Direct-Gap Semiconductors

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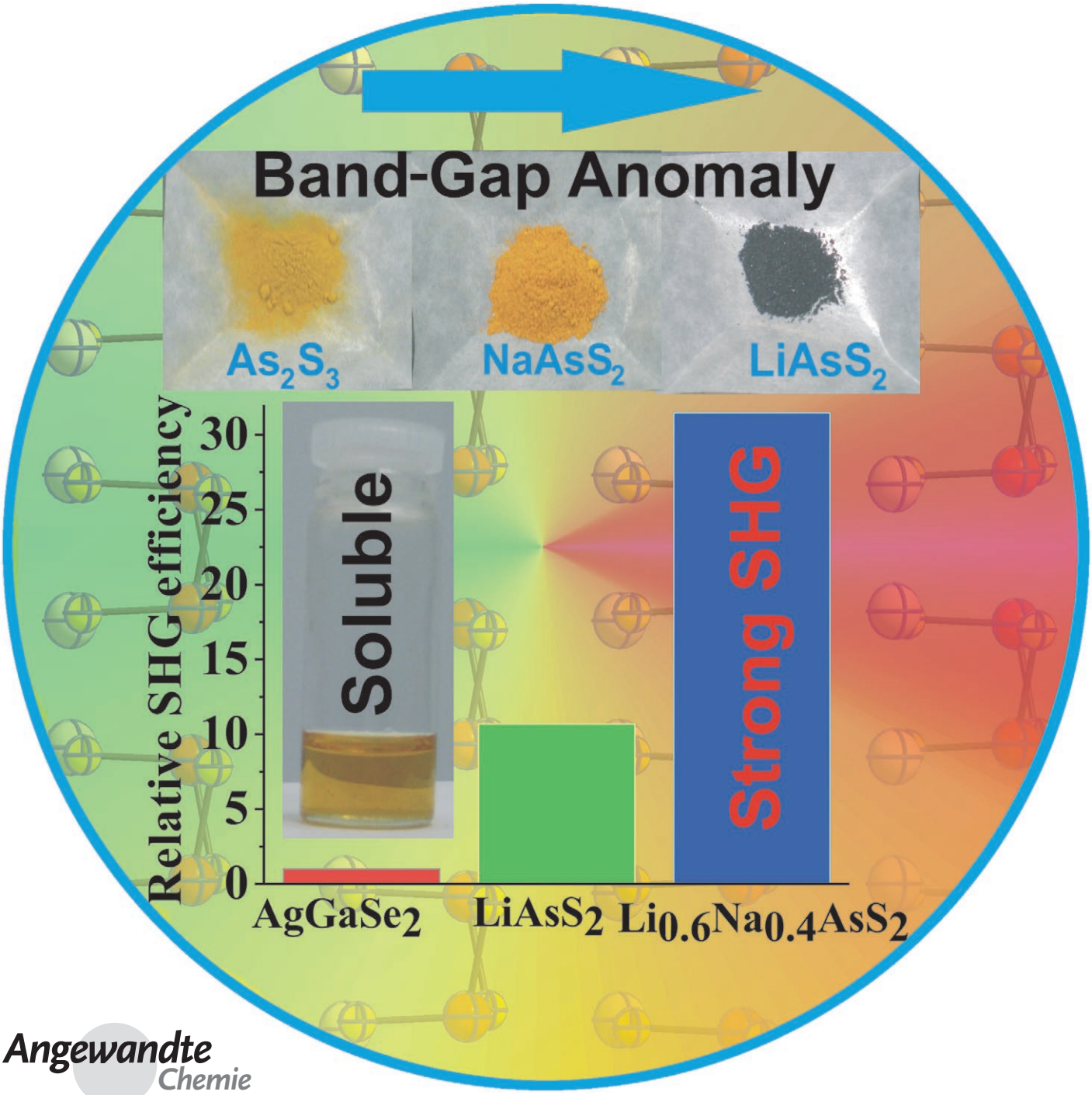
Soluble Direct-Band-Gap Semiconductors $LiAsS_2$ and $NaAsS_2$: Large Electronic Structure Effects from Weak As···S Interactions and Strong Nonlinear Optical Response**

