Second Harmonic Generation Response of the

Cubic Chalcogenides $Ba_{(6-x)}Sr_x[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$

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ABSTRACT

We synthesized barium/strontium solid solution the sequence $Ba_{6-x}Sr_x[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ for nonlinear optical (NLO) applications in the infrared (IR) via a flux synthesis route. All title compounds are isotypic, crystallizing in the cubic space group $I\overline{4}3d$ and are composed of a three-dimensional (3D) anionic framework of alternating corner-sharing SnS₄ and AgS₄ tetrahedra charge balanced by Ba and Sr. The shrinkage of Ba/Sr–S bond lengths causes the tetrahedra in the anionic framework to become more distorted, which results in a tunable band gap from 1.58 to 1.38 eV with increasing x values. The performance of the barium limit (x = 0) is also superior to that of Sr (x = 6), but surprisingly second harmonic generation (SHG) of the solid solution remains strong and is insensitive to the value of x over the range 0 to 3.8. Results show that the non-type-I phase-matched SHG produced by these cubic chalcogenides display intensities higher than the benchmark $AgGaSe_2$ from 600 - 1000 nm.

KEYWORDS

metal chalcogenide, second harmonic generation, infrared nonlinear optical material, tunable band gap, solid solutions

INTRODUCTION

The mid-IR is a current focus for NLO material investigation since it is difficult to produce coherent, tunable laser sources in this region of the electromagnetic spectrum.¹ Applications for mid-IR technologies include chemical sensing,² telecommunications,³ and biomedicine.⁴ Chalcogenides are top-notch materials for NLO applications in the mid-IR because of their large nonlinear susceptibility, extensive IR transparency, and high thermal stability.⁵

Only a few NLO mid-IR materials are currently used commercially, and these are the chalcopyrites including AgGaS₂,⁶ AgGaSe₂,^{6d, 7} and ZnGeP₂.^{6d, 8} However, each of these materials have their own limitations, so more work is needed to discover better materials for mid-IR NLO applications.⁹ The exploratory synthesis of NLO materials often utilizes asymmetric building units to target noncentrosymmetric structures. Specifically, having high polarity on the preferred domains has been shown to yield high nonlinear susceptibilities. For example, A_3 Ta₂AsS₁₁ (A = K, Rb)¹⁰ and AAsS₂ (A = Li, Na)¹¹ are comprised of chains condensed from [AsS₃]³⁻ units, which are highly polar along the chain due to the severely distorted polyhedra caused by the lone pair on As. Additionally, structures with tetrahedral building blocks oriented in the same direction can accumulate induced dipole moments to give high polarity. For instance, the NLO materials $APSe_6$ (A = K, Rb),¹² β -K₂Hg₃Ge₂S₈,¹³ CaZnOS,¹⁴ Na₂Ge₂Se₉,¹⁵ Li₂MGeS₄ (M = Cd, Mn, Zn),¹⁶ BaGa₂Ge₂G₆ (Q = S, Se),¹⁷ Ba₂₃Ga₈Sb₂S₃₈,¹⁸ and Ba₄CuGa₅Q₁₂ (Q = S, Se)¹⁹ all contain aligned tetrahedra.

We have previously reported the solid solution series $Ba_6Ag_{2.67+4\delta}Sn_{4.33-\delta}S_{16-x}Se_x$, which is comprised of aligned tetrahedra to give a noncentrosymmetric structure and strong NLO response in the range of 600 – 800 nm.²⁰ The enhancement of polarity through substituting *x* (i.e. more Se) on anions optimized SHG signal at longer wavelengths. Here, we have advanced the work on this system by making substitutions on cations and discovered the solid solution series $Ba_{6-x}Sr_x[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ [x = 0 (1a), 1.9 (1b), 2.8 (1c), 3.8 (1d), 6 (1e)]. In the solid solution series, 1a-e, the SnS₄ and AgS₄ tetrahedra become more distorted with increasing Sr substitution. The band gap of these materials spans from 1.30-1.58 eV and generally decreases with increasing Sr substitution. The title compounds share the same crystal system $\overline{43m}$ with the semiconductor GaAs, which isotropic structure lacks birefringence for the tuning of phase matching. The technique of quasi-phase-matching has been applied to assist these cubic materials with high SHG signals performed in the frequency conversion.²¹ We examined SHG responses of 1a-e to have SHG intensity greater than the benchmark AgGaSe₂ in the range from 600 – 1000 nm and equivalent signal from 1100 – 1150 nm.

