

View Article Online View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Zhou, C. Li, X. Li, J. Yao and Y. Wu, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT00143B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/dalton

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

View Article Online DOI: 10.1039/C6DT00143B

K₂Sn₂ZnSe₆, Na₂Ge₂ZnSe₆, and Na₂In₂GeSe₆: A New Series of Quaternary Selenides with Intriguing Structural Diversity and Nonlinear Optical Properties

Molin Zhou,^{†,‡,§} Chao Li,^{†,‡,§} Xiaoshuang Li,^{†,‡,§} Jiyong Yao^{†,‡,*} and Yicheng Wu^{†,‡}

Three new compounds (*i.e.*, $K_2Sn_2ZnSe_6$, $Na_2Ge_2ZnSe_6$, and $Na_2In_2GeSe_6$) with intriguing structural diversity and nonlinear optical properties were discovered for the first time. They crystallize in space groups *P4/ncc*, *I4/mcm* and *Cc*, respectively. In $K_2Sn_2ZnSe_6$ and $Na_2Ge_2ZnSe_6$, the [Sn(Ge)Se_4] tetrahedra and [ZnSe_4] tetrahedra are linked via edge-sharing to build up a 1D [Sn_2ZnSe_6] infinite chain separated by $K^+(Na^+)$ cations along the c direction, while the structure of $Na_2In_2GeSe_6$ is an interesting three-dimensional framework composed of [InSe_4] and [GeSe_4] tetrahedra via corner-sharing with Na^+ cations in the cavities. The experimental optical band gaps of these compounds were determined as 1.71(2) eV, 2.36(4) eV and 2.47(2) eV, respectively, according to UV-vis-NIR diffuse reflectance spectroscopy. Interestingly, in addition to the large band gap (1.80 eV for AgGaSe_2, as a comparison), $Na_2In_2GeSe_6$ exhibits phase-matchable nonlinear optical (NLO) property with a

[†]Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

[‡]Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

[§]University of Chinese Academy of Sciences, Beijing 100049, P.R. China

[†]Electronic supplementary information (ESI) available: Crystallographic data in CIF format for $K_2Sn_2ZnSe_6$, $Na_2Ge_2ZnSe_6$, and $Na_2In_2GeSe_6$

powder second harmonic generation signal about 0.8 times that of AgGaS₂. Moreover, Na₂In₂GeSe₆ melts congruently at a rather low temperature of 671 \Box , which suggests bulk crystals can be easily obtained by the Bridgman–Stockbarger method. Our preliminary results indicate that Na₂In₂GeSe₆ has promising applications in IR nonlinear optics.

Introduction

The research on metal chalcogenides has been a very active area owing to their great structural diversity and many important physical properties.¹⁻³ Recently, extensive exploration has been carried out in search for new Mid-far IR NLO materials in metal chalcogenides because IR NLO materials have great civil and military applications and the current commercially available chalcopyrite-type IR NLO crystals (e.g., AgGaS₂,⁴ AgGaSe₂⁵ and ZnGeP₂⁶) have severe drawbacks.⁷ Many new compounds with attractive NLO properties such as large NLO responses and large band gaps (possibly high laser damage thresholds) have been synthesized. Examples include $BaGa_4S_7$,⁸ $BaGa_4Se_7$,⁹ $BaGa_2MSe_6$ (M = Si, Ge; Q = S, Se),¹⁰ $Pb_4Ga_4GeQ_{12}$ (Q = S, Se),¹¹ Ba₂₃Ga₈Sb₂S₃₈,¹² Cs₅BiP₄Se₁₂,¹³ Ln₄GaSbS₉ (Ln = Pr, Nd, Sm, Gd-Ho),¹⁴ and Ba₂InYQ₅ (Q = Se, Te),^{15,16} LiGaS₂,¹⁷ LiGaSe₂,¹⁸ Li₂In₂MS₆ (M = Si, Ge),¹⁹ SnGa₄Q₇ (Q = S, Se),²⁰ AAsQ₂ (A = Li,Na; Q = S,Se),²¹ AZrPSe₆ (A = K, Rb, Cs)¹ and Na₄MgM₂Se₆ (M = Si, Ge).²² Generally speaking, a large macroscopic NLO response originates from the cooperative arrangement of the microscopic NLO building units, including the MX₄ tetrahedra (M = Ga, In, Si, Ge, Sn etc.; X = S, Se), the polyhedra centered by the second-order Jahn-Teller (SOJT) distorted d^0 (e.g., Ta⁵⁺, Zr^{4+}) or d¹⁰ (e.g., Ag⁺, Zn²⁺, Cd²⁺) metal cations, and some polar structural units centered by cations with stereochemically active lone pair electrons (e.g., As³⁺, Sb³⁺, Pb^{2+}). Meanwhile, it is well-known that the shorter and stronger interactions caused by smaller cations (e.g., Li⁺, Na⁺, Mg²⁺, K⁺, Ca²⁺) can draw the NLO-active microscopic groups closer to each other forming a denser packing to produce larger NLO effects.^{23–25} Besides, numerous exploration have proven that the inclusion of an alkali metal will effectively enlarge the band gap, which can in turn increase the laser damage threshold.^{17–19}

In this work, we intended to combine different microscopic NLO-active building units with alkali metal into one compound to obtain new IR nonlinear optical materials. We thoroughly investigated the A-M-M'-Q (A = Na, K; M, M' = Ga, In, Ge, Sn, Zr, Zn, Cd, Sb, Pb; Q = S, Se) quaternary system and successfully discovered three new compounds $K_2Sn_2ZnSe_6$, $Na_2Ge_2ZnSe_6$, and $Na_2In_2GeSe_6$. The above compounds crystallize in space groups P4/ncc, I4/mcm and Cc, respectively. Although the former two crystallize in centrosymmetric structures, Na₂In₂GeSe₆ adopts a noncentrosymmetric (NCS) structure type and shows good NLO property with a large band gap of 2.47(2) eV, good phase-matchability and a powder second harmonic generation (SHG) response about 0.8 times that of benchmark $AgGaS_2$ at a laser radiation of 2.09 μ m. Moreover, Na₂In₂GeSe₆ exhibits congruent-melting behavior with low melting point (671 \Box), which is very important for growing bulk single crystals for the practical application. In addition, K₂Sn₂ZnSe₆ and Na₂Ge₂ZnSe₆ clearly illuminate the influence of alkali cations on the packing of anionic groups, resulting in the intriguing structural diversity. Here, we report the syntheses, crystal structures, thermal, linear and nonlinear optical properties of the title compounds.

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

Experimental Section

Syntheses

The following reagents were used as obtained: Na (Sinopharm Chemical Reagent Co., Ltd, 99%), K (Sinopharm Chemical Reagent Co., Ltd, 99.9%), In (Sinopharm Chemical Reagent Co., Ltd, 99.9%), Ge (Sinopharm Chemical Reagent Co., Ltd, 99.9%), Sn (Sinopharm Chemical Reagent Co., Ltd, 99.9%), Se (Sinopharm Chemical Reagent Co., Ltd, 99

Traditional solid state reaction technique can be applied to grow the single crystals of the title compounds. During the process, all reactants were mixed and loaded into fused-silica tubes under an Ar atmosphere in a glovebox, then flame-sealed under a high vacuum of 10^{-3} Pa. The tubes were then placed in a computer-controlled furnace and heated. Compared with Na₂Se–In₂Se₃–GeSe₂ system, the K(Na)₂Se–Sn(Ge)Se₂–ZnSe system has higher sintering and melting temperatures. Thus, these compounds were heated to and cooled to different temperatures in our approach to obtain the single crystals. Detailed heating profiles are discussed below.

 $K_2Sn_2ZnSe_6$ and $Na_2Ge_2ZnSe_6$. The mixtures of binary materials (K₂Se (0.5 mmol), SnSe₂ (1.1 mmol) and ZnSe (0.5 mmol) for K₂Sn₂ZnSe₆; Na₂Se (0.5 mmol), GeSe₂ (1.1 mmol) and ZnSe (0.5 mmol) for Na₂Ge₂ZnSe₆) were heated to 1273 K within 15 h, left for 48 h, cooled to 623 K at a rate of 3 K/h, and finally cooled to room

temperature by switching off the furnaces. Many prism-shaped crystals were found in the tubes for both compounds. The crystals are stable in air.

 $Na_2In_2GeSe_6$. The mixtures of Na₂Se (0.5 mmol), In₂Se₃ (0.5 mmol) and GeSe₂ (0.5 mmol) were heated to 1173 K within 15 h, left for 48 h, cooled to 573 K at a rate of 3 K/h, and finally cooled to room temperature by switching off the furnace. Many chip-shaped crystals were found in the tubes. The crystals are stable in air.