*Tarun K. Bera, Jung-Hwan Song, Arthur J. Freeman, Joon I. Jang, John B. Ketterson, and Mercouri G. Kanatzidis**



Polarity is essential for various technologically important properties, such as nonlinear optics (NLO), piezoelectricity, and ferroelectricity,[1] and a direct gap is important for optoelectronic applications, such as light-emitting diodes (LED), lasers, and solar cells.[2] Chalcopyrite-based materials are polar direct-gap semiconductors that are used both in optoelectronic and NLO applications as second harmonic generators (SHGs) in the IR region,[3] where the use of oxides such as $BaBa_2O_4$, $LiNbO_3$, or $KTiOPO_3$ is limited. The non-centrosymmetric packing of asymmetric building units can result in highly polar compounds.[4] Today, materials design exploiting asymmetric building units, such as Jahn–Teller-distorted d^0 metal centers (e.g. Ti^{4+}, Nb^{5+}, Mo^{6+}),[5] anionic groups with stereochemically active lone pairs (e.g. $(IO_3)^-$, $(TeO_x)^{n-}$),[6] and non-centrosymmetric π-orbital systems (e.g. $(BO_3)^{3-}$, $(B_3O_6)^{3-}$),[7] is of broad scientific and technological interest. Corresponding units of the heavier chalcogenides have been little explored. These would be the trigonal-pyramidal building anions (e.g. $[AsS_3]^{3-}$, $[SbS_3]^{3-}$, $[TeS_3]^{2-}$).[4]

Herein we present the unusual properties of the new thioarsenate $LiAsS_2$ (**I**) and its analogue $NaAsS_2$ (**II**),[8] which have $^1_\infty[AsS_2^-]$ chains made of condensed trigonal-pyramidal units $[AsS_3]^{3-}$. From a combined experimental and theoretical investigation, we find that the size of the alkali metal influences the symmetry and polarity of the structure. Remarkably, it also leads to unexpected trends in the size of the band gap in these compounds. The polar $LiAsS_2$ and the centrosymmetric $NaAsS_2$ are found to be direct-gap semiconductors, with the lithium analogue having a substantially narrower energy gap. Surprisingly, the band gap of both compounds is substantially narrower than that of the parent binary compound As_2S_3, a trend which, as we will explain below, is opposite to what is expected. Our ab initio density functional calculations of their ground- and excited-state properties with the full-potential linearized augmented plane wave method (FLAPW)[9a] reveal that the anomalously large differences in the energy band gap of the two compounds are mainly due to the weak interchain As···S interactions. We also report a strong SHG response for $LiAsS_2$ and its dramatic enhancement in the solid solutions $Li_{1-x}Na_xAsS_2$ up to 30 times larger than the benchmark material $AgGaSe_2$ and 120 times larger than $LiNbO_3$.

$LiAsS_2$ (**I**) was first prepared by the alkali metal polychalcogenide flux method,[10] but it can also be prepared by the direct reaction of Li_2S, As, and S. $Li_{1-x}Na_xAsS_2$ ($x = 0.4$, 0.5) and $NaAsS_2$ (**II**) were also synthesized by direct combination reactions. The crystal structures were determined with single-crystal X-ray diffraction analysis. Differential thermal analyses (DTA) show that **I** and **II** melt congruently, as indicated by the full recovery of the compounds upon cooling the melts.[11] The compounds are stable in air and water.