EXPERIMENTAL SECTION

Reagents. Starting materials used in the reactions include barium (rod, 99.99%, Aldrich), silver (shot, 99.9%), tin (pieces, 99.9%, Aldrich), sulfur (powder, 99.98%, Aldrich), and potassium bromide (crystals, 99.9%, J. T. Baker).

Synthesis. The stoichiometric ratios of chemical elements listed below and KBr (0.5 g, 4.2 mmol) were loaded into 8 mm fused-silica tubes in a dry N₂ atmosphere in an OMNI-LAB glovebox then sealed under vacuum ($<10^{-4}$ Torr). All the reactions were heated to 300°C for 4h, raised to 800 °C and held for 48 h, then cooled to 300 °C by a rate of 5 °C/h. The experiment was finished by turning off the power. Deionized water was used to remove the KBr flux in an ultrasonic cleaner. Dark-red and chunk-shaped crystals with dimensions around 0.2 mm were observed for compounds **1a-e**. The yield was decreased by crystals sticking on the wall of the quartz tube. A very small amount of black clods or light-yellow SnS₂ crystals were easily

removed by using a needle under a microscope. All products are air and water stable. AgGaSe₂ was prepared by heating a stoichiometric ratio of the respective elements at 1000 °C for 24 h, followed by slow cooling to 700 C, then further cooling to room temperature by tuning off the furnace power.

 $Ba_6[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (1a): A mixture of Ba (0.824 g, 6.0 mmol), Ag (0.345 g, 3.2 mmol), Sn (0.499 g, 4.2 mmol), and S (0.513 g, 16.0 mmol) giving a yield of ~72%. The average composition of three crystals using energy-dispersive X-ray spectroscopy (EDS) was $Ba_{6.0(2)}Ag_{3.9(2)}Sn_{4.2(2)}S_{16.4(4)}$.

 $Ba_{4.1}Sr_{1.9}[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (1b): A mixture of Ba (0.577 g, 4.2 mmol), Sr (0.158 g, 1.8 mmol), Ag (0.367 g, 3.4 mmol), Sn (0.499 g, 4.2 mmol), and S (0.513 g, 16.0 mmol) giving a yield of ~54%. The average composition of three crystals using EDS was $Ba_{3.9(2)}Sr_{1.9(2)}Ag_{3.2(3)}Sn_{4.2(3)}S_{16.0(7)}$.

 $Ba_{3.2}Sr_{2.8}[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (1c): A mixture of Ba (0.453 g, 3.3 mmol), Sr (0.228 g, 2.6 mmol), Ag (0.367 g, 3.4 mmol), Sn (0.499 g, 4.2 mmol), and S (0.513 g, 16.0 mmol) giving a yield of ~79%. The average composition of three crystals using EDS was $Ba_{2.9(2)}Sr_{2.8(3)}Ag_{3.4(3)}Sn_{4.2(2)}S_{16.0(7)}$.

 $Ba_{2.2}Sr_{3.8}[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (1d): A mixture of Ba (0.343 g, 2.5 mmol), Sr (0.307 g, 3.5 mmol), Ag (0.388 g, 3.6 mmol), Sn (0.487 g, 4.1 mmol), and S (0.513 g, 16.0 mmol) giving a yield of ~77%. The average composition of three crystals using EDS was $Ba_{2.3(2)}Sr_{3.5(3)}Ag_{3.7(3)}Sn_{4.3(3)}S_{16.0(7)}$.

 $Sr_6[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (1e): A mixture of Sr (0.526 g, 6.0 mmol), Ag (0.410 g, 3.8 mmol), Sn (0.487 g, 4.1 mmol), and S (0.513 g, 16.0 mmol) giving a yield of ~62%. The average composition of three crystals using EDS was $Sr_{6.0(2)}Ag_{3.5(2)}Sn_{4.8(2)}S_{16.7(4)}$.

