0.034 )</td>
<td></td>
</tr>
<tr>
<td>Absorption Coefficient, ( \mu ) [( \text{[mm}^{-1}\text{]} )]</td>
<td>3.761</td>
<td>4.3</td>
<td>30.425</td>
<td>30.48</td>
<td></td>
</tr>
<tr>
<td>( \sin(\theta_{\text{max}})/\lambda ) [( \text{[Å]} )]</td>
<td>0.89</td>
<td>–</td>
<td>1.00</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Data/parameters</td>
<td>2500/84</td>
<td>–</td>
<td>2059/38</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.005(14)</td>
<td>–</td>
<td>0.014(10)</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>0.98</td>
<td>–</td>
<td>1.06</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
We redetermined the crystal structures of both compounds (Figure 1 and Table 1). Our SCXRD investigation of the crystal structure of RuSi$_4$P$_4$ is in good agreement to the original report, with interatomic distances outlined in Table S1, Supporting Information. However, our crystal structure of IrSi$_3$P$_3$ showed a deviation from the original report. The space group was found to be $Cm$ (No. 8) with fully occupied Si and P sites, instead of $C2$ with mixed sites of Si and P. Upon initial determination of the IrSi$_3$P$_3$ structure, it was ambiguous between the assignments of space group as $C2$, $C2/m$, or $Cm$. Therefore, to find the true space group, high-resolution SCXRD datasets were collected ($\sin \theta_{max}/\lambda = 1.00$ Å$^{-1}$) and structures were solved and refined in all three space groups. $Cm$ structure was found to be the more convincing solution for several reasons. Based off the SHG activity observed, the $C2/m$ space group can be ruled out due to the inversion center present; only NCS space groups would show SHG activity.[13] Furthermore, the original solution using the $C2$ space group resulted in mixed occupancies of two 4c atomic sites with arbitrarily assigned site occupancy refinements of Si (25%) and P (75%), which leads to the presence of Si–Si and P–P bonds. For the crystal structure of RuSi$_4$P$_4$ we observed separate sites for Si and P with only Si–P bonds present, and we expect the same for the crystal structure of IrSi$_3$P$_3$. This can be achieved in the $Cm$ space group. Individual site refinements of Si and P reveal the most reasonable ADP values (Table S2, Supporting Information) for the final assignments presented here for IrSi$_3$P$_3$. The ability to distinguish Si from P via single crystal X-ray diffraction is limited due to their similar X-ray scattering factors.

$^{29}$Si and $^{31}$P Magic Angle Spinning (MAS) NMR spectroscopy was used to assign the Si/P sites and confirms the $Cm$ space group models and structures of RuSi$_4$P$_4$ and IrSi$_3$P$_3$. In the $^{29}$Si and $^{31}$P MAS NMR spectra for RuSi$_4$P$_4$, there are four distinct and sharp signals with nearly equivalent ratios of 1:1:1:1 with chemical shifts of 52.8, 39.2, 28.1, −12.3 ppm ($^{29}$Si) and −70.6, −93.1, −121.4, −135.5 ppm ($^{31}$P) (Figure 2, top panel). We note that the $^{29}$Si NMR may not be fully quantitative because of lengthy $^{29}$Si longitudinal relaxation times. The $^{29}$Si NMR signal observed around −111 ppm corresponds to a silica (SiO$_2$) impurity from the reaction ampoule.[14] The observation of four distinct $^{31}$P and $^{29}$Si signals correspond well to the RuSi$_4$P$_4$ crystal structure, that has four unique and fully occupied Si sites, as well as four unique and fully occupied P sites. Similarly, the IrSi$_3$P$_3$ NMR spectra showed two distinct signals for both $^{29}$Si and $^{31}$P with shifts of −1.7, −29.2 ppm ($^{29}$Si) and −160.2, −184.9 ppm ($^{31}$P). The observed spectra agree with the crystal structure model in $Cm$ space group that has two Si sites (2a and 4b) and two P sites (2a and 4b). Additionally, a 2:1 ratio of integration of the two NMR signals is expected based off both Si and P site multiplicities. In the previously reported $C2$ structural model, P−P bonds would occur 50% of the time, based on the two connected 4c sites each assigned with 75/25% P/Si occupancy (bottom panel, Figure 2). Therefore, the incorrect $C2$ model would be expected to have at least 3 Si peaks with a 4:1 integration ratio and at least 2 P peaks with a 1:1 integration ratio, which is clearly not the case. Importantly, the observed $^{29}$Si and $^{31}$P peak widths in the spectra of IrSi$_3$P$_3$ and RuSi$_4$P$_4$ are comparable. If IrSi$_3$P$_3$ existed in the $C2$ structure, then we would expect significant peak broadening because of the mixed occupancy of the Si and P neighbors. Thus, solid-state NMR data support the hypothesis that IrSi$_3$P$_3$ crystallizes in the $Cm$ space group.

Finally, we note that no Knight or paramagnetic shifts are observed in either the $^{29}$Si or $^{31}$P SSNMR spectra, consistent with the semiconducting nature of the compounds. The chemical shifts observed for both phases, −20–80 ppm ($^{29}$Si) and −200–0 ppm ($^{31}$P), are within expected values for other semiconducting phosphides, and are comparable to SiP (δ($^{29}$Si) = −6.0 to −34.5 ppm), BaAu$_3$P$_4$ (δ($^{31}$P) = −11.4 ppm), mP–BaP$_3$ (δ($^{31}$P) = ranging from −3 to −103 ppm), and La$_3$Zn$_4$P$_6$Cl (δ($^{31}$P) = ranging from +125 to −147 ppm).[17,35–38]

To examine the underlying lack of inversion symmetry of RuSi$_4$P$_4$ and IrSi$_3$P$_3$, we can zoom-in on their respective structural units, namely octahedral and tetrahedral units (Figure 1). For the RuSi$_4$P$_4$ structure, there are fac-[RuSi$_3$P$_3$] octahedral units with 3 Si atoms forming one of the faces and 3 P atoms forming an opposite face of the octahedron. These octahedra are connected throughout the structure by Si–P bonds, where two of the P sites of one octahedra are connected to two of the Si sites on another octahedra. Octahedra are additionally linked by SiP$_4$ tetrahedral units that are corner-sharing P atoms with octahedra. For IrSi$_3$P$_3$, the structure is composed of distorted fac-[IrSi$_3$P$_3$] octahedra. The 4b sites, labeled as Si1 and P1 in Figure 2, exhibit slightly elongated bonds to the central metal, as compared to the 2a sites, labeled as Si2 and P2. These octahedra are connected through Si–P bonds, where a P corner of one octahedra is bonded to a Si corner of another octahedra. The NCS nature of these structures stem from the fac-arrangements of the Si and P around the metal and the respective packing of these units in both the Ru and Ir structures.

Due to the small difference of electronegativities between the M and main group elements of Si and P in RuSi$_4$P$_4$ and
IrSi₃P₃, the ability for the metal to bond with both Si and P leads to more structural diversity and the ability to adopt NCS structures easily. For electropositive metals such as Ba (Pauling electronegativity 0.9), both Si (1.9) and Ba are surrounded by most electronegative P (2.2) atoms without any Ba–Si interactions. In contrast to Ba–Si–P compounds, the relative electronegativities of Ir (2.2) and Ru (2.2) are comparable to that for P making Si the most electropositive element in these systems. This unusual trend of electronegativities allow for both metal-silicon and metal-phosphorus bonding and resulted in ordered local coordination which may hold the key to why so many of M–Si–P compounds crystallize in NCS structures.

A general trend is observed for M–Si versus M–P bond lengths for both title compounds, where the M–P bonds are longer on average than the M–Si bonds (Figure 2). This is in contrast to the expectations based on the covalent radii for Si (1.17 Å) and P (1.11 Å). We hypothesized that the larger difference of electronegativities between M and Si as compared to similar electronegativities of M and P resulted in a more ionic character of M–Si bonds, causing slightly shorter distances. Specifically, the Ru–Si bond distances of 2.34–2.36 Å in RuSi₄P₄ are similar in length to distances in Ru₂Si₂ (2.32–2.52 Å) and TiRuSi (2.37–2.50 Å) and not as short as the previously reported Ru–Si in RuSi₃P₄ (2.25–2.32 Å). However, the Ru–P distances ranging from 2.40–2.44 Å seem slightly longer than most Ru–P distances, but are comparable to distances found in LaRu₄P₁₂ (2.36 Å), RuP₆Si (2.45 Å), RuP₄ (2.28–2.41 Å), α-RuP₄ (2.28–2.44 Å) and β-RuP₄ (2.41–2.64 Å).

For IrSi₃P₃, the distances follow a similar pattern to RuSi₄P₄, where the Ir–Si distances (2.36–2.41 Å) are comparable to those found in BaIr₄Si₂ (2.31–2.42 Å), CeIrSi₃ (2.30–2.36 Å) and IrSi (2.32–2.56 Å) while Ir–P distances (2.41–2.51 Å) are slightly longer than most Ir–P distances but are close to the range of distances found in BaIr₄P₂ (2.36 Å), LaIrP (2.45–2.46 Å) and IrP (2.40 Å). As for the non-metal bonds of Si–P of 2.22–2.32 Å (RuSi₄P₄) and 2.24–2.31 Å (IrSi₃P₃), these correspond well to distances found in AuSiP (2.26 Å), SiP (2.26–2.30 Å), α-RuP₄ (2.28–2.44 Å) and β-RuP₄ (2.41–2.64 Å). It is interesting to note that no Si–Si or P–P bonding is observed for either RuSi₄P₄ or IrSi₃P₃, regardless of the high Si and P content. To maintain the 1:1 composition of silicon to phosphorus in the RuSi₄P₄ and IrSi₃P₃ phases, Si–P bonding is preferred. However, this is not the case for binary SiP, that is composed of Si-Si dumbbells arranged in [P₃Si–SiP₃] trigonal antiprism motifs.

2.3. Quantum Chemical Calculations

To further determine the bonding schemes in RuSi₄P₄ and IrSi₃P₃, electron localization function (ELF) analysis (Figure 3) and basin analysis (Figure S4, Supporting Information) were conducted. ELF analysis was used to visualize the chemical bonding. Bader analysis of the corresponding ELF basins allows to determine electron density per chemical bond. The ELF computations show attractors between Si–P, M–Si, and M–P bonds for both RuSi₄P₄ and IrSi₃P₃ compounds. The
ELF analysis suggests that the metals Ru and Ir are each covalently bonded to 3 Si and 3 P via an octahedral arrangement. ELF slices of [RuSi2P2] and [IrSi2P2] portions of the octahedra are shown in Figure 3 that highlight the ELF maxima between atoms. No significant shifting of the attractors away from the line connecting atoms is observed for any of the bonds involved. Furthermore, topological basin analysis reveals the disynaptic (bonding basins only directly touching two core basins) basins for all bonds in RuSi4P4 and IrSi3P3. Integration of the bonding basins indicated approximately two electrons per chemical bond for all bonds in both compounds (Table S3, Supporting Information), apart from a single Ir–P bond showing a lower count of 1.7 electrons. This corresponds to the longest Ir–P bond. Thus, chemical bonding analysis confirms covalent nature of M–Si, M–P, and Si–P bonding.

Density of states for RuSi4P4 and IrSi3P3 calculated using PBE[60] exchange-correlation functional with spin–orbit coupling are plotted in Figure 4. Both compounds have a sizable band gap. With projection on atomic orbitals, it shows that the contribution to the conduction bands are not dominated by the M in both compounds and agrees with the mostly covalent bonding picture. There is a strong hybridization between M d orbitals and Si and P p orbitals in a large energy range as seen in the filled states. The Ir 5d derived bands are broader than Ru 4d because of the relativistic effect and the center of Ir 5d band is shifted to lower energy due to one more d electron. The bond structures of RuSi4P4 and IrSi3P3 are plotted in Figure 5 for using both PBE and also the modified Becke–Johnson (mBJ)[61] exchange-correlation potential, a meta-GGA, to effectively correct the underestimated band gap. For both compounds, the band gap is indirect, and the size is comparable. With PBE, the band gap is 1.46 and 1.53 eV for RuSi4P4 and IrSi3P3, respectively. With mBJ, the band dispersion for both valence and conduction bands in the two compounds does not change much, but the band gap increases with valence (conduction) bands being shifted to lower (higher) energy. The predicted band gap with mBJ is 1.81 and 1.93 eV for RuSi4P4 and IrSi3P3, respectively. To corroborate the bandgap value, optical
measurements were conducted via diffuse reflectance. The estimated optical direct bandgaps from the Tauc plots (Figure 6) were found to be 1.88(5) eV (RuSi$_4$P$_4$) and 1.80(5) eV (IrSi$_3$P$_3$). The optical spectra agree with the calculations, as well as with the red color of the powders observed.

Additionally, two-probe thermal transport properties were conducted on sintered pellets of RuSi$_4$P$_4$ and IrSi$_3$P$_3$. Both title compounds were found to be $p$-type wide bandgap semiconductors, a consistent finding to the band gap calculations and optical measurements. The temperature-dependence of the electrical resistivity shows the expected exponential increase upon cooling. In addition to the large bandgap, the pellets measured were low density (>80% geometric density) and therefore the resistivity was too high to reliably measure below $≈$ 180 K.