$LiAsS_2$ (**I**) crystallizes in the space group Cc[12] and $NaAsS_2$ (**II**) in $P2_1/b$.[8] Both **I** and **II** feature the same polymeric $^1_\infty[AsS_2^-]$ chains, but these are stacked in a different manner (Figure 1a,b). The chains are made from corner-sharing AsS_3 trigonal pyramids having two different sulfur atoms: a bridging atom S2 and a terminal atom S1 (Figure 1c). A non-centrosymmetric packing of the $^1_\infty[AsS_2^-]$ chains in **I** and the corresponding centrosymmetric packing in **II** are shown in Figure 1a,b.

The arsenic-centered trigonal pyramids are distorted, as evidenced by the As–S bond lengths (2.176(2)–2.331(2) Å) and S-As-S angles (94.52–102.64°). By comparison, the As–S and S-As-S metrics in As_2S_3 are 2.243–2.293 Å and 92.76–

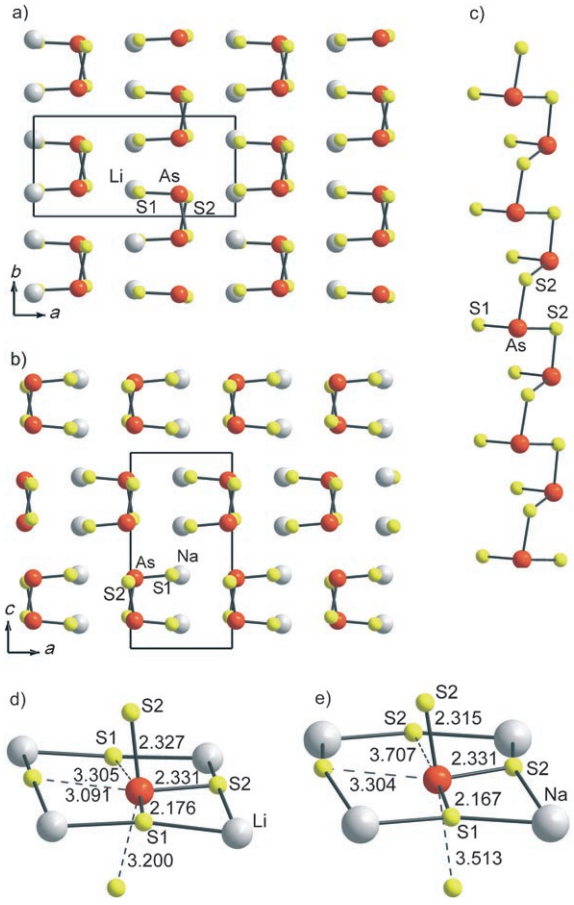


Figure 1. Extended unit cell view of a) $LiAsS_2$ with non-centrosymmetric packing of $^1_\infty[AsS_2^-]$ chains, and b) centrosymmetric packing in $NaAsS_2$. c) A single $^1_\infty[AsS_2^-]$ chain. d, e) The coordination environment of As in $LiAsS_2$ (d) and $NaAsS_2$ (e), showing three strong As–S interactions (solid lines) and three weak interactions (dashed lines).

[*] T. K. Bera, Prof. Dr. M. G. Kanatzidis
Department of Chemistry, Northwestern University
2145 Sheridan Rd., Evanston, IL 60208 (USA)
Fax: (+1) 847-491-5937
E-mail: m-kanatzidis@northwestern.edu
Dr. J.-H. Song, Prof. A. J. Freeman, Dr. J. I. Jang, Prof. J. B. Ketterson
Department of Physics and Astronomy, Northwestern University
2145 Sheridan Rd., Evanston, IL 60208 (USA)

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104.99°, respectively.[13] Each arsenic atom has three weakly interacting sulfur atoms in addition to the three covalently bonded sulfur atoms (a so-called [3+3] coordination, Figure 1d,e).

The alkali-metal ions in **I** and **II** are in a distorted octahedral environment of sulfur atoms with A–S (A = alkali metal) distances of 2.620(12)–2.880(12) Å in **I** and 2.800(12)–3.060(13) Å in **II**. The AS_6 octahedron forms a three-dimensional network by itself through edge sharing in the *bc* plane and corner sharing along the *a* direction.[11] The NaS_6 octahedron is much more distorted than the LiS_6 octahedron.