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Powder X-ray Diffraction (PXRD) Analysis. The PXRD patterns were collected with a Bruker AXS D2 Phaser using a Cu K α tube (1.5406 Å) at 30 kV and 10 mA. A one-dimensional LYNXEYE detector designed with more than 150 integrated slits recorded 2 θ positions with an angular accuracy of <0.02°. The experimental PXRD patterns compared well with the theoretical ones for **1a-e** can be observed in Figure S1–S5.

Scanning Electron Microscopy. Semiquantitative analyses of crystals were performed using a Hitachi SU-1500 scanning electron microscope equipped with a Horiba EMAX-ENERGY energy dispersive spectrometer. The data were acquired using an accelerating voltage of 10 kV and analyzed using the EMAX Suite version 1.90 software.

Single Crystal X-ray Diffraction. Single crystals were selected for indexing and data collection on a Bruker APEXII CCD diffractometer and irradiated with graphitemonochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Data integrations and empirical absorption corrections were performed using the SAINT and SADABS functions, respectively, in the APEX2 package.²² Data was recorded at 296(2) K. The space group is $I\bar{4}3d$ for all the structures based on the intensity distributions and systematic absence of the observed structure factors. Direct methods were used to locate atomic positions on the electron density maps. Crystal data and refinement details for **1a-e** are listed in Table 1. Atomic coordinates and anisotropic displacement parameters for all the structures can be found in Tables S1-S10.

For 1a-e: First all atomic positions were determined isotropically keeping the Ag(1)/Sn(2) shared occupancy site as Ag only. The site occupancies of Ag(1), Ag(1A) and Ag(1B) were first freely refined with all three Ag sites constrained to have the same thermal parameters. Here the Ag(1A) and Ag(1B) sites falling on a 2-fold axis were apart from the Ag(1) site on a $\overline{4}$ axis. Once converged, the site occupancies of Ag(1A) and Ag(1B) were constrained

to be that determined occupancy, and these occupancies remained unchanged throughout the final refinement of the structures. The Sn(2) site was then added and constrained to have the same atomic coordinates as Ag(1) and the same thermal parameters as Ag(1), Ag(1A) and Ag(1B). The occupancies of Ag(1) and Sn(2) were algebraically determined and constrained to give the total distorted Ag position (including Ag(1), Ag(1A), Ag(1B), and Sn(2)) an occupancy of 1 with an overall charge of +1.33, which is necessary to charge balance the structure. This always yielded an occupancy of 0.11 for Sn(2). The *y*-variable in the chemical formula for these compounds represents the substitution of Sn(2) onto the Ag(1) site. A higher residual electron density as a B alert in the *CHECKCIF* report for **1c** is found around these deficient positions. Finally, all the atoms in **1a**, **1b**, **1c**, **1d** and **1e** were refined anisotropically after constraining the occupancies.

Solid State UV/Vis/Near-IR Spectroscopy. Diffuse reflectance spectra were recorded using a Hitachi U-4100 UV-Vis-NIR spectrophotometer covering a wavelength range from 300 to 3300 nm. This system was equipped with a single monochromator, photomultiplier detector for the UV/Vis region, and PbS-based detector for the NIR region. The powder sample was measured with respect to BaSO₄ powder as a reference. The absorption data (α /S) were calculated from the reflectance data using the Kubelka–Munk function: α /S = $(1 - R)^2/2R$ where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. The band gap was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge. The absorption spectra of **1a-e** indicating their band gaps can be observed in Figure S6–S10. We notice that the absorption edges for compounds **1a** and **1e** with full Ba and Sr cations, respectively, are the most smooth and clean. For the mixed Ba/Sr cations observed in **1b**, **1c**, and **1d**, the absorption edges displayed slight fluctuations and that phenomena could be related to the structural defects and compositional phase width.