Polycrystalline sample of $Na_2In_2GeSe_6$ was synthesized by mixtures of the corresponding binary materials in the stoichiometric ratio. The mixtures were heated to 973 K in 15 h and kept at that temperature for 48 h, and finally the furnaces were turned off.

Powder X-ray diffraction (PXRD) pattern of the ground powder was performed at room temperature on a Bruker D8 Focus diffractometer with Cu K α (λ = 1.5418 Å) radiation. The scanning step width of 0.05° and a fixed counting time 0.2 s/step were applied to record the patterns in the 2 θ range of 10–70°. The measured XRD powder pattern was found to match the simulated pattern generated using the CIF of the refined structure. (Figure 1).

Structure Determination

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

Single-crystal X-ray diffraction experiment was performed on a Rigaku AFC10 diffractometer equipped with a graphite-monochromated Mo-K_{α} (λ = 0.71073 Å) radiation at 293 K. The collection of the intensity data and cell refinement was carried

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

Dalton Transactions

View Article Online DOI: 10.1039/C6DT00143B

out with Crystalclear software.²⁶ Face-indexed absorption corrections were performed numerically with the use of the program XPREP.²⁷

The structure was solved with the direct methods SHELXTLS program and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs.²⁷ Relevant crystallographic information from the single-crystal structure refinements are given in Table 1 and selected metrical distances are given in Table 2–4. Further information may be found in Supplementary Material.

Diffuse Reflectance Spectra

A Cary 5000 UV-vis-NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectra of the title compounds and $BaSO_4$ as a reference in the range 300 nm (4.1 eV) to 2000 nm (0.62 eV). Appropriate amounts of single crystals of the title compounds were thoroughly ground for the measurements.

Thermal Analysis

The thermal property of Na₂In₂GeSe₆ was investigated by the differential scanning calorimetric (DSC) analysis using the LabsysTM TG-DTA16 (SETARAM) thermal analyzer. Appropriate amounts of small Na₂In₂GeSe₆ single crystals were manually selected and thoroughly ground into powder, and were then placed in a silica tube (5 mm o.d. \times 3 mm i.d.) and sealed under a high vacuum. The heating and the cooling rates were both 15 K min⁻¹.

The optical SHG response of $Na_2In_2GeSe_6$ was measured by means of the Kurtz–Perry method.²⁸ The fundamental light was the 2090 nm light generated with a Q-switched Ho: Tm: Cr: YAG laser. Enough $Na_2In_2GeSe_6$ polycrystalline sample was ground to powder with the particle size range from 50–300 µm for the measurement. Microcrystalline AgGaS₂ of particle size (105–150 µm) served as a reference.

Results and Discussion

Crystal Growth

Three new quaternary selenides (*i.e.*, K₂Sn₂ZnSe₆, Na₂Ge₂ZnSe₆ and Na₂In₂GeSe₆) have been obtained by spontaneous nucleation method for the first time. We also tried to synthesize their sulfide and telluride analogues. Unfortunately, the sulfide crystals were of poor quality in our synthesis and no telluride analogues were found. Thus, we only report the study on those three selenides here.

Structures

 $K_2Sn_2ZnSe_6$ belongs to the $K_2Sn_2MnSe_6^{29}$ structure type in space group *P4/ncc*, while $Na_2Ge_2ZnSe_6$ adopts the KInSnSe₄³⁰ structure type in space group *I4/mcm*. The asymmetric unit of $K_2Sn_2ZnSe_6$ contains two crystallographically independent K atoms, one Sn atom, one Zn atom and two independent Se atoms, occupying Wyckoff sites 4*c*, 4*c*, 8*e*, 4*b*, 16*g* and 8*f*, respectively, while the asymmetric unit of $Na_2Ge_2ZnSe_6$ contains one crystallographically independent Na atom, one Ge atom, one Zn atom and two independent Se atoms of Na₂Ge₂ZnSe₆ contains one crystallographically independent Na atom, one Ge atom, one Zn atom and two independent Se atoms occupying Wyckoff sites 8*f*, 8*g*, 4*b*, 8*h* and 16*l*, respectively. All sites are occupied with occupancy of 100% in both compounds.

