

Article

Ultralow Thermal Conductivity and High Temperature Thermoelectric Performance in n-Type K2.5Bi8.5Se14

Zhong-Zhen Luo, Songting Cai, Shiqiang Hao, Trevor P. Bailey, Xiaobing Hu, Riley Hanus, Runchu Ma, Gangjian Tan, Daniel G. Chica, G. Jeffrey Snyder, Ctirad Uher, Christopher Wolverton, Vinayak P. Dravid, Qingyu Yan, and Mercouri G. Kanatzidis

Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.9b02327 • Publication Date (Web): 11 Jul 2019 Downloaded from pubs.acs.org on July 12, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Ultralow Thermal Conductivity and High Temperature Thermoelectric Performance in n-Type K_{2.5}Bi_{8.5}Se₁₄

Zhong-Zhen Luo,^{1,2} Songting Cai,^{2,3} Shiqiang Hao,³ Trevor P. Bailey,⁴ Xiaobing Hu,⁵ Riley Hanus,³ Runchu Ma,⁴ Gangjian Tan,⁶ Daniel G. Chica,² G. Jeffrey Snyder,³ Ctirad Uher,⁴ Christopher Wolverton,³ Vinayak P. Dravid,³ Qingyu Yan,^{1,*} Mercouri G. Kanatzidis^{2,*}

¹School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue 639798, Singapore

²Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

³Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

⁴Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, United States

⁵Department of Materials Science and Engineering, NUANCE Center, Northwestern University, Evanston, Illinois 60208, United States

⁶State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, China

ABSTRACT

We studied the narrow bandgap (0.55 eV) semiconductor $K_{2.5}Bi_{8.5}Se_{14}$, as a potential thermoelectric material for power generation. Samples of polycrystalline $K_{2.5}Bi_{8.5}Se_{14}$ prepared by spark plasma sintering exhibit exceptionally low lattice thermal conductivities (κ_{lat}) of 0.57 – 0.33 Wm⁻¹K⁻¹ in the temperature range of 300 – 873 K. The physical origin of such low κ_{lat} in $K_{2.5}Bi_{8.5}Se_{14}$ is related to the strong anharmonicity and low phonon velocity caused by its complex low-symmetry, large unit cell crystal structure and mixed-occupancy of Bi and K atoms in the lattice. High-resolution scanning transmission electron microscopy (HRSTEM) studies and micro-analysis indicates that the $K_{2.5}Bi_{8.5}Se_{14}$ sample is a single phase without intergrowth of the structurally related $K_2Bi_8Se_{13}$ phase. The undoped material exhibits n-type character and a figure of merit (*ZT*) value of 0.67 at 873 K. Electronic band

structure calculations indicate that $K_{2.5}Bi_{8.5}Se_{14}$ is an indirect bandgap semiconductor with multiple conduction bands close to the Fermi level. Phonon dispersion calculations suggest $K_{2.5}Bi_{8.5}Se_{14}$ has low phonon velocities and large Grüneisen parameters that can account for the observed ultralow κ_{lat} . The degree of n-type doping can be controlled by introducing Se deficiencies in the structure providing a simple route to increase the *ZT* to ~1 at 873 K.

INTRODUCTION

Thermoelectric materials can achieve direct conversion of heat to electrical power and can play an important role in increasing energy utilization efficiency, harvesting waste heat and producing power in places where neither solar cells not windmills can. The conversion efficiency of a thermoelectric material depends on the dimensionless figure of merit, $ZT = S^2 \sigma T / (\kappa_{\text{lat}} + \kappa_{\text{ele}})$, where S, σ , T, κ_{lat} and κ_{ele} are the Seebeck coefficient, electrical conductivity, absolute temperature, lattice and charge carrier thermal conductivity, respectively.¹⁻² The most fundamental challenge of obtaining a high ZT is attaining the simultaneous enhancement in power factor (*PF*, $S^2\sigma$) and reduction in total thermal conductivity ($\kappa_{\text{tot}} = \kappa_{\text{lat}} + \kappa_{\text{ele}}$).