Raman Spectroscopy. The Raman spectra were recorded using a Renishaw inVia Raman microscope with a 785 nm, 36 mW diode laser. The exposure time was 10 s. The data collection was done by Renishaw's RenCam CCD detector.

IR Spectroscopy. The mid-IR transmittance spectra were recorded using a Perkin Elmer Rx1 FTIR spectrophotometer. The pressed pellets were prepared by grinding the powdered samples with KBr and then drying at 70 °C for 1 day. The IR spectroscopic measurements covered a wavelength range from 500 to 4000 cm⁻¹.

Differential Thermal Analysis (DTA). DTA was performed using a computercontrolled Shimadzu DTA-50 thermal analyzer. The sample and a reference α -Al₂O₃ were loaded with the same weight of ~25 mg and were sealed in fused silica ampoules under vacuum. The heating and cooling rates of the DTA chamber were ±20 °C·min⁻¹. The thermal measurement was monitored by multiple cycles of melting and recrystallization. Differential thermal analyses on the reference AgGaSe2 and samples **1a**, **1b**, **1c**, **1d**, and **1e** are displayed in Figure S11. The reference AgGaSe2 melts congruently around 860 °C. Compounds **1a-1e** were thermally stable without the appearance of a melting point before the highest temperature of 800 °C or 925 °C.

Sample Preparation for SHG Measurements. Each compound was crushed into a powder and the crystallites were sieved to separate them into 8 different particle size ranges (20 – 32 μ m, 32 – 45 μ m, 45 – 53 μ m, 53 – 63 μ m, 63 – 90 μ m, 90 – 106 μ m, 106 – 125 μ m, 125 – 150 μ m). Material from each size range was placed into borosilicate capillary tubes (1.5 – 1.8 mm outer diameter × 90 mm) in air. The filled capillaries were evacuated, set into a dry nitrogen

environment, capped with clay to retain the dry nitrogen atmosphere, and finally flame sealed to prevent sample oxidation or hydrolysis.

SHG Measurements. The fundamental of an Nd:YAG laser pulsed at 10 Hz with a $(5.4\pm0.5)\times10^{-11}$ s full width half-maximum pulse duration was frequency-tripled (to 355 nm) and used to pump a home-made optical parametric amplifier (OPA). A long wavelength pass filter was used to remove the signal beam, and the idler beam was focused onto the samples with a 100 mm focusing lens to a spot size of about 1 mm. In order to check the SHG efficiency as a function of the excitation energy, we tuned the wavelengths of the incident light. The spectral bandwidth of the light from the OPA is approximately 2 meV full width at half-maximum. The SHG signal was collected off axis and focused onto a fiber optic bundle, which was coupled to an Andor 303 mm focal length Czerny-Turner spectrograph. A grating with 150 grooves/mm was used. The SHG spectrum was recorded with a DU420A-BEX2-DD CCD camera. We did not observe dielectric breakdown or thermal damage under these conditions.

RESULTS AND DISCUSSION

Structure. The structures of compounds **1a-e** are analogous and crystallize in the cubic space group $I\bar{4} 3d$ (Table 1). The materials Ba₆Cd₂Sn₄S₁₆,²³ Ba₆CdAg₂Sn₄S₁₆,²³ and our previously reported solid solution sequence, Ba₆Ag_{2.67+4δ}Sn_{4.33-δ}S_{16-x}Se_x,²⁰ also crystallize in this space group with the same structure-type. Here we will first discuss the structure of compound **1a** in detail then explain the differences between the other title compounds. The structure of **1a** is 3D and made of alternating corner sharing SnS₄ and AgS₄ tetrahedra (Figure 1). The SnS₄ tetrahedra have three bridging (i.e. corner sharing) S and one terminal S. The AgS₄ tetrahedra have all four bridging S. This creates a 3D anionic framework, and the holes are filled with barium to charge balance.

There is both occupancy and positional disorder of the Ag site, and it is well known that Ag⁺ ions have low energy barriers in chalcogenides, which can lead to mobility in the structure.²⁴ The Ag position splits into three crystallographically distinct ones: Ag(1), Ag(1A), and Ag(1B). There is a $\overline{4}$ rotation centered at the Ag(1) position and a $\overline{2}$ rotation centered at both Ag(1A) and Ag(1B) positions so that there are 2 possible positional sites for each Ag(1A) and Ag(1B): the main Ag(1) and two Ag(1A) and two Ag(1B) sites surrounding Ag(1) (Figure 2). The distances between Ag(1), Ag(1A), and Ag(1B) are all less than 2 Å, therefore these silver sites are not occupied simultaneously. If the occupancy of all Ag positions is restricted to a $\overline{4}$ position, then each unit of the crystal structure has a charge of -1. Therefore, a small fraction of Sn^{4+} (0.111) shares occupancy with Ag(1) to charge balance the structure (Tables S1). The y-variable in the chemical formula $Ba_{6-x}Sr_x[Ag_{(4-\nu)}Sn_{(\nu/4)}](SnS_4)_4$ represents this shared occupancy. The crystal structure was refined to charge balance and have full occupancy of the overall Ag position so that there is never a vacancy in the middle of a tetrahedron. Selected bond distances and angles for 1a are displayed in Tables 2 and 3 and discussed below. Additional structural details of 1a can be found elsewhere.²⁰

Compounds **1b-e** are the solid solution progression of compound **1a** substituting Sr for Ba, with $Ba_{4.1}Sr_{1.9}$ for **1b**, $Ba_{3.2}Sr_{2.8}$ for **1c**, $Ba_{2.2}Sr_{3.8}$ for **1d**, and **1e** is the limit containing only Sr. This solid solution sequence follows Vegard's Law because there is a linear correlation between lattice parameter and amount of Sr (Figure 3). The SnS₄ and MS_4 [M = Ag(1)/Sn(2)] tetrahedra from **1a** to **1e** become more distorted with increasing percentage of Sr. This is due to the smaller size of Sr²⁺ compared to Ba²⁺, and the trend is easily visualized by examining the Ba/Sr–S bond lengths. The Ba/Sr shared occupancy site has 8 short contacts with S atoms, and the range of these distances decreases as the amount of Sr in the unit cell increases. For example, the Ba/Sr–S bond lengths are distributed in the ranges of 3.153(1)-3.503(2) Å and 3.058(3)-3.425(3) Å for both ends, **1a** and **1e**, respectively. To accommodate the shrinkage of Ba/Sr–S distances, Sn(1)S₄ tetrahedra have S–Sn(1)–S angles gradually deviate from 111.74(6)° and 107.11(6)° in **1a** to 112.49(10)° and 106.29(10)° in **1e** (Table 2). The bridging angles *M*–S(2)– Sn(1) are affected correspondingly and compress from 107.15(6)° in **1a** to 103.98(10)° in **1e** (Table 3).

Optical Absorption. The experimental band gaps of the title compounds range from 1.30-1.58 eV (Figure 4 and Figures S6-S10). The overall trend for the solid solution series (**1a**-e) is that the band gap decreases with increasing Sr substitution. This redshift is due to the more distorted tetrahedra caused by the shrinkage of Ba/Sr–S distances, which destabilizes the bonding interaction in the anionic framework and therefore narrows the band gaps. The fully Sr substituted **1e** is anomalous to this trend and has a band gap slightly larger than **1c**. The bandgap anomaly in the full Sr analog is difficult to explain. As the fraction of Sr rises in the series there is a type of chemical pressure that is created by the shrinkage of the lattice constant and this could be a reason for the decreasing band gap. However, when the Sr fraction reaches 100% it is possible that it results in some form of structural relaxation that relieves this chemical pressure. This is of course speculation but we are unable to provide a better explanation. Bandgap anomalies (often referred to as bowing) in solid solution semiconductors are known, see for example the chalcopyrite series $Ag_xGa_{1-x}S_2^{25}$ and the perovskite series $CH_3NH_3Sn_{1-x}Pb_xI_3^{26}$

Raman and IR Spectroscopy. The Raman spectra of the full Ba of **1a** and the full Sr of **1e** compounds exhibit one strong peak at 336 cm^{-1} (Figure S13). Substituting Sr for Ba does not

affect the Raman properties. These spectra are similar to that of $Ag_4Sn_3S_8$,²⁹ displaying a strong peak at 314 cm⁻¹. Although the crystal classes of **1a-e** ($\overline{4}3m$) and $Ag_4Sn_3S_8$ (432) and therefore vibrational modes are different, these materials have similar masses, local structure, and force constants of the *M*–S (*M* = Ag, Sn) bonds, which explains the comparable frequencies. The six compounds are transparent in the IR range, and the spectra can be observed in Figure 5.