The influence of the alkali metal (Li and Na) on the crystal symmetry was further investigated by studying the mixed alkali-metal system $Li_{1-x}Na_xAsS_2$. The non-centrosymmetric structure of **I** holds up to 40% sodium.[14] The resultant $Li_{0.6}Na_{0.4}AsS_2$ (referred to as **Ia**) is isostructural with **I**. A further increase in the sodium fraction leads to a structural transition from monoclinic *Cc* to orthorhombic *Pbca*.

The 50% sodium-substituted compound $Li_{0.5}Na_{0.5}AsS_2$ (referred to as **IIa**) is centrosymmetric and very closely related to **II**. Structure solutions and refinements of **Ia** and **IIa** reveal that the alkali-metal site has a mixed occupation of both lithium and sodium. Following the Végard law,[15] there is a linear increase of the unit cell volume with increasing *x*, as expected from the fact that sodium is larger than lithium (Figure 2a). The slope of the plot (normalized unit cell volume vs. composition *x*) in the composition range $0 \le x \le 0.4$ is different from that in the composition range $0.5 \le x \le 1$ (Figure 2a). A sudden increase of the unit cell volume on going from $x = 0.4$ to 0.5 signifies the structural change and also reveals that the polar structure is more dense than the centrosymmetric one.

The denser packing of $^1_\infty[AsS_2^-]$ chains in **I** leads to a shortening of the weaker interchain As···S interactions (3.091, 3.200, and 3.305 Å in $LiAsS_2$) compared to those in $NaAsS_2$ (3.304, 3.513, and 3.707 Å; Figure 1d,e). These weak As···S interactions turn out to have a considerable effect on the electronic structures and the band gaps of the compounds.

The solid-state UV/Vis optical absorption spectra of **I**, **II**, **Ia**, **IIa**, and As_2S_3 show very strong and steep absorption onsets almost parallel to the absorption axis, suggestive of direct band-edge absorption (Figure 2b). A striking contrast in the spectra is that the band gap of $LiAsS_2$ (**I**) at 1.60 eV is anomalously smaller than that of $NaAsS_2$ (**II**) at 2.23 eV, which can be seen visually in Figure 2c. Generally, changes in the alkali metal do not have a profound influence on the energy gap of the covalent network structure because of the generally ionic bonding with the network. Thus, the observed 0.63 eV difference in band gap is too large for such a compositional change.

Another unexpected finding is that the energy gaps of the two ternary compounds are found to be smaller than that of the parent As_2S_3 (ca. 2.44 eV). Generally, when the structure of a binary solid is modified by the introduction of a nucleophilic agent, as for example in the case of $A_2Q + m\,MQ \rightarrow A_2M_mQ_{m+1}$, the $[M_mQ_{m+1}]^{2-}$ part of the structure is generally typified by two prominent characteristics 1) less dense structure with same dimensionality or lower dimensionality and 2) higher-energy gap compared to the binary

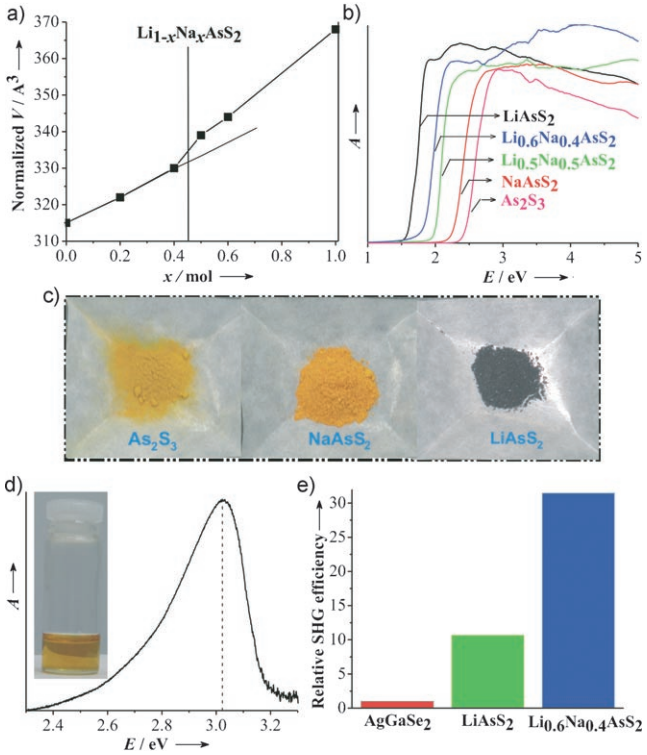

Figure 2. a) Normalized unit cell volume versus composition in the $Li_{1-x}Na_xAsS_2$ system. The vertical line indicates the region of the structural transition. b) Solid-state UV/Vis absorption spectra of **I**, **II**, **Ia**, **IIa**, and As_2S_3. c) Photos of the as-synthesized powdered materials showing color trend. d) Solution UV/Vis absorption spectrum of **I**. Inset shows the clear solution of **I** in hydrazine. e) A plot of the relative SHG efficiency of **I** and **Ia** compared with that of $AgGaSe_2$ (particle sizes of 45–63 μm were used for the SHG efficiency comparison).

material.[16] In other words, the introduction of ionic A_2Q dismantles the dense MQ framework to a less dense $[M_mQ_{m+1}]^{2-}$ framework of lower dimensionality. The $[M_mQ_{m+1}]^{2-}$ framework has less dispersed energy bands than MQ and consequently a larger band gap. Therefore, it is surprising that $LiAsS_2$ and $NaAsS_2$ (which derive from $A_2S + As_2S_3 \rightarrow 2\,AAsS_2$) absorb light at lower energies than As_2S_3 itself. The structures of the two compounds appear to meet the lower dimensionality characteristic, yet they possess a lower-energy gap compared to the binary material. This result may be attributed to the different hybridization of arsenic associated with the weak As···S interactions between the derived (interchain in $LiAsS_2$ and $NaAsS_2$) and the parent (interlayer in As_2S_3) compounds, as explained below.

To understand these unusual optical properties, we performed band-structure calculations for the ground and excited states using the highly precise full-potential linearized augmented plane wave (FLAPW) method[9a] with the screened-exchange local density approximation (sX-LDA)[9b] as well as the Hedin–Lundqvist form of the exchange-correlation potential (LDA).[9c]

The results show the title compounds to be direct-gap materials, and the reasons for the narrower gaps are highly insightful. Here too, the sX-LDA method with the FLAPW approach shows great improvements of the excited electronic

states over the LDA and again has yielded excellent estimates of the band gaps and band dispersions.[17] Careful investigation of the band structure revealed that the fundamental absorption edge in As_2S_3 corresponds to an indirect gap, but with several other indirect and direct transitions within a few tenths of an electronvolt of the indirect edge, consistent with previous studies and also in accord with most of the optical absorption studies.[18] Interestingly, the fundamental absorption edges in both $LiAsS_2$ (**I**) and $NaAsS_2$ (**II**) correspond to direct gaps.

The band structure of **I** is shown in Figure 3a (for **II**, see the Supporting Information). The DOS plots (see the Supporting Information) show that the bands around the Fermi level (E_F) are predominantly As and S states. The valence band edge is mainly S 3p in nature, whereas the conduction band edge has mainly As 4p character in all three compounds. The fundamental band edge excitation is mostly from the S 3p to the As 4p orbital. The calculated band gaps ($E_{calcd} = 1.68$ eV for $LiAsS_2$, 2.19 eV for $NaAsS_2$, and 2.7 eV for As_2S_3) show very good agreement with the measured band gaps (1.60, 2.23, and 2.44 eV, respectively). A direct band gap of 1.6 eV is nearly ideal for maximum capture of solar radiation, suggesting $LiAsS_2$ could be promising for solar-cell investigations.

To explain the anomalous band-gap difference between $LiAsS_2$ and $NaAsS_2$, three factors were considered: 1) the strong As–S covalent interactions, 2) the average S-As-S bond angles, and 3) the weak As···S interactions (intrachain and interchain). The differences in the average As–S separations and the S-As-S bond angles[11] on going from As_2S_3 to $NaAsS_2$ to $LiAsS_2$ were insufficient to explain the band-gap variation. Then the role of the weak As–S interactions (mainly interchain) was investigated by calculating the band structures of the individual $^1_\infty[AsS_2^-]$ chains. This calculation was done on a model system in which the chains were set apart from each other by up to approximately 8 Å, to essentially eliminate any interaction between them. The calculated band gap of this model system is approximately 3.5 eV (Figure 3b), which is considerably larger than the band gaps of all three compounds (including As_2S_3). This finding suggests a dominant role for interchain interactions on defining the band gap. The single-chain band structure in Figure 3b shows the same gross features along Γ-B-D-Y as in Figure 3a of the real compounds, but the flat bands along Γ-X-S-Y-Γ are due to a lack of interchain interactions.[19] The shorter interchain separations in $LiAsS_2$ than $NaAsS_2$ result in stronger hybridization between the weakly interacting As 4p and S 3p states, which results in more dispersive bands (Figure 3a) and consequently narrower band gaps.

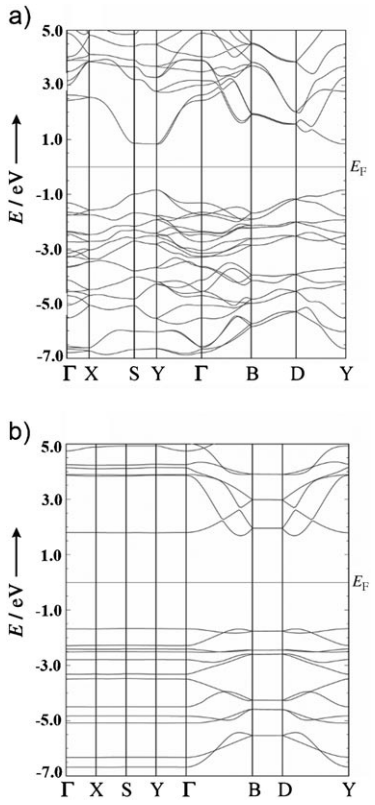

Figure 3. The calculated band structures of a) $LiAsS_2$, $E_{calcd} = 1.68$ eV and b) a single $^1_\infty[AsS_2^-]$ chain, $E_{calcd} = 3.36$ eV. See the Supporting Information for calculated band structures of $NaAsS_2$, $E_{calcd} = 2.19$ eV, and the projection of the electronic density-of-states (DOS) of $LiAsS_2$ for individual elements (As and S).

$LiAsS_2$ and $NaAsS_2$ are highly soluble (ca. 0.3 mol L^{-1}) in hydrazine and produce yellow solutions (inset in Figure 2d) with identical optical absorption maxima at 3.05 eV (Figure 2d). This finding suggests that the two solutions contain the same separated $^1_\infty[AsS_2^-]$ chains. Good agreement between the measured solution UV/Vis absorption and the calculated energy gap (ca. 3.5 eV) for the separated $^1_\infty[AsS_2^-]$ chains (Figure 3b) suggests well-separated $^1_\infty[AsS_2^-]$ chains in dilute solution and confirms the significant role of the interchain interactions on the band-edge formation.[11] The λ_{max} in the spectra of these solutions shifts progressively to longer wavelengths with increasing concentration, indicative of chain–chain interactions at higher concentration. The high solubility of these compounds makes them good candidates for solution processing investigations to fabricate thin films of the materials.[20] The polarity and one-dimensional structure could be helpful to prepare highly oriented films.[21]

The nonlinear optical SHG efficiency of the polar $LiAsS_2$ (**I**) and $Li_{0.6}Na_{0.4}AsS_2$ (**Ia**) was measured with a modified Kurtz–NLO system using a 1580 nm laser.[22a] The particle size versus SHG efficiency measurement revealed that these compounds are not type I phase-matchable.[11,22b] An efficiency comparison with the commercially used material $AgGaSe_2$ was also made (Figure 2e), because the transparency window for **I** and **Ia** is in the same region as for $AgGaSe_2$.[11] We found that **I** is about 10 times and compound **Ia** is about 30 times more efficient than $AgGaSe_2$. The highly polar structure that results from the alignment of dipoles in $LiAsS_2$ is responsible for the enhanced SHG intensity compared to weakly polar $AgGaSe_2$. This enhanced SHG intensity of the sodium-substituted **Ia** could be attributed to the higher polarizability of sodium vis-à-vis lithium in the structure; this conclusion is supported by the progressive SHG intensity enhancement observed in $Li_{1-x}Na_xAsS_2$ with increasing x.[11]

In conclusion, $LiAsS_2$ and $NaAsS_2$ are direct-gap semiconductors with a band gap which is anomalously lower than that of As_2S_3. The SHG response of $LiAsS_2$ is up to 30 times

larger than $AgGaSe_2$. The 1.6 eV direct energy gap of $LiAsS_2$ coupled with its high solubility makes it promising as an efficient light-harvesting component in solar cells.

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[12] Crystal data for $LiAsS_2$ (**I**): Monoclinic space group *Cc*, $Z=4$; $a=11.847(4)$, $b=5.4076(10)$, $c=5.3508(18)$ Å, $\beta=113.25(3)°$, $V=315$ Å^3 at 100 K; θ_{max} ($Mo_{K\alpha}$) = 29.15°; number of data measured: 1416; number of unique data $F_o^2>2\sigma(F_o^2)$: 755; number of variables: 37; $\mu=11.794$ mm^{-1}; $\rho_{calcd}=3.079$ g cm^{-3}; $R_{int}=2.87\%$; GOF = 1.078; $R_1=2.22\%$; $R_w=4.33$ for $I>2\sigma(I)$.

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[14] Crystal data for $Li_{1-x}Na_xAsS_2$($x=0.4$, **Ia**): Monoclinic space group *Cc*, $Z=4$; $a=12.104(3)$, $b=5.4839(9)$, $c=5.4176(14)$ Å, $\beta=113.188(19)°$, $V=330.54(13)$ Å^3 at 100 K; θ_{max} ($Mo_{K\alpha}$) = 29.03°; number of data measured: 1487; number of unique data $F_o^2>2\sigma(F_o^2)$: 827; number of variables: 38; $\mu=11.293$ mm^{-1}; $\rho_{calcd}=3.062$ g cm^{-3}; $R_{int}=2.86\%$; GOF = 1.088; $R_1=2.36\%$; $R_w=5.62\%$ for $I>2\sigma(I)$. Crystal data for $Li_{1-x}Na_xAsS_2$($x=0.5$, **IIa**): Orthorhombic *Pbca*, $Z=8$; $a=11.0913(6)$, $b=5.4291(2)$, $c=22.5383(12)$ Å, $V=1357.16(11)$ Å^3 at 100 K; θ_{max} ($Mo_{K\alpha}$) = to 29.17°; number of data measured: 11222; number of unique data $F_o^2>2\sigma(F_o^2)$: 1824; number of variables: 73; $\mu=11.015$ mm^{-1}; $\rho_{calcd}=3.015$ g cm^{-3}; $R_{int}=4.70\%$; GOF = 1.168; $R_1=3.91\%$; $R_w=6.40\%$ for $I>2\sigma(I)$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-419059, 419060, and 419061 for $LiNaAs_2S_4$, $Li_{1-x}Na_xAsS_2$, and $LiAsS_2$, respectively.

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