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

The arrangements of the structural units are similar between those two compounds, which are illustrated in Figure 2(a) and Figure 3(a). Their packing characteristic can be described as follows: two $[Sn(Ge)Se_4]$ tetrahedra are first connected to each other by sharing two Se2 atoms to form the $[Sn(Ge)_2Se_6]$ block, which is further linked via edge-sharing two Se1 atoms with one $[ZnSe_4]$ tetrahedron to build up a 1D $[Sn(Ge)_2ZnSe_6]$ infinite chain along the c direction. The chains are separated from each other by $K(Na)^+$ cations residing in the cavities. Figure 2(b) and Figure 3(b) demonstrate the coordination environments of K⁺ and Na⁺ cations, respectively. As is shown, all K⁺ and Na⁺ cations are coordinated by eight Se atoms in a bicapped trigonal prismatic arrangements. Moreover, The K and Sn in K₂Sn₂ZnSe₆ are more electropositive and larger than Na and Ge in Na₂Ge₂ZnSe₆, respectively, leading to the more loose packing and larger commensurate spaces for holding K⁺.

Selected interatomic distances for the two compounds are displayed in Tables 2–3. For example, The Sn–Se distances and Se–Sn–Se angles are in the range of 2.4986(8)–2.5672(7) Å and 102.137(21)–117.340(16)°, respectively, which are comparable to those of 2.565(10)–2.582(1) Å and 115.180(57)° in KSnSe₂.³¹ The Ge–Se bonds range from 2.3318(9) Å to 2.3929(9) Å with the Se–Ge–Se angles in the range of 96.177(8)°–114.081(20)°, which are in good agreement with those of 2.255(6)–2.395(10) Å and 97.651(31)–116.572(40)° in Na₂Ge₂Se₅.³² In K₂Sn₂ZnSe₆, the Zn atom is bound to four Se atoms to form a ZnSe₄ tetrahedron and all the Zn–Se bonds share the same length 2.5142(7) Å with Se–Zn–Se angles ranging from 101.263(21)–113.725(21)°, while in Na₂Ge₂ZnSe₆, the Zn–Se bond distances and

Se–Zn–Se angles are 2.4833(7) Å and 96.054(22)–116.569(23)°, respectively. Such values are consistent with those in $In_2ZnSe_4^{33}$ (2.447 Å and 111.599°). The calculated bond valence sums $(BVS)^{34}$ (*i.e.*, 1.273, 1.173, 3.956, 1.840, 1.972 and 2.155 for K1, K2, Sn, Zn, Se1 and Se2 in K₂Sn₂ZnSe₆, respectively; 0.962, 3.905, 2.001, 1.938 and 1.970 for Na, Ge, Zn, Se1 and Se2 in Na₂Ge₂ZnSe₆, respectively) are close to the expected value, and further proves the validity of the atoms assignments.

As for Na₂In₂GeSe₆, it belongs to the Li₂In₂MQ₆ (M = Si, Ge; Q = S, Se)¹⁹ structure type and crystallizes in the noncentrosymmetric space group *Cc* of the monoclinic system with unit cell parameters of a = 12.707(3) Å, b = 8.1157(16) Å, c = 12.760(3) Å, $\beta = 108.70(3)^{\circ}$ and Z = 4. In the asymmetric unit, there are two crystallographically independent Na atoms, two independent In atoms, one Ge atom, and six Se atoms. All atoms are at general positions with 100% occupancy, and there is no detectable disorder in the structure.

Fig 4(b) demonstrates the coordination environments of Na cations, the 5-coordinated Na1 atoms and 4-coordinated Na2 atoms are in a trigonal biyramidal and tetrahedral arrangements, respectively. Selected bond distances are listed in Table 4, for instance, the Na–Se distances of 2.863(1)–3.168(3) Å are in good agreement of NaInSe₂ (3.010 Å).³⁵ The distances of In–Se range from 2.558(2) to 2.571(3) Å, a little shorter than those in NaInSe₂ (2.758 Å).³⁵ The Ge–Se bond lengths of 2.335(1)–2.361(3) Å are a little longer than those of 2.313(1)–2.336(3) Å in Ag₂In₂GeSe₆.³⁶ The calculated bond valence sums (BVS)³⁴ (1.158, 1.245, 3.180, 3.220, 4.295, 1.869, 1.974, 2.134, 2.177, 2.071 and 2.167 for Na1, Na2, In1, In2, Ge,

Se1, Se2, Se3, Se4, Se5 and Se6, respectively) are also close to the expected value.

The crystal structure of Na₂In₂GeSe₆ is illustrated in Figure 4(a), it is an interesting three-dimensional framework composed of corner-sharing [InSe₄] and [GeSe₄] tetrahedra with Na⁺ cations residing in the cavities. As is shown, the basic building unit of Na₂In₂GeSe₆ can be determined as a [In₄Ge₂Se₁₆] block comprised of two smaller [In₂GeSe₉] blocks. Firstly, two [InSe₄] tetrahedra, namely, [In1Se₄] and [In2Se₄], and one [GeSe₄] tetrahedron, are linked to each other via sharing corner Se₂, Se₃ and Se₆ atoms to form a [In₂GeSe₉] block, which is further bridged with another [In₂GeSe₉] block by sharing corner Se₁ and Se₄ atoms. Then, the [In₄Ge₂Se₁₆] blocks are connected to each other by sharing corner Se₅ atoms to generate the three-dimensional framework. Obviously that the alignment of [GeSe₄] groups is fully co-parallel while [InSe₄] tetrahedra deviate from the fully co-parallel alignment to some degree, the interplay of [InSe₄] and [GeSe₄] tetrahedra in this particular arrangements may increase the NLO properties.

Compared with the related $Li_2In_2GeSe_6$ compound, the larger and more ionic alkali metal Na⁺ in Na₂In₂GeSe₆ acts as a counter ion to balance the negative charge of the $[In_2GeSe_6]^{2^-}$ framework, while the smaller and more covalent Li⁺ in $Li_2In_2GeSe_6$ becomes part of the complicated three-dimensional framework built by $[LiSe_4]$, $[InSe_4]$ and $[GeSe_4]$ tetrahedra. It is obvious that different ionic radius and electronegativity of alkali metal cations have strong influences on the structures and properties of the materials.

Experimental Band Gaps

Dalton Transactions

Figure 5 shows the UV-vis-NIR diffuse reflectance spectra of the title compounds in the region of 300-2000 nm. The experimental optical band gaps of 1.71(2) eV, 2.36(4)eV and 2.47(2) eV for K₂Sn₂ZnSe₆, Na₂Ge₂ZnSe₆, and Na₂In₂GeSe₆ respectively were determined by the straightforward extrapolation method.³⁷ Consequently the absorption edges are 725 nm, 525 nm and 502 nm, respectively. The band gaps are consistent with their colors. For the NLO compound $Na_2In_2GeSe_6$, the value is comparable to the common commercial crystals (e.g., AgGaS₂-2.64 eV). Hence, $Na_2In_2GeSe_6$ may effectively avoid the two-photon absorption problem of the conventional 1(Nd:YAG) or 1.55(Yb:YAG) lasers, which has severely limited the application of the NLO AgGaSe₂ and ZnGeP₂ crystals.

Thermal Analysis

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

The DSC curve of $Na_2In_2GeSe_6$ is shown in Figure 6. It is clearly shown that $Na_2In_2GeSe_6$ melts congruently at a rather low temperature 671 \Box . This valuable thermal behavior makes it feasible to use the Bridgman-Stockbarger technique to grow bulk crystals, which are needed for the practical application. Additionally, the low melting point can effectively reduce the corrosion of the quartz tubes, which is helpful for single crystal growth with better quality. As a comparison, the melting points of several infrared crystals are much higher: (860 \square for AgGaSe₂, 915 \square for LiGaSe₂, 998 \Box for AgGaS₂, 1025 \Box for ZnGeP₂).

SHG Measurement

View Article Online DOI: 10.1039/C6DT00143B

Owing to its non-centrosymmetric structure (NCS) structure, Na₂In₂GeSe₆ is expected to possess NLO properties. As shown in Figure 7, the SHG signal intensity of Na₂In₂GeSe₆ with the 2090 nm laser as the fundamental wavelength is about 0.8 times that of AgGaS₂ with a similar particle size 105–150 µm. Considering the large NLO effect of AgGaS₂, the above value is relatively large. In addition, the plot of SHG response versus particle size reveals the phase matching feature of Na₂In₂GeSe₆, which is an essential criteria for practical application. As the particle size increasing, the orientations of different particles change from canceling out each other to working in concert, until the saturation is reached. As discussed in the structure section that the alignment of [GeSe₄] groups is fully co-parallel while [InSe₄] tetrahedra deviate from the fully co-parallel alignment to some degree, such packing characteristics of the [InSe₄] and [GeSe₄] tetrahedra may explain the relatively large SHG response.

Conclusion

Single crystals of K₂Sn₂ZnSe₆, Na₂Ge₂ZnSe₆, and Na₂In₂GeSe₆ were grown and characterized for the first time. They possess the same stoichiometric ratio but crystallize in different space groups *P*4/*ncc*, *I*4/*mcm* and *Cc*, respectively due to the modification of metal cations with different electronegativities and ionic radii. The structures of K₂Sn₂ZnSe₆ and Na₂Ge₂ZnSe₆ are similar and can be described as [Sn(Ge)Se₄] tetrahedra and [ZnSe₄] tetrahedra are linked via edge-sharing to build up a 1D [Sn₂ZnSe₆] infinite chain separated by K⁺(Na⁺) cations along the c direction, while the structure of Na₂In₂GeSe₆ is an interesting three-dimensional framework

Dalton Transactions

composed of [InSe₄] and [GeSe₄] tetrahedra via corner-sharing with Na⁺ cations in the cavities. The experimental band gaps of these compounds were determined as 1.71(2) eV, 2.36(4) eV and 2.47(2) eV, respectively, according to UV-vis-NIR diffuse reflectance spectroscopy. Interestingly, in addition to the large band gap, Na₂In₂GeSe₆ exhibits a phase matchable feature NLO property with a powder SHG response at 2 μ m that is approximately 0.8 times that of the benchmark material AgGaS₂ at a particle size of 105–150 μ m. Moreover, Na₂In₂GeSe₆ melts congruently at a rather low temperature of 671 \Box , which makes it feasible to use the Bridgman–Stockbarger technique to grow bulk crystals needed for the practical application. Our preliminary experimental results suggest that Na₂In₂GeSe₆ has promising applications in IR nonlinear optics and further research is in progress.

Acknowledgments

This research was supported the National Natural Science Foundation of China (No. 51472251, and No. 21271178).

References

- S. Banerjee, C. D. Malliakas, J. I. Jang, J. B. Ketterson and M. G. Kanatzidis, J. Am. Chem. Soc., 2008, 130, 12270.
- T. K. Bera, J. I. Jang, J. B. Ketterson and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2009, **131**, 75.
- W. Chen, G. Mouret, D. Boucher and F. K. Tittel, *Appl. Phys. B: Lasers Opt.*, 2001, 72, 873.
- G. D. Boyd, H. Kasper and J. H. Mcfee, *IEEE J. Quantum Electron.*, 1971, 7, 563.
- 5. B. Tell and H. M. Kasper, Phys. Rev. B: Solid State., 1971, 4, 4455.
- 6. G. D. Boyd, E. Buehler and F. G. Storz, Appl. Phys. Lett., 1971, 18, 301.
- 7. P. G. Schunemann, Aip Conf. Proc., 2007, 916, 541.
- 8. X. S. Lin, G. Zhang and N. Ye, Cryst. Growth Des., 2009, 9, 1186.
- J. Y. Yao, D. J. Mei, L. Bai, Z. S. Lin, W. L. Yin, P. Z. Fu and Y. C. Wu, *Inorg. Chem.*, 2010, 49, 9212.
- W. L. Yin, K. Feng, R. He, D. J. Mei, Z. S. Lin, J. Y. Yao and Y. C. Wu, *Dalton Trans.*, 2012, 41, 5653.
- Y. K. Chen, M. C. Chen, L. J. Zhou, L. Chen and L. M. Wu, *Inorg. Chem.*, 2013, 52, 8334.
- M. C. Chen, L. M. Wu, H. Lin, L. J. Zhou and L. Chen, J. Am. Chem. Soc., 2012, 134, 6058.
- 13. I. Chung, J. H. Song, J. I. Jang, A. J. Freeman, J. B. Ketterson and M. G.

Kanatzidis, J. Am. Chem. Soc., 2009, 131, 2647.