Phase-Matchability. The type-I phase-matchability of each material was determined at $\lambda_{SHG} = 1000$ nm using a modified Kurtz-Perry method.²⁷ SHG measurements for the 8 different particle sizes (20 – 150 µm) are shown in Figure S12. For type-I phase-matchability, the SHG intensity should increase then level off for increasing particle size. For non-type-I phase-matchability, the SHG signal should increase until the coherence length (l_c) is reached. Then the SHG intensity has an inverse relationship with particle size. This is because once the particle size is larger than l_c , destructive interference between the incident laser and SHG light occurs, decreasing SHG efficiency. Samples **1a-e** are all non-type-I phase-matchable at 1000 nm. All of these compounds have $l_c \leq 20$ µm because the SHG intensity only decreases from smallest to largest particle size. The quasi-phase-matching technique may help these cubic materials featuring with isotropic refractive index in the application of frequency conversion.²¹

Broadband SHG. Broadband SHG measurements are important because the NLO efficiency of a material varies with wavelength, hence examining just one wavelength does not give complete information about the SHG strength of a material. The SHG responses of **1a-e** were obtained with $\lambda_{SHG} = 600 - 1150$ nm in increments of 50 nm. The smallest particle size range, $20 - 32 \mu$ m, was used to obtain the strongest SHG signal since all materials are non-type-I phase-matchable. The SHG responses of the examined materials were compared to a benchmark mid-IR SHG material, AgGaSe₂, which is also non-type-I phase-matchable up to a fundamental

wavelength of 3000 nm. The SHG intensities of the examined materials were divided by that of AgGaSe₂ for each wavelength and are plotted on a log scale in Figure 6. The ratio to AgGaSe₂ served to both show how efficient these materials were compared to AgGaSe₂, and it also removed unwanted intensity changes due to differences in illumination and detection efficiency in the equipment used.

All materials produced a detectable SHG signal for all examined wavelengths. The strength of SHG is greater than or comparable to $AgGaSe_2$ for all tested wavelengths for all compounds. $AgGaSe_2$ is an inefficient second harmonic generator at wavelengths less than 678 nm (1.83 eV) because of its small band gap. From 600 – 1000 nm **1a-e** have greater SHG signal than $AgGaSe_2$, and from 1100 – 1150 nm the responses are comparable to $AgGaSe_2$. Presumably, the heavier Sn atoms together with tetrahedral distortion caused by mobile Ag ions enhance the polarities of the covalent bonds for the examined materials with narrower band gaps than $AgGaSe_2$ (1.83 eV) to generate higher SHG response. The enhanced SHG response of **1a** compared to $AgGaSe_2$ is aligned with the previous SHG measurement of **1a**.²⁰

The general trend between materials for SHG intensity shows $\mathbf{1a} \approx \mathbf{1b} \approx \mathbf{1c} \approx \mathbf{1d} > \mathbf{1e}$. With the full Ba analogue in $\mathbf{1a}$, $Ba_{4.1}Sr_{1.9}$ in $\mathbf{1b}$, $Ba_{3.2}Sr_{2.8}$ in $\mathbf{1c}$, and $Ba_{2.2}Sr_{3.8}$ in $\mathbf{1d}$, there are no major differences in SHG signal for the overall wavelength range. However, the fully substituted Sr analogue in $\mathbf{1e}$ exhibits slightly lower signal. This trend shows substituting over half of Sr for Ba doesn't affect the SHG response, but after a certain limit, substituting the less polarizable Sr for Ba weakens the SHG intensity. Recent reports on NLO materials such as $A_4 \text{GeP}_4 S_{12}^{28}$ and $ACd_4 \text{Ga}_5 \text{Se}_{12}^{29}$ with A varied from K to Rb and Cs have shown that the cations arranged within the cages of their respective anionic frameworks slightly influence the intensity of the SHG signals.