Research efforts in developing good thermoelectric materials include enhancing power factor and reducing κ_{lat} . The power factor can be enhanced *via* the electronic band structure engineering (*eg.* band convergence,³ resonant states,⁴ gap states,⁵ Fermi level pinning,⁶ multiple bands,⁷ and band alignment using secondary phases⁸). The hierarchical architectures on all length scales (*eg.* solid-solution alloying,⁹⁻¹¹ nanostructures,^{1, 12} grain boundaries,¹³ off-center atoms,¹⁴⁻¹⁵ and defect engineering¹⁶) can reduce κ_{lat} . Another strategy is to discover entirely new materials with intrinsically low κ_{lat} and favorable electronic structures.¹⁷⁻¹⁸

In general, materials with very low κ_{lat} are those that exhibit intrinsic bond anharmonicity, anisotropic structures,^{17, 19-21} complex crystal structures,²² relatively low-symmetry and large unit cells,²³⁻²⁴ heavy constituent elements,²⁵⁻²⁶ atomic disorder,²⁷ metals with stereochemically active lone-pairs of electrons,²⁸⁻³² "rattler" vibrations,³³ *etc*. Thus, studying materials with such attributes is a promising strategy to identify new advanced thermoelectrics.

The Bi-/Sn-based chalcogenide semiconductors with stereochemically active lone-pair of electrons, such as CsBi₄Te₆,²⁵ K₂Bi₈Se₁₃,³⁴⁻⁴² K_{2.5}Bi_{8.5}Se₁₄,^{34, 43} BiSe,⁴⁴ AgBi₃S₅,⁴⁵ AgBiS₂,⁴⁶ SnSe,⁴⁷⁻⁴⁸ *etc.*, have emerged as a promising family of thermoelectric materials, owing to their ultralow κ_{lat} . Recently, high ZT ~1.3 at 873 K for the monoclinic β -K₂Bi₈Se₁₃ based material has been attained by Cl doping. However, its synthetic process is tedious, including long reaction time (~21 days), high energy-consuming, and complex multi-step reactions.⁴⁰ Moreover, the second phase (~20-30% K_{2.5}Bi_{8.5}Se₁₄) often co-exist in the β -K₂Bi₈Se₁₃ sample, which makes it complicated for the study of the intrinsic thermoelectric properties of pure β -K₂Bi₈Se₁₃.⁴⁰ Like β -K₂Bi₈Se₁₃, the second phase, K_{2.5}Bi_{8.5}Se₁₄, also has a low-symmetry complex monoclinic crystal structure and a large unit cell with two different interconnected types of Bi/Se building blocks and K⁺ atoms in tunnels, showing low κ_{lat} at T < 300 K.³⁴

In this work, we focus of pure single phase samples of n-type $K_{2.5}Bi_{8.5}Se_{14}$ and Se deficient samples, and assessed the charge transport, thermal transport and thermoelectric properties as a function of temperature.³⁴ We find that undoped polycrystalline n-type $K_{2.5}Bi_{8.5}Se_{14}$ samples show an ultralow κ_{lat} of 0.35 Wm⁻¹K⁻¹ and a *ZT* value of ~0.67 at 873 K. We report elastic measurements which reveal low average phonon velocities, v_a (1610 ms⁻¹), small Young's modulus, *E* (35.8 GPa), large Grüneisen parameter, γ (1.96) and low Debye temperature, Θ_D (126 K), in agreement with the phonon dispersion calculations and consistent with the ultralow κ_{lat} . Furthermore, we demonstrate controlled electron doping by introducing Se deficiencies, of the type $K_{2.5}Bi_{8.5}Se_{14-x}$, which improves the power factor and yields a *ZT* value of ~1 at 873 K.

EXPERIMENTAL SECTION

Raw materials. The starting materials used were Bi shot (99.999%, American Elements, USA), Se pieces (99.99%, American Elements, USA), K chunks (99.99%, Aldrich Chemical Co., USA). K₂Se was synthesized by a stoichiometric reaