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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b06373 • Publication Date (Web): 15 Aug 2017 Downloaded from http://pubs.acs.org on August 15, 2017

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Homologous 2D Chalcogenides Cs-Ag-Bi-Q (Q = S, Se) with Ion-exchange Properties

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ABSTRACT: Four new layered chalcogenides $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ and $Cs_2Ag_{2,5}Bi_{8,5}Se_{15}$ are described. $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ are isostructural and have a hexagonal $P6_3/mmc$ space group; their structures consist of $[Ag/Bi]_2Q_3$ (Q = S, Se) quintuple layers intercalated with disordered Cs cations. $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ also adopts a structure with the hexagonal $P6_3/mmc$ space group and its structure has $[Ag/Bi]_3S_4$ layer intercalated with a Cs layer. $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ can be ascribed to a new homologous family $A_x[M_mS_{1+m}]$ ($m = 1, 2, 3 \dots$). $Cs_2Ag_{2,5}Bi_{7,5}Se_{15}$ is orthorhombic with *Pnnm* space group and it is a new member of the $A_2[M_{5+n}Se_{9+n}]$ homology with n = 6. The Cs ions in $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ can be exchanged with other cations, such as Ag^+ , Cd^{2+} , Co^{2+} , Pb^{2+} and Zn^{2+} forming new phases with tunable band gaps between 0.66 and 1.20 eV. $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ possess extremely low thermal conductivity (< 0.6 W·m⁻¹·K⁻¹).

Introduction

A layered structure is one where intralayer bonding is more significant than interlayer bonding. When anionic covalent frameworks are charge balanced by alkali metal ions,¹⁻³ the presence of alkali metals force the covalent frameworks to form around them. Thus, alkali metal chalcogenides tend to form chain, layered or tunneled structures depending on the A₂Q/MQ ratios (Q= S, Se, Te).⁴ The highly anisotropic nature of the materials may lead to the possibilities of tailoring the band gaps^{5,6} and can give rise to attractive and unusual physical properties that makes them outstanding for applications in the fields of topological quantum science,⁷⁻¹³ thermoelectricity,¹⁴⁻¹⁶ γ -ray detection^{17,18} second-harmonic generation,¹⁹ optical data storage,²⁰ superconductivity,^{21,22} charge density wave formation and photovoltaics.^{23,24}

Bismuth chalcogenide compounds are a special class because they exhibit amazingly diverse compositions and structures.^{25,26} The trivalent Bi atoms in the structures can have coordination numbers varying from 3 to 9 and the inert $6s^2$ lone pair of electrons defines the electronic character of the compounds. In these compounds the BiQ₆ (Q = S, Se, Te) octahedra can combine by edge or face sharing to form blocks or modules that are fragments excised from the NaCl-, Bi₂Te₃-, CdI₂- and Sb₂Se₃-type structures.^{4,25,27,28} Furthermore, Bi atoms can share sites with similar sized cations, such as alkali or alkaline earth metals, Cu⁺, Pb²⁺, Sn²⁺, Ag⁺, Cd²⁺or lanthanides.^{29-31,32} Ternary or quaternary alkali metal chalcogenides A/M/Bi/Q (A = Li, K, Rb, Cs; M = Sn, Pb, Ag, Cd; Q = S, Se Te)²⁸ form readily and tend to possess tunneled or layered structures. For example, the $A_m[M_{1+}Se_{2+i}]_{2m}[M_{1+2l+n}Se_{3+3l+n}]$ (A = alkali metal, M = Sn and Bi) homologous superseries^{33,34,29} features compounds with tunneled structures, while the members of the Cs₄[Bi_{2n+4}Te_{3n+6}],⁴ CsM_mBi₃Te_{5+m},^{35,36} [MTe]_n[Bi₂Te₃]_m (M = Ge, Sn, Pb)³⁷⁻⁴⁵ and A₂[M_{5+n}Se_{9+n}] (A = Rb, Cs; M = Bi, Ag, Cd)³⁰ series possess layered structures. Recently, we reported the family A_xCd_xBi₄, xQ_6 (A = Cs, Rb, K; Q = S and A = Cs; Q = Se) of new compounds which also possess a layered structure.⁴⁶

The discovery and classification of homologous series makes structure design and prediction possible and they are part of a growing toolbox for the creation of new materials.^{26,47,48} Herein, we present the synthesis, structure and characterization of four new compounds $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_{6}$, $Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_{6}$, $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_{4}$ and $Cs_{2}Ag_{2.5}Bi_{8.5}Se_{1.5}$. They crystallize in three different structure types. All compounds have layered structures with intercalated Cs^+ cations. We show that Cs cations reside between the layers of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_{6}$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_{4}$ and can be ion-exchanged with other cations without structural change of the frameworks (topotactically). Thus, they provide a "soft chemistry" route to generate new materials.^{46,49-51} $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_{6}$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_{4}$ are members of a new homologous family $A_x[M_mS_{1+m}]$

Table 1. Crystal Data and Structural Refinement Statistics for $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, $Cs_{1,2}Ag_{0,6}Bi_{3,4}Se_6$, $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ and $Cs_2Ag_{2,5}Bi_{8,5}Se_{15}$ at 293(2) K^a

empirical formula	$Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$	$Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_6$	$Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$	Cs ₂ Ag _{2.5} Bi _{8.5} Se ₁₅			
formula weight	1130.08	1399.95	754.05	3496.22			
crystal system	hexagonal	hexagonal	hexagonal	orthorhombic			
space group	P6 ₃ /mmc	<i>P</i> 6 ₃ / <i>mmc</i>	P6 ₃ /mmc	Pnnm			
<i>a</i> (Å)	4.0300(14)	4.1456(8)	4.0331(6)	12.448(3)			
<i>b</i> (Å)	4.0300(14)	4.1456(14)	4.0331(6)	32.342(6)			
<i>c</i> (Å)	24.212(5)	25.449(5)	30.438(6)	4.1399(8)			
volume (Å ³)	340.5(2)	378.77(16)	428.77(15)	1666.7(6)			
Z	1	1	2	2			
density (calculated) (g/cm ³)	5.510	6.137	5.840	6.967			
absorption coefficient (mm ⁻¹)	48.635	57.705	50.229	64.656			
F(000)	474	577	634	2886			
crystal size (mm ³)	0.2252×0.1041×0.0123	0.2945×0.1289× 0.0013	0.1474×0.0945× 0.009	0.1434×0.1206×0.0055			
θ range for data collection (deg.)	1.682-29.043	3.202-24.900	4.017-24.981	1.753 to 23.498°			
	$-4 \leq h \leq 5$,	$-4 \leq h \leq 4$,	$-4 \leq h \leq 4$,	-14≤ <i>h</i> ≤14,			
index ranges	$-5 \leq k \leq 5$,	-4≤ <i>k</i> ≤4,	-4≤ <i>k</i> ≤4,	-38≤ <i>k</i> ≤38,			
	-33 <i>≤l≤</i> 33	-30 <i>≤l≤</i> 30	-36 <i>≤l≤</i> 35	-4≤ <i>l</i> ≤4			
reflections collected	2994	1847	2177	9867			
independent reflections	227 [$R_{\rm int} = 0.0920$]	$167 [R_{int} = 0.1872]$	$190 [R_{int} = 0.0683]$	1428 [$R_{int} = 0.1722$]			
completeness to $\theta = 25.242^{\circ}$	100%	98.8%	97.4%	99.6%			
refinement method	full-matrix least-squares on F^2						
goodness-of-fit	1.340	1.392	0.703	1.064			
final <i>R</i> indices $[> 2\sigma(I)]$	$R_1 = 0.0594,,$ $wR_1 = 0.1096,$	$R_1 = 0.0810,$ $wR_1 = 0.1883$	$R_1 = 0.0447,$ $wR_1 = 0.1233$	$R_1 = 0.0753,$ $wR_1 = 0.1342$			
R indices [all data]	$R_2 = 0.0638,$ $wR_2 = 0.1113$	$R_2 = 0.0981,$ $wR_2 = 0.1953$	$R_2 = 0.0491,$ $wR_2 = 0.1299$	$R_2 = 0.1351,$ $wR_2 = 0.1504$			
largest diff. peak and hole $(e \cdot Å^{-3})$	2.527 and -1.862	3.468 and -2.622	2.295 and -1.240	2.414 and -2.277			
${}^{a}R = \Sigma F_{o} - F_{c} / \Sigma F_{o} , wR = {}^{1/2}$ and	calc $w=1/[\sigma^2(Fo^2)+(0.052)]$	$(P)^2 + 3.9364P$] where $P = (F)^2 + 3.9364P$	$o^2 + 2Fc^2)/3$				

(m = 1, 2, 3 ...) while $Cs_2Ag_{2.5}Bi_{7.5}Se_{15}$ is a new member of the $A_2[M_{5+n}Se_{9+n}]$ homology with n = 6.

Experimental Section

Reagents. All chemicals were used as obtained, silver metal (99.99%, Sigma Aldrich), bismuth metal (99.9 %, Strem Chemicals), sulfur pellets (99.99%, Sigma Aldrich) and selenium pellets (99.99%, Sigma Aldrich), AgNO₃ (ACS Grade, Sigma Aldrich), CdCl₂ (ACS Grade, Mallinckrodt Baker, Inc.), Co(NO₃)₂·6H₂O (ACS Grade, Mallinckrodt Baker, Inc.), ZnCl₂ (ACS Grade, Columbus Chemical Industries, Inc.) and Pb(NO₃)₂ (ACS Grade, Columbus Chemical Industries, Inc.). Cs₂S and Cs₂Se were synthesized by reacting stoichiometric amounts of the elements in liquid ammonia as described elsewhere.⁵²

Synthesis.

Cs_{1.2}**Ag**_{0.6}**Bi**_{3.4}**S**₆. Single crystals of Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ were obtained by combining 0.0894 g Cs₂S (0.3 mmol), 0.0539 g Ag (0.5 mmol), 0.3030 g Bi (1.45 mmol) and 0.0706 g S (2.2 mmol) together in a 9 mm carbon coated fused silica tube and it was flame sealed at a vacuum of $\sim 10^{-4}$ mbar. The tube was put into a programmable furnace and heated to 300 °C in 6 h, held at this temperature for 5 h for totally melt of sulfur, then heated to 880 °C in 7 h and held at 880 °C for 72 h, then cooled down to 450 °C in 96 h and held at this temperature for 1 h followed by cooling to RT in 2 h. Black plate-like crystals with the longest edge up to 0.1 mm were obtained. Pure phase (with no observable impurities from PXRD pattern) of Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ can be obtained with the same starting ratio but with a faster cooling rate of cooling from 880 °C to 450 °C in 24 h.

 $Cs_{1,2}Ag_{0.6}Bi_{3,4}Se_6$. Single crystals of $Cs_{1,2}Ag_{0.6}Bi_{3,4}Se_6$ were obtained by the same staring molar ratio of $Cs_{1,2}Ag_{0.6}Bi_{3,4}S_6$ but changing sulfur to selenium by mixing 0.103 g Cs_2Se (0.3)

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mmol), 0.0539 g Ag (0.5 mmol), 0.3030 g Bi (1.45 mmol) and 0.1737 g Se (2.2 mmol) together in a 9 mm carbon coated fused silica tube and flame sealed at $\sim 10^{-4}$ mbar. Using the same heating profile as $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, this experiment yielded black plate-like crystals of $Cs_{1,2}Ag_{0,6}Bi_{3,4}Se_6$ large enough for single crystal X-ray diffraction measurement. The phase purity of the obtained sample is $\sim 90\%$, Figure S1.

Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄. Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ crystals were obtained by using the starting materials of 0.0745 g Cs₂S (0.25 mmol), 0.0539 g Ag (0.5 mmol), 0.209 g Bi (1 mmol) and 0.0722 g S (2.25 mmol). The mixture was loaded in a 9 mm carbon coated fused silica tube in a dry, nitrogen-filled glovebox. The tube was then placed in a programmable furnace and heated to 350 °C in 10 h and held at 350 °C for 6 h for the totally melt of S, then heated to 750 °C in 12 h and soaked for 18 h, followed by slow cooling to 300 °C in 96 h and then held for 1 h, finally cooled to RT in 3 h. Black plate-like crystals were obtained. Pure phase of Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ was obtained by combining 0.834 g Cs₂S (2.8 mmol), 0.0895 g Ag (0.83 mmol), 0.3521 g Bi (1.69 mmol) and 0.0926 g S (2.89 mmol) together in a carbon coated fused silica tube. The tube was heated to 350 °C in 6 h and held for 6 h, then heated to 750°C in 12 h and soaked for 24 h, followed by slow cooling to 300 °C in 32 h and then held for 1 h, finally cooled to RT in 2 h. The Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ pure phase was obtained with no observable extra peaks from PXRD pattern.

Cs₂Ag_{2.5}Bi_{8.5}Se₁₅. Synthesis was conducted to obtain Cs_{0.6}Ag_{0.8}Bi_{2.2}Se₄ crystals with the same starting molar ratio used to obtain Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄. The starting materials are 0.0862 g Cs₂Se (2.8 mmol), 0.539 g Ag (0.83 mmol), 0.209 g Bi (1.69 mmol) and 0.1777 g Se (2.89 mmol). The starting materials were combined together in a 9 mm fused silica tube in a dry, nitrogen-filled glovebox. The tube was evacuated to ~10⁻⁴ mbar and flame sealed. The tube was heated to 300 °C in 6 h, held for 6 h, and then heated to 750 °C in 12 h and held for 18 h, then cooled down to 300 °C in 96 h and held for 1 h followed by cooling to room temperature (RT) in 3 h. Bar like crystals were obtained for single crystal diffraction and the purity of the obtained phase is ~90%, Figure S1.

Finally, $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$ (with a nominal formula of $Cs_{0.53}Ag_{0.67}Bi_{2.26}Se_4$) with *Pnnm* space group instead of $Cs_{0.6}Ag_{0.8}Bi_{2.2}Se_4$ (*P6*₃/*mmc* space group) was obtained. When trying to obtain better crystals of $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$ with different starting material ratios, a reported compound $Cs_2Ag_{1.5}Bi_{7.5}Se_{13}^{30}$ was also obtained but the structure of this compound was re-refined and the CIF file is given in the supporting information.

Powder X-ray Diffraction. The purity of the samples was characterized by Rigaku Miniflex powder X-ray diffractometer with Ni-filtered Cu K α radiation operating at 40 kV and 15 mA. The scanning width is 0.02° and a collecting rate of 10°/min was used. Simulated powder X-ray diffraction (PXRD) pattern was obtained by using the CIF file of the refined structure by using the Visualizer software package of the program FINDIT.

Single Crystal X-ray Diffraction. The single crystals used to conduct X-ray diffraction measurements were adhered to the tips of glass fibers with glue. STOE IPDS II single crystal diffractometer was operating at 50 kV and 40 mA with Mo K α radiation ($\lambda = 0.71073$ Å). Data collection were conducted by using X-Area software,⁵³ integration were operated in X-RED, and numerical absorption corrections were applied with X-SHAPE.⁵³ The crystal structures were solved via direct meth-

od and refined by SHELXTL program package.⁵⁴ Table S1 to 12 show the atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters and bond lengths of the title compounds.

Scanning Electron Microscopy. Quantitative microprobe analyses and crystal imaging of the compounds were performed by using Hitachi S-3400 scanning electron microscope equipped with a PGT energy-dispersive X-ray analyzer. The data were acquired by an accelerating voltage of 25 kV, a probe current of 70 mA, and 60 s acquisition time. The compositions reported here are an average of a large number of independent measurements from given samples.

Differential Thermal Analysis. The ground single crystals of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ with a mass about 40 mg were sealed in silica ampoules under a vacuum of $\sim 10^{-4}$ mbar. Differential Thermal Analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50 thermal analyzer. A silica ampoule containing alumina was placed on the reference side of the detector. The $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ sample was heated to 750 °C and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ was heated to 620 °C at 10 °C/min followed by cooling at 10 °C/min to room temperature and finally this cycle was repeated. The DTA products were examined with PXRD after the experiment.

Ultraviolet-Visible Spectroscopy. The ultraviolet-visible spectrums were recorded, in the infrared region 500-2000 nm, with the use of UV-3600 Shimadzu UV-3600 PC double-beam, double-monochromator spectrophotometer. Finely ground samples were used to do the measurements at room temperature. By using Kubelka–Munk equation absorption (α /*S*) data was obtained: α /*S* = $(1-R)^2/2R$, where *R* is reflectance, α is absorption coefficient, and *S* is scattering coefficient.⁵⁵ The fundamental absorption edge was obtained by linearly fitting the absorbance of the converted data.

Ion-Exchange Experiments. Ion-exchange experiments of Cs_{1,2}Ag_{0,6}Bi_{3,4}S₆ and Cs_{0,6}Ag_{0,8}Bi_{2,2}S₄ were conducted. The crystals of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ (~10.0 mg) were added into 0.2 mol/L water solution (10 mL) of AgNO₃, $CdCl_2$, $Co(NO_3)_2 \cdot 6H_2O$, $ZnCl_2$ and $Pb(NO_3)_2$, respectively. The mixture kept shaking for 24 hours at RT and then isolated by filtration (through filter paper, Whatman no. 1); washed several times with water and acetone then dried in air. Crystals after ion-exchange were hand-picked and analyzed with energy dispersive spectroscopy (EDS) analysis. The ground powder of Cs_{1,2}Ag_{0,6}Bi_{3,4}S₆ and Cs_{0,6}Ag_{0,8}Bi_{2,2}S₄ (~100 mg) were added in 0.2 mol/L water solution (20 mL) of AgNO₃, CdCl₂, $Co(NO_3)_2 \cdot 6H_2O$, ZnCl₂ and Pb(NO₃)₂, respectively. The mixture kept under magnetic stirring for 24 hours at RT. The solution was filtered and washed as previously mentioned and characterized with PXRD and UV-visible spectroscopy.

Spark Plasma Sintering. Phase pure samples of $Cs_{1,2}Ag_{0.6}Bi_{3,4}S_6$ and $Cs_{0.6}Ag_{0.8}Bi_{2,2}S_4$ were pulverized and hand grounded into fine powders in N₂-filled glove box. The powders were then loaded into graphite dies with a diameter of 10 mm for SPS at 763 K for 10 min under an axial pressure of 30 MPa. The relative mass density of the SPSed sample is about 97% for $Cs_{1,2}Ag_{0.6}Bi_{3,4}S_6$ and 93% for $Cs_{0.6}Ag_{0.8}Bi_{2,2}S_4$.

Thermal Conductivity. The SPSed pellets were cut and polished into desired geometry with dimensions of $\sim 6 \text{ mm} \times 6 \text{ mm} \times 2 \text{ mm}$ and coated with a thin layer of graphite to minimize the emissivity of the material. By using the laser flash diffusivity method in Netzsch LFA457 thermal diffusivity (*D*) coefficients were measured perpendicular to the SPS pressure direction. The thermal diffusivity data were analyzed using a

Cowan model with pulse correction. The total thermal conductivity was calculated from $\kappa_{tot} = DC_p d$, density (d) is determined by using the dimensions and mass of the SPSed sample. The specific heat capacity (C_p) was estimated by Dulong-Petit law $C_p = 3R/\overline{M}$, in which *R* is gas constant 8.314 J·mol⁻¹K⁻¹ and \overline{M} is average molar mass. The uncertainty of the thermal conductivity is estimated to be ~8%.⁵⁶

Electrical Properties. SPS-processed pellet were cut into bars (~3 mm × 3 mm × 8 mm) perpendicular to the sintering pressure direction and the samples were spray-coated with boron nitride to minimize outgassing, except where needed for electrical contact. The Seebeck coefficients and electrical conductivities were measured simultaneously on an Ulvac Riko ZEM-3 instrument under a low-pressure helium atmosphere. The uncertainty of the Seebeck coefficients and electrical conductivity measurements is ~ 5%.⁵⁶

Density Functional Theory (DFT) Calculations. The total energies and relaxed geometries were calculated by DFT using the exchange correlation functional within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof the exchange correlation functional with Projector Augmented Wave potentials.⁵⁷ We use periodic boundary conditions, a plane wave basis set, and Projector Augmented Wave potentials⁵⁷ as implemented in the Vienna ab initio simulation package.⁵⁸ The total energies were numerically converged to approximately 3 meV/cation using a basis set energy cutoff of 500 eV and dense k-meshes corresponding to 4000 k-points per reciprocal atom in the Brillouin zone. Our theoretically relaxed CsAgBi₂S₄ lattice constants for the P6₃/mmc crystal structure are a = 7.04 Å, b = 4.09 Å, and c = 28.11 Å, which are in reasonable agreement with the experimentally measured lattice parameters, a = 4.0331(6) Å, b = 4.0331(6) Å, c =30.438(6) Å. Building a small-unit-cell periodic atomic structure to represent $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ is difficult, since Cs sites are partially occupied and certain Bi atoms occupy the Ag site. We thus used a simplified CsAgBi₂S₄ stoichiometry, with no partially occupied Wyckoff sites as a model to simplify the problem.

Phonon Dispersion Calculations. To quantitatively explore the origin of lattice thermal conductivity at the atomic level, we utilize the Debye-Callaway model to quantitatively evaluate the value of lattice thermal conductivity of CsAg-Bi₂S₄. It is known that the Grüneisen parameters, which characterize the relationship between phonon frequency and crystal volume change, serve as a useful measure of the lattice anharmonicity and thus helpful to interpret the physical nature of lattice thermal conductivity behavior.^{59,60} The phonon and Grüneisen dispersions are calculated using first-principles DFT phonon calculations within the quasi-harmonic approximation. The CsAgBi₂S₄ phonon dispersions are calculated on a 128 atom cell at two volumes, one is the equilibrium volume V_0 and an isotropically compressed volume $0.98V_0$. Details of Grüneisen parameter calculations are given in the supporting information.

Results and Discussion

Synthesis and Thermal Stability. Single crystals of $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, $Cs_{1,2}Ag_{0,6}Bi_{3,4}Se_6$, $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ and

 $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$ were obtained with a relatively slow cooling rate (~5 °C/h). Pure phases of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ can be obtained by heating a mixture of Cs_2S , Ag, Bi and S in sealed fused silica tubes at 750 °C as indicated by the powder X-ray diffraction (PXRD) patterns, Figure 1(a). All compounds are black and stable in air, water and acetone. Energy-dispersive X-ray spectroscopy (EDS) was performed as semiquantitative elemental analysis of Cs, Ag, Bi, S and Se. The EDS results of all these compounds are in agreement with the compositions obtained from the refinements of the crystal structure, Figure S2. The $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$ was found in the products of the reaction performed to obtain $Cs_{0.6}Ag_{0.8}Bi_{2.2}Se_4$ as an isostructural analog of $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$.



Figure 1. (a) Comparison of powder X-ray diffraction spectrum between synthesized and the simulated ones. A: $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ simulated, B: $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ synthesized, C: $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ simulated, D: $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ synthesized; (b) The DTA curves of $Cs_{0.94}Ag_{0.56}Bi_{2.2}A_4$.

Differential thermal analysis (DTA) of $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ was conducted with a heating and cooling rate of 10 °C/min to 750 °C for two consecutive cycles. DTA revealed an endothermic peak at 687 °C and one exothermic peak at 688 °C, Figure 1(b). PXRD of the DTA-derived products showed that the compound melts congruently, Figure S3. $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ is stable up to 620 °C as indicated by DTA, Figure S4.

Crystal Structures. $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$, $Cs_{1,2}Ag_{0,6}Bi_{3,4}Se_6$, $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ and $Cs_2Ag_{2,3}Bi_{8,5}Se_{15}$ crystallize in three differ ent structure types. $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and $Cs_{1,2}Ag_{0,6}Bi_{3,4}Se_6$ are

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Figure 2. The crystal image (left), (a) the unit cell of $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and (b) the unit cell of $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$; The scale bar is 100 μ m.

isostructural with the space group of $P6_3/mmc$, see Table 1. The unit cell of Cs_{1.2}Ag_{0.6}Bi_{3.4}Se₆ is slightly larger than that of Cs₁₂Ag_{0.6}Bi_{3.4}S₆ because of the larger radius of Se.⁶¹ Herein, we describe in detail only the representative crystal structure of Cs₁₂Ag₀₆Bi₃₄S₆. Cs₁₂Ag₀₆Bi₃₄S₆ consists of infinite anionic $[Ag_{x}Bi_{2-x}S_{3}]_{n}^{-2x}$ quintuple slabs separated by Cs⁺ cations. SEM images show a step-like texture on the plate-like crystals of Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ which arise from the stacking of the individual layers, Figure 2. There is only one crystallographic position for the Ag/Bi atoms. Each $[Ag_{x}Bi_{2-x}S_{3}]_{n}^{-2x}$ slab is two octahedra thick and they are isostructural to the layers of Bi₂Se₃, and has mixed occupancy of Ag/Bi1 (15% Ag and 85% Bi) octahedral sites bound to six sulfur atoms, Figure 2(a). The Ag/Bi-S bond distances range from 2.62(2) to 3.10(3) Å. The average Ag/Bi-S distance is 2.830 Å, which is very similar to the Bi-S distances reported in KBi6 33S10 and $K_2 Bi_8 S_{13}$.⁶² The Cs⁺ cations partially occupy two different Wyckoff positions 2b and 2d making these ions highly disordered in the *ab*-plane.

The Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ structure is similar to the A_xCd_xBi_{4.x}Q₆ (A = Cs, Rb, K; Q = S and A = Cs; Q = Se) compounds.⁴⁶ The A_xCd_xBi_{4.x}Q₆ structure consists of infinite anionic [Cd_xBi_{4.} xS₆]_n^{-x} layers which adopt the hexagonal motif of the Bi₂Se₃ structure type, separated by disordered Cs cations. Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ is derived from A_xCd_xBi_{4.x}Q₆ by changing the six coordinated Cd²⁺ to Ag⁺ with the extra negative charge balanced by accommodating more alkali metals between the layers i.e. A_{2x}Ag_xBi_{4.x}Q₆.

Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ also adopts the *P*6₃/*mmc* space group, see Table 1. The structure is composed of $[Ag_xBi_{3-x}S_4]_n$ slabs and disordered Cs⁺ cations. These slabs are thicker than the $[Ag_xBi_{2-x}S_3]_n^{-2x}$ layer described above. In comparison, the unit cell parameters along *a* and *b* directions of Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ are the same as Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ but the *c*-axis of Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ is lengthened by 6.223 Å compared to Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆. Figure 2(b) shows how adding a layer of $[Ag/BiS]_n$ atoms the $[Ag_xBi_{2-x}S_3]_n$ slab leads to the thicker $[Ag_xBi_{3-x}S_4]_n$ slabs. The $[Ag_xBi_{3-x}S_4]_n$ are three octahedra thick, and feature two crystallographically different Ag/Bi sites 2a and 4f. The Ag/Bi1 (58% Bi and 42% Ag) site forms regular octahedral coordination with Ag/Bi1-S2 distances of 2.818(6) Å. The Ag/Bi2 (82% Bi and 18% Ag) site has three long Ag/Bi2-S2 and three short Ag/Bi2-S1 bonds with an average bond distance of 2.891 Å. The Cs cation layer resembles that observed in $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$.