- M. C. Chen, L. H. Li, Y. B. Chen and L. Chen, J. Am. Chem. Soc., 2011, 133, 4617.
- W. L. Yin, K. Feng, W. D. Wang, Y. G. Shi, W. Y. Hao, J. Y. Yao and Y. C. Wu, *Inorg. Chem.*, 2012, **51**, 6860.
- W. L. Yin, W. D. Wang, L. Bai, K. Feng, Y. G. Shi, W. Y. Hao, J. Y. Yao and Y. C.
 Wu, *Inorg. Chem.*, 2012, **51**, 11736.
- Z. Z. Kish, V. V. Loshchak, E. Y. Peresh and E. E. Semrad, *Inorg. Mater.*, 1989, 25, 1658.
- V. Petrov, A. Yelisseyev, L. Isaenko, S. Lobanov, A. Titov and J. J. Zondy, *Appl Phys B-Lasers O*, 2004, **78**, 543.
- W. L. Yin, K. Feng, W. Y. Hao, J. Y. Yao and Y. C. Wu, *Inorg. Chem.*, 2012, 51, 5839.
- Z. Z. Luo, C. S. Lin, H. H. Cui, W. L. Zhang, H. Zhang, Z. Z. He and W. D. Cheng, *Chem. Mater.*, 2014, 26, 2743.
- T. K. Bera, J. I. Jang, J. H. Song, C. D. Malliakas, A. J. Freeman, J. B. Ketterson and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2010, **132**, 3484.
- 22. K. Wu, Z. H. Yang and S. L. Pan, Inorg. Chem., 2015, 54, 10108.
- H. W. Huang, J. Y. Yao, Z. Lin, X. Y. Wang, R. He, W. J. Yao, N. X. Zhai and C. T. Chen, *Chem. Mater.*, 2011, 23, 5457.
- G. S. Yang, G. Peng, N. Ye, J. Y. Wang, M. Luo, T. Yan and Y. Q. Zhou, *Chem. Mater.*, 2015, 27, 7520.

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

View Article Online DOI: 10.1039/C6DT00143B

- 25. H. Huang, J. Yao, Z. Lin, X. Wang, R. He, W. Yao, N. Zhai and C. Chen, *Angew. Chem. Int. Edit.*, 2011, **50**, 10274.
- 26. Rigaku Corporation, Tokyo, Japan, CrystalClear 2008.
- 27. Sheldrick, G. M. Acta. Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64,

112.

- 28. Kurtz, S. K.; Perry, T. T. J. Appl. Phys., 1968, 39, 3798.
- X. Chen, X. Y. Huang, A. H. Fu, J. Li, L. D. Zhang and H. Y. Guo, *Chem. Mater.*, 2000, **12**, 2385.
- S. J. Hwang, R. G. Iyer, P. N. Trikalitis, A. G. Ogden and M. G. Kanatzidis, *Inorg. Chem.*, 2004, 43, 2237.
- L. D. Zhang, Y. G. Wei, X. L. Feng and H. Y. Guo, *Chem J Chinese U*, 2005, 26, 1395.
- 32. B. Eisenmann, J. Hansa and H. Schafer, Rev Chim Miner, 1984, 21, 817.
- 33. L. Gastaldi, M. G. Simeone and S. Viticoli, J. Solid State Chem., 1987, 66, 251.
- 34. I. D. Brown and D. Altermatt, Acta. Crystallogr., Sect. B, 1985, 41, 244.
- 35. R. Hoppe, W. Lidecke and F. C. Frorath, Z. Anorg. Allg. Chem., 1961, 309, 49.
- O. V. Krykhovets, L. V. Sysa, I. D. Olekseyuk and T. Glowyak, *J. Alloys Compd.*, 1999, **287**, 181.
- 37. O. Schevciw and W. B. White, Mater. Res. Bull., 1983, 18, 1059.

Figure captions

- Figure 1 Experimental (black) and simulated (red) X-ray powder diffraction data of Na₂In₂GeSe₆. The differences in peak intensity between the two patterns may be caused by the preferential orientation of the powder samples.
- Figure 2 Crystal packing structure of K₂Sn₂ZnSe₆ with the unit cell marked, in which the red and turquoise polyhedra represent GeS₄ and ZnS₄ tetrahedra, respectively (a), coordination environments of K cations (b).
- Figure 3 Crystal structure of the unit cell of Na₂Ge₂ZnSe₆, in which the red and turquoise polyhedra represent GeS₄ and ZnS₄ tetrahedra, respectively (a), coordination environments of Na cations (b).
- **Figure 4** Crystal packing characteristics of $Na_2In_2GeSe_6$ along the *b* axis with a single $[In_4Ge_2Se_{16}]$ group marked by a black circle, in which the red and turquoise polyhedra represent InS_4 and GeS_4 tetrahedra, respectively (a), coordination environments of Na cations (b).
- Figure 5 Diffuse reflectance spectra of the title compounds.
- Figure 6 DSC curve of Na₂In₂GeSe₆.
- Figure 7 Oscilloscope traces of SHG signals for Na₂In₂GeSe₆ with AgGaS₂ as a reference at a particle size of 105–150 μm (a), Phase-matching curve for Na₂In₂GeSe₆ (*i.e.*, SHG response versus particle size) (b).