### 2.4. Second Harmonic Generation and Laser Damage Threshold

Since the requirements for second harmonic generation (SHG) have been fulfilled by having both NCS structures and relatively wide bandgaps ($≈$2 eV), optical powder SHG measurements were conducted. The Kurtz and Perry method was used for both RuSi$_4$P$_4$ and IrSi$_3$P$_3$ compounds using a Q-switch 2.09 µm laser source (3 Hz, 50 ns).[62] Even though the SHG response may be weakened due to their narrow optical bandgaps (1.8–1.9 eV) and long shortwave absorption edge (up to 1 µm), the SHG activities for both the title compounds are still higher than the AgGaS$_2$ (AGS) standard (Figure 7). Specifically, when compared at the 54–88 µm particle size, RuSi$_4$P$_4$ (1.4 $×$ AGS) and IrSi$_3$P$_3$ (1.6 $×$ AGS) both outperform the recently discovered MgSiAs$_2$.
Together with recent report of LDT for MnSiP₂ (70 MW cm⁻²) under identical conditions and versus identical standard, but are not as strong as MnSiP₂ (6 × AGS), despite the latter was measured under different excitation conditions.[21] Moreover, stronger SHG response is expected under longer wavelength irradiation (such as 10.6 μm of CO₂ laser), as reported for CdGeAs₂ with large nonlinear optical efficiency (236 pm V⁻¹) at a longer wavelength (>2.5 μm).[6] Both RuSi₄P₄ and IrSi₃P₃ compounds are expected to be promising infrared NLO materials under suitable excitation sources. Unfortunately, the phase matchability was not reliably determined due to the small crystallite size (Figure S6, Supporting Information). Attempts to sieve sample to separate fraction with >75 μm sizes resulted in selection of agglomerates of smaller crystallites. Additionally, since phase matchability is a wavelength-dependent phenomenon, other laser source measurements would be needed.

Generally, phosphides have narrow bandgaps as compared to chalcogenides which induces the low laser damage threshold (LDT) since the bandgap has the positive relationship with LDT. Nevertheless, the (LDT) values are particularly outstanding for RuSi₄P₄ and IrSi₃P₃ phases are found to be p-type widegap semiconductors. 1.8–1.9 eV. Most importantly, RuSi₄P₄ and IrSi₃P₃ are found to have strong SHG activities and outstanding LDT values as compared to AgGaS₂. Based off the reported work presented here, we anticipate the title compounds to be good candidates for longer wavelength state-of-the-art infrared NLO materials.

[Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76 344 Eggenstein–Leopoldshafen (Germany), on quoting the depository CSD numbers 2041854 and 2041855]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors thank Professors Javier Vela and Julia Zaikina (Iowa State University) for access to the solid-state UV–vis spectrometer and SPS instrument; and Professor Vitalij Pecharsky of Ames Lab, US DOE for the use of the arc-melting setup in his laboratory. The authors also thank Dr. SuYin Grass Wang and Dr. Yu-Sheng Chen for their help conducting the synchrotron single crystal diffraction experiment at 15-ID beamline at the Advanced Photon Source at Argonne National Lab. G.A. is grateful to the Ames Laboratory Spedding Postdoctoral Fellowship for financial support. This work was supported by the Ames Laboratory’s Laboratory Directed Research and Development (LDRD) program (G.A., S.L., K.K.). The Ames Laboratory is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Data available on request from the authors.

Table 2. LDT values for RuSi₄P₄ and IrSi₃P₃ as compared to the standard of AgGaS₂ (AGS).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Damage Energy [mJ]</th>
<th>Spot Diameter [mm]</th>
<th>LDT [MW cm⁻²]</th>
<th>LDT (&gt;AGS)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGaS₂</td>
<td>0.58</td>
<td>0.5</td>
<td>29.6</td>
<td>1</td>
</tr>
<tr>
<td>RuSi₄P₄</td>
<td>1.13</td>
<td>0.5</td>
<td>57.7</td>
<td>2.0</td>
</tr>
<tr>
<td>IrSi₃P₃</td>
<td>0.94</td>
<td>0.5</td>
<td>48.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

¹AGS = AgGaS₂

Figure 7. Second harmonic generation signals (volt) diagram of RuSi₄P₄, IrSi₃P₃, and AgGaS₂ powders at the 54–88 μm particle size.