Cs₂Ag_{2.5}Bi_{8.5}Se₁₅ adopts the *Pnnm* space group and its structure belongs to the A₂[M_{5+n} Se_{9+n}] homology with n = 6.⁶³ The n = 1, 2, 3, 4 members of the series were reported previously.⁶³ The discovery of Cs₂Ag₂₅Bi₈₅Se₁₅ validates the predictive function of the homologous series. In terms of the homology it can be expressed as $Cs_2[(Ag/Bi)_{11}Se_{15}]$ featuring the $[M_{11}Se_{15}]^{2}$ (M = Ag/Bi) modules, Figure 3(b). This module is four "BiSe6" octahedra wide and three octahedra thick, and is propagated by linking with identical neighboring modules through sharing an edge of the Ag/Bi4-Se octahedron to form a stepwise slab. The structure has six crystallographically different Ag/Bi atoms. Except for Bi1, all metal sites have mixed occupancy by Bi and Ag. Ag/Bi6 forms a regular octahedron and other Ag/Bi atoms are in distorted octahedral coordination environments. The bond distances of Ag/Bi-Se vary from 2.780(5) to 3.194(5) Å with an average Ag/Bi-Se distance of 2.941 Å. The Cs⁺ cations are in a bicapped trigonal prismatic coordination with Cs–Se distances range between 3.579(7) and 3.579(7) Å.63

Homologous series of compounds are families of related structures that are composed of similar building blocks whose number increases by regular increments. Homologous series provide an ideal playground to predict new materials.^{27,32} These structural characteristics make it possible to manipulate

the physical properties through a controlled modification of the crystal structure and/or chemical composition.⁶⁴ These compounds with flat layers intercalated with Cs^+ cations can

be summarized into a new homologous series $A_x[M_mQ_{1+m}]$ (Q = S and Se). $K_{2x}Mn_xSn_{3-x}S_6$ (KMS-1)⁶⁵, $K_{2x}Mg_xSn_{3-x}S_6$ (KMS-2)⁶⁶ and RbBiS₂⁶⁷ contain [MS₂] monolayers. $K_{2x}Mn_xSn_{3-x}S_6$ and $K_{2x}Mg_xSn_{3-x}S_6$ can be denoted as $K_{2x/3}$ (M/Sn)S₂ (M = Mn



Figure 3.

and Mg) with m = 1. The monolayer in KMS-1 and KMS-2 derives from the simplest of octahedral layers SnS₂ by substituting some Sn⁴⁺ atoms for divalent Mg²⁺ and Mn²⁺ atoms with the resulting negative charge being balanced by K^+ atoms. $Cs_{1,2}Ag_{0,6}Bi_{3,4}Q_6$ and $Cs_xCd_xBi_{4,x}Q_6$ (Q = S, Se) can be denoted as $A_x(M/Bi)_2Q_3$ (m = 2) with structure possessing $[M_2Q_3]$ double octahedral layers.⁶⁷ $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ possesses $[M_3S_4]_n$ triple octahedral layer with m = 3. $[M_3S_4]_n$ layers are also found in the three dimensional PbBi₂Se₄ compound which is a member of the galenobismuthite homologous series.38 Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ can be derived from a [PbBi₂Se₄] slab by substituting Pb²⁺ atoms with Ag⁺. This renders the slab negatively charged and the Cs⁺ balance the charge by residing between the layers.



Figure 4. The band gaps of A: $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ with $E_g = 1.20$ eV; B: $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ with $E_g = 1.09$ eV; C: $Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_6$ with $E_g = 0.67 \text{ eV}$; D: $Cs_2Ag_{2.5}Bi_{7.5}Se_{15}$ with $E_g = 0.65 \text{ eV}$.

Optical Absorption and Electronic Structure Calculations. The four title compounds are semiconductors as indicated by the solid state electronic absorption spectra which reveal the presence of bandgaps. Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ shows a sharp and strong optical absorption edge at 1.20 eV, Figure 4. Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ shows a smaller band gap (1.09 eV) than Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ due to the thicker layer. Cs_{1.2}Ag_{0.6}Bi_{3.4}Se₆ possesses a band gap of 0.67 eV. Cs₂Ag_{2.5}Bi_{7.5}Se₁₅ has the smallest band gap of 0.65 eV.

The DFT calculated electronic structures indicate an indirect band gap of 0.51 eV for CsAgBi₂S₄ and a direct band gap of

The unit cell of (a) $Cs_2Ag_{1,5}Bi_{7,5}Se_{1,3}$ and (b) $Cs_2Ag_{2,5}Bi_{8,5}Se_{1,5}$ and the evolution of the layers (middle).

0.21 eV for Cs₂AgBi₃S₆, see Figure 5. This underestimation of the calculated bandgaps compared to experiment is a wellknown tendency of semi-local exchange-correlation functionals like PBE.^{68,6}



Figure 5. Electronic band structure of CsAgBi₂S₄ (a) and $Cs_2AgBi_3S_6(b)$.

Ion-Exchange Chemistry. The interlayer space available for the disordered Cs^+ cations in $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ with their weak ionic interactions, gives ample room for ion mobility and this suggested to us that these atoms could participate in ion-exchange reactions with other cations. In fact, the study of metal sulfide as ion-exchangers is an emerging field and promises materials with unique applications.⁷⁰ We find that when these two compounds are immersed in a water solution of Ag^+ , Cd^{2+} , Co^{2+} , Pb^{2+} and Zn^{2+} ions for 24 h the ion-exchange proceeds with apparent ease. Table 2 lists

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Figure 6. The ion-exchange mechanism and band gaps changes after ion exchange (a) C_{1.2}Ag_{0.6}Bi_{3.4}S₆ and (b) Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄.

the EDS elemental analysis results of the materials after ion exchange. The Table shows that in $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ the Cs^+ can be completely replaced by Cd^{2+} , Pb^{2+} and Zn^{2+} and most exchanged by Co²⁺ and the exchanged cations distribute homogeneously in the layered crystal, Figure S5. In the case of $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ the Cs^+ cations can be completely exchanged by Ag^+ , Cd^{2+} , Co^{2+} , Pb^{2+} and Zn^{2+} , Figure S6. The ionexchange process is illustrated in Figure 6 and the ion exchange was further confirmed by the shift of the PXRD peaks, i.e. (002), which are shown in Figure 7. Taking Pb^{2+} as an example, after ion exchange the (002) basal peak moved to higher angles indicating a decrease of the interlayer distance as a result of ion exchange which is consistent with the smaller size of Pb²⁺ than Cs⁺.

 Table 2.
 Energy-dispersive X-ray Spectroscopy (EDS)
Elemental Analyses Results of Ion-exchange Products

	Cs	X *	Ag	Bi	S
Cs _{1.2} Ag _{0.6} Bi _{3.4} S	6				
As- synthesized	0.92	-	0.70	3.20	6
Ag-exchanged	-	-	10.74	0.41	6
Cd-exchanged	-	0.32	0.68	3.20	6
Co-exchanged	0.20	0.50	0.62	3.40	6
Pb-exchanged	-	0.50	0.62	4.00	6
Zn-exchanged	-	0.40	0.70	3.00	6
Cs _{0.6} Ag _{0.8} Bi _{2.2} S	4				
As-synthesizd	0.94	-	0.56	2.24	4
Ag-exchanged	-	-	1.23	2.49	4
Cd-exchanged	-	0.30	0.60	2.70	4
Co-exchanged	0.02	0.12	0.64	2.11	4
Pb-exchanged	-	0.20	0.82	2.30	4
Zn-exchanged	-	0.21	0.75	2.14	4



Figure 7. (a) The PXRD of $C_{1,2}Ag_{0,6}Bi_{3,4}S_6$ before and after ion exchange; (b) The PXRD of Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ before and after ion exchange.

The process of ion exchange can be described by the following equations:

 $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6(s) + 0.6 Pb(NO_3)_2(aq) \rightarrow Pb_{0.6}Ag_{0.6}Bi_{3.4}S_6$ $(s) + 1.2 \text{ CsNO}_3(aq)$ $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4(s) + 0.3 Pb(NO_3)_2(aq) \rightarrow Pb_{0.3}Ag_{0.8}Bi_{2.2}S_4$ $(s) + 0.6 \text{ CsNO}_3 (aq)$



Figure 8. (a) Electrical conductivity, (b) Seebeck coefficient and (c) Thermal conductivity values as a function of temperature for $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ (black) and $Cs_{0,6}Ag_{0,8}Bi_{2,2}S_4$ (red).

It is characteristic that the ion-exchange process results in materials with a red-shifted optical absorption. The Pb²⁺ exchanged materials of both $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_6$ and Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ show the largest red shift and thus smallest band gaps of 0.66 and 0.76 eV, respectively. This large band gap narrowing is due to the inter layer bonding change from ionic in $Cs^+ \cdots S^{2-}$ to covalent in Pb-S so the structure become more three-dimensional.⁷¹ When the Cs ions in $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ are ion exchanged with Zn^{2+} , Cd^{2+} , and Co^{2+} the band gap also narrows from 1.20 eV of the pristine sample to 1.05, 1.03 and 0.85 eV, respectively. When immersed in solution of Ag⁺ PXRD measurements reveal that Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ decomposes partially to Ag₂S after ion exchange, Figure 7(a). This is attributed to the great thermodynamic and kinetic stability of the Ag₂S phase. The Cs⁺ in $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ can be ion exchanged with Zn^{2+} , Co^{2+} , Cd^{2+} and Ag⁺ resulting in band gaps of 1.00, 0.96, 0.94, 0.85 and 0.76 eV, respectively. Unlike in Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ no Ag₂S was observed in the case of Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ under the same ion exchange conditions, Figure 6(b). Both $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_{6}$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ exhibit partial ion exchange in Co^{2+} solution giving products with formula (derived by EDS) of Cs0.20Co0.50Ag0.26Bi3.40S6 and Cs0.02Co0.12Ag0.64Bi2.11S4, respectively. The ion exchange process provides a direct "soft chemistry" route to new compounds which are not readily accessible by traditional solid state synthesis techniques.

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Thermal Electrical and Transport **Properties.** $Cs_{1,2}Ag_{0,6}Bi_{3,4}S_{6}$ features a low electrical conductivity (< 1 $S \cdot cm^{-1}$) and a relatively high Seebeck coefficient (-440 $\mu V \cdot K^{-1}$ ¹) at room temperature, which suggests a relatively low carrier concentration, Figure 8 (a) and (b). With temperature increasing, the electrical conductivity rises rapidly while the absolute value of Seebeck coefficient decreases, indicating semiconducting transport behavior, with the highest electrical conductivity of 11 S·cm⁻¹, and the Seebeck coefficient of -183 μ V·K⁻¹ at 775K. The Seebeck coefficients are negative in the entire temperature range, suggesting electrons as the majority carriers. The conductivity of $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ is 0.05 S cm⁻¹ and the Seebeck coefficient is relatively large with -432 μ V·K⁻¹ at 373 K. When heating both electrical conductivity and Seebeck coefficient have the same trend as that of Cs1.2Ag0.6Bi3.4S6 with the highest conductivity of 11 S \cdot cm⁻¹ and Seebeck coefficient of -185 $\mu V \cdot K^{-1}$ at 820 K.

Another noteworthy feature of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$ is its ultralow thermal conductivity of ~0.45 $W \cdot m^{-1} \cdot K^{-1}$ at 300 K, Figure 8(c). Moreover, the thermal conductivity shows very

weak tempera ture dependence. This low value is comparable to compounds known for their ultralow thermal conductivity and excellent thermoelectric performance, i.e., $Cu_{2,x}Se(0.66-1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$,⁷² $Cu_{2,x}S(0.25-0.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$,⁷³ AgSbSe₂ $(0.23-0.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$,⁷⁴ CsAg₃Te₃ $(0.18-0.14 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$,⁷⁵ etc. $Cs_{0.6}Ag_{0.8}Bi_{2,2}S_4$ also possesses a lower thermal conductivity of 0.6 W $\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature, Figure 8(c). It decreases with increasing temperature with the lowest value of 0.49 W $\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 825K. The origin of this ultralow thermal conductivity could be related to its layered structure and the disordered Cs ion distribution that lends them to "rattle". Rattler atoms have been invoked as phonon scattering centers in many compounds including $Cs_2Hg_6S_7$,⁷⁶ $Ba_8Au_{16}P_{30}^{77}$, $CsAg_5Te_3^{75}$, Skutterudites⁷⁸⁻⁸² and recently in a family of Ba_2AuBi and related Heusler compounds.⁸³

To understand the origin of the low thermal conductivity of CsAgBi₂S₄, the phonon dispersions and Grüneisen dispersions were calculated by using DFT. Grüneisen parameters can characterize the relationship between phonon frequency and crystal volume change, thus provide an insight into the lattice anharmonicity.^{60,75} The Grüneisen parameters for the acoustic modes in CsAgBi₂S₄ are all large and give rise to large average acoustic Grüneisen parameters of $\gamma_{TA}=2.87$, $\gamma_{TA}=2.07$, γ_{LA} =1.61, Figures 9a and b. Thus, the Gruneisen parameters of CsAgBi₂S₄ indicate strongly anharmonic vibrational properties. The low frequency vibration modes originate from the Cs, Ag and Bi contributions which exhibit a rattler-like behavior. These modes are identified as three low frequency peaks in Figure 9c. Similar to CsAg₅Te₃, where the concerted rattling modes account for the low lattice thermal conductivity, ⁷⁵ rattling vibrations in CsAgBi₂S₄ contribute strongly to suppressing the lattice thermal conductivity. On the basis of the phonon dispersions and Grüneisen parameters, the calculated lattice thermal conductivities (calculated via a Debye- Grüneisen model) of CsAgBi₂S₄, are shown in Figure 9d. The calculated value is about 2.1 W·m⁻¹·K⁻¹ at 300 K, which is significantly larger than the measurements of total thermal conductivity around 0.6 $W \cdot m^{-1} \cdot K^{-1}$ for $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$. On one hand, the discrepancy could be due to the difference in composition between the calculated ideal structure of CsAgBi₂S₄ and the experimentally determined one at Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄, which is really difficult to represent by a simple supercell (due to the disorder-linked mixed occupancy of Cs). This discrepancy suggests the presence of extra phonon scattering induced by the disorder in the Cs layers and the mixed occupancy disorder of Bi in Ag which are not considered in our calculations.

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Figure 9. (a) Phonon and (b) Grüneisen dispersions for $CsAgBi_2S_4$. (c) The projected phonon density of states for $CsAgBi_2S_4$. (d) The temperature dependent lattice thermal conductivities of $CsAgBi_2S_4$, calculated by the Debye-Callaway model.

Concluding Remarks

 $Cs_{1,2}Ag_{0.6}Bi_{3.4}S_6,\ Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_6$ and $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ together with other reported compounds which possess flat MSe₆ octahedral layers form a new homologous series $A_x[M_mQ_{1+m}]$ (Q = S and Se). In the context of this homology, Cs12Ag06Bi34S6, Cs12Ag06Bi34Se6 and Cs06Ag08Bi22S4 can be denoted as $Cs_{0.6}(Ag/Bi)_2S_3$ with m = 2, $Cs_{0.6}(Ag/Bi)_2Se_3$ with m = 2 and $Cs_{0.6}(Ag/Bi)_3S_4$ with m = 3, respectively. The $Cs_2Ag_{2.5}Bi_{7.5}Se_{15}$ is new member of the known $A_2[M_{5+n}Se_{9+n}]$ homology with n = 6 and its synthesis enlarges this homologous family and inspires the pursuit of additional new members. The Cs⁺ ions intercalated between the layers of Cs_{1.2}Ag_{0.6}Bi_{3.4}S₆ and Cs_{0.6}Ag_{0.8}Bi_{2.2}S₄ structure can be topotactically exchanged with Ag^+ , Cd^{2+} , Co^{2+} , Pb^{2+} and Zn^{2+} at room temperature to give new compound red-shifted band gaps tunable from 1.20 to 0.66 eV. Thermal conductivity measurements show both Cs1.2Ag0.6Bi3.4S6 and Cs0.6Ag0.8Bi2.2S4 compounds possess extremely low thermal conductivity. Although a full study of the thermoelectric properties is not the focus of this paper future systematic doping studies should explore their potential as high performance materials.

ASSOCIATED CONTENT

X-ray crystallographic data of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$, $Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_6$, $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$ and $Cs_2Ag_{1.5}Bi_{7.5}Se_{13}$ in CIF format. Tables of atomic coordinates and displacement parameters of $Cs_{1.2}Ag_{0.6}Bi_{3.4}S_6$, $Cs_{1.2}Ag_{0.6}Bi_{3.4}Se_6$, $Cs_{0.6}Ag_{0.8}Bi_{2.2}S_4$ and $Cs_2Ag_{2.5}Bi_{8.5}Se_{15}$; SEM image and Energydispersive X-ray spectroscopy spectrum; PXRD after DTA was given in supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported in part by National Science Foundation (Grant DMR-1708254). This work made use of the EPIC facility (NUANCE Center-Northwestern University), which has received support under the State of Illinois, Northwestern University, and the National Science Foundation with grants DMR-1121262 through the MRSEC program at the Materials Research Center, and EEC-0118025/003 through The Nanoscale Science and Engineering Center. S.H. and C.W. (DFT calculations) acknowledge support from the Department of Energy, Office of Science Basic Energy Sciences under grant DE-SC0014520.

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TOC Graphic