CONCLUSION

We synthesized the new cubic solid solution series $Ba_{6-x}Sr_x[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ (x = 0-6) with a molten salt flux synthesis technique. The structure of these materials contains aligned tetrahedra of MS_4 (M = Ag and Sn), inducing net noncentrosymmetry. This is a robust cubic structure due to the compositional flexibility seen in Ag/Sn stoichiometric ratio 20 , S/Se 20 substitution and Ba/Sr replacement that provide a complete solid solution to display the composition-property correlations. In the title solid solution series, with increasing Sr substitution, the MS₄ tetrahedra become increasingly distorted. Compounds 1a-e exhibited stronger or similar SHG response to the reference, AgGaSe₂. Overall, 1b shows the best performance for generating the harmonic of the Erbium telecom window ($\lambda_{SHG} \approx 770$ nm). The band gaps of these materials generally decrease with increasing Sr substitution; hence, these materials have high tunability in the band gap and can be tailored to specific NLO applications based on the needed gap. When Sr is partially substituted for Ba, the SHG efficiency is nearly maintained while the band gap is tuned, which may be useful for IR sensing applications. The compounds **1a-e** are thermally stable up to 800 °C (Figure S12), suggesting they have high resistance to thermal damage, which is a beneficial property for some NLO applications.

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SOPPORTING INFORMATION AVAILABLE: The crystallographic CIF files, atomic coordinates and occupancies, displacement parameters, PXRD patterns, UV/Vis/Near-IR absorption spectra, DTA curves, and SHG variable particle size measurements.

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Compound	1 a	1b	1c	1d	1e
Chemical Formula	$\begin{array}{c} Ba_{6} \\ Ag_{2.7}Sn_{4.3}S_{16} \end{array}$	$\begin{array}{c} Ba_{4.1}Sr_{1.9} \\ Ag_{2.7}Sn_{4.3}S_{16} \end{array}$	$\begin{array}{c} Ba_{3.2}Sr_{2.8}\\ Ag_{2.7}Sn_{4.3}S_{16} \end{array}$	$\begin{array}{c} Ba_{2.2}Sr_{3.8}\\ Ag_{2.7}Sn_{4.3}S_{16} \end{array}$	$Sr_6 \\ Ag_{2.7}Sn_{4.3}S_{16}$
Formula Weight	2138.70	2044.26	1999.52	1949.81	1840.46
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	I43d	I 4 3d	I 4 3d	I 4 3d	I 4 3d
<i>a</i> (Å)	14.7432(2)	14.6346(4)	14.5646(4)	14.5142(4)	14.3637(4)
$V(\text{\AA}^3)$	3204.61(8)	3134.31(15)	3089.55(15)	3057.59(15)	2963.46(14)
Ζ	4	4	4	4	4
Calculated ρ (g/cm ³)	4.433	4.326	4.271	4.238	4.127
$\mu (\mathrm{mm}^{-1})$	13.179	14.374	14.836	15.582	17.131
F(000)	3736	3595	3513	3464	3305
Reflns Collected	11660	11318	11099	10959	10656
Indep Reflns	673	657	649	645	621
R _{int}	0.0429	0.0329	0.0389	0.0339	0.0370
Data / Restraints / Parameters	673 / 0 / 27	657 / 1 / 28	649 / 1 / 28	645 / 1 / 28	621 / 0 / 26
Goodness-of-fit	1.148	1.154	1.171	1.159	1.199
$\mathbf{R}_1 \left[\mathbf{I} > 2\sigma(\mathbf{I}) \right]^a$	0.0228	0.0236	0.0305	0.0281	0.0386
$\mathbf{wR}_2 \left[\mathbf{I} > 2\sigma(\mathbf{I})\right]^b$	0.0578	0.0675	0.0798	0.0738	0.1034
Largest diff. peak and hole $(e \cdot Å^{-3})$	1.401 and -1.326	2.257 and -1.039	3.811 and -0.764	2.513 and -1.280	3.441 and -0.878

Table 1. Crystal data and structure refinement for compounds 1a-e.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, {}^{b}wR_{2} = \{\Sigma [w(|F_{o}|^{2} - |F_{c}|^{2})^{2}] / \Sigma [w(|F_{o}|^{4})]\}^{1/2}$ and calc w=1/[$\sigma^{2}(Fo^{2})$ +(0.0219P)²+55.5105P] where P=(Fo²+2Fc²)/3.

Cpd.	S(1)–Sn(1)	S(2)–Sn(1)	S(1)–Sn(1)–S(2)	S(2)–Sn(1)–S(2)
1a	2.359(2)	2.404(2)	111.74(6)	107.11(6)
1b	2.357(2)	2.400(2)	111.88(7)	106.96(6)
1c	2.364(2)	2.402(2)	112.27(7)	106.54(7)
1d	2.356(2)	2.400(2)	112.14(8)	106.68(7)
1e	2.358(3)	2.402(3)	112.49(10)	106.29(10)

Table 2. Bond distances (Å) and angles (°) of $Sn(1)S_4$ in 1a-e.

Table 3. Ba/Sr–S bond distances (Å), bond distances (Å) and angles (°) of MS_4 , and angles between Sn(1) and M (M = Ag(1)/Sn(2) in **1a-e**.^{*a*}

Cpd	Ba/Sr–S	S(2)–M	S(2)– <i>M</i> –S(2)	M-S(2)-Sn(1)
1 a	3.153(1)-3.503(2)	2.587(2)	96.60(5)-140.37(5)	107.15(6)
1b	3.132(1)-3.497(2)	2.591(2)	95.82(6)-142.85(6)	106.25(7)
1c	3.110(2)-3.487(2)	2.594(2)	95.47(6)-144.03(6)	105.47(7)
1d	3.106(2)-3.467(2)	2.585(2)	95.37(6)-144.38(6)	105.32(8)
1e	3.058(3)-3.425(3)	2.584(3)	94.68(9)-146.83(9)	103.98(10)



Figure 1. Crystal structure of **1a-e**. (a) Unit cell in the [111] direction with SnS_4 tetrahedra (white), $(Ag/Sn)S_4$ tetrahedra (purple), and barium and strontium atoms omitted for clarity. (b) Building blocks of the anionic structure with atoms labeled and thermal ellipsoids set to 90%. Ag disorder was removed for simplicity.



Figure 2. Representation of the silver atom disorder and silver and tin shared occupancy with thermal ellipsoids set at 90%. Note that only one atom can occupy one of the 3 sites (Ag1, Ag1A, Ag1B) per unit due to the Ag–Ag bond lengths.



Figure 3. Lattice parameter (Å) vs Sr fraction for **1a-e** exhibiting a linear trend, which follows Vegard's Law.



Figure 4. Band gap comparison of the solid solution series 1a-e. The measured band gaps are 1.58 eV for 1a, 1.44 eV for 1b, 1.35 eV for 1c, 1.30 eV for 1d and 1.38 eV for 1e.



Figure 5. Infrared transmission spectra of compounds 1a, 1b, 1c, 1d and 1e. The KBr background was removed from all of the spectra, and it is also depicted at the bottom of this figure.



Figure 6. Broadband SHG intensity ratio comparison to AgGaSe₂ plotted on a log-scale from $\lambda_{SHG} = 600 - 1150$ nm at particle size $20 - 32 \mu m$ with all compounds **1a-e**.

For Table of Contents Only



A series of new cubic chalcogenides $Ba_{(6-x)}Sr_x[Ag_{(4-y)}Sn_{(y/4)}](SnS_4)_4$ display superior SHG intenisties compared to AgGaSe₂ from 600 – 1000 nm. With the substitutions of cations (x = 0-6), the SHG signal remains strong while providing tunability in the band gap for these isotropic NLO materials.