Figure 2

ez Se2

Se1



Se2

b

Se1

e1 Se1















Chemial content	$K_2Sn_2ZnSe_6$	Na ₂ Ge ₂ ZnSe ₆	Na ₂ In ₂ GeSe ₆
Fw	854.71	730.29	821.97
<i>a</i> (Å)	8.1511(12)	7.7568(12)	12.707(3)
$b(\text{\AA})$	8.1511(12)	7.7568(12)	8.1157(16)
$c(\text{\AA})$	19.570(4)	18.734(4)	12.760(3)
$\beta(°)$	90	90	108.70(3)
Space group	P4/ncc	I4/mcm	Сс
$V(Å^3)$	1300.2(4)	1127.2(3)	1246.4(4)
Ζ	4	4	4
T(K)	293(2)	293(2)	293(2)
λ(Å)	0.71073	0.71073	0.71073
$\rho_c(g/cm^3)$	4.366	4.303	4.380
$\mu(\text{mm}^{-1})$	23.024	26.797	23.597
$R(F)^{a}$	0.0451	0.0451	0.0280
$R_{\rm W}(F_{\rm o}^{2})^{b}$	0.0767	0.0998	0.0488

Published on 21 March 2016. Downloaded by Gazi Universitesi on 29/03/2016 04:51:56.

Table 1. Crystal data and structure refinement for K2Sn2ZnSe6, Na2Ge2ZnSe6, andNa2In2GeSe6.

 ${}^{a}R(F) = \Sigma \Box \Box F_{o} \Box - \Box F_{c} \Box \Box / \Sigma \Box F_{o} \Box \text{ for } F_{o}^{2} > 2\sigma(F_{o}^{2}). {}^{b}R_{W}(F_{o}^{2}) = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / C_{o}^{2} = \{\Psi [w(F_{o}^{2} - F_{c}^{2})^{2} \} / C_{o}^{2} = \{\Psi [w(F_{o}^{2} - F_{c}^{2})^{2}] / C_{o}^{2} = \{\Psi [w(F_{o}^{2} - F_{c}^{2})^{2} \} / C_{o}^{2} = \{\Psi [w(F_{o}^{2} - F_{c}^{2})^{2}] / C$

 $\Sigma w F_0^4$ ^{1/2} for all data. $w^{-1} = \sigma^2 (F_0^2) + (zP)^2$, where $P = (Max(F_0^2, 0) + 2F_c^2)/3$.

K1–Se1	3.4589(18)×4	Sn-Se1	2.4986(8)×2
K1–Se2	3.3666(15)×4	Sn–Se2	2.5672(7)×2
K2–Se1	3.3359(13)×4	Zn-Se1	2.5142(7)×4
K2–Se1	3.5863(21)×4		

Table 2. Selected bond lengths(Å) for $K_2Sn_2ZnSe_6$.

Table 3. Selected bond lengths(Å) for Na₂Ge₂ZnSe₆.

Na-Se1	3.6412(46)×4	Ge–Se2	2.3318(9)×2
Na–Se2	3.0019(22)×4	Zn–Se2	2.4833(7)×4
Ge-Se1	2.3929(9)×2		

Na1–Se2	2.968(5)	In1–Se3	2.579(2)
Na1–Se3	2.876(5)	In1-Se4	2.568(3)
Na1–Se4	2.863(2)	In2–Se3	2.570(6)
Na1–Se5	3.234(2)	In2–Se4	2.557(7)
Na1–Se6	2.949(2)	In2–Se5	2.613(7)
Na2–Se1	3.168(5)	In2–Se6	2.599(2)
Na2–Se3	2.852(1)	Ge-Se1	2.335(1)
Na2–Se4	2.875(1)	Ge–Se2	2.341(9)
Na2–Se5	2.870(3)	Ge–Se5	2.361(3)
In1–Se1	2.615(2)	Ge-Se6	2.345(6)
In1–Se2	2.599(3)		

Table 4. Selected bond lengths(Å) for Na₂In₂GeSe₆.

Table of Contents Entry

New selenides K₂Sn₂ZnSe₆, Na₂Ge₂ZnSe₆, and Na₂In₂GeSe₆ exhibit diverse structures

and Na₂In₂GeSe₆ possesses a moderate second harmonic generation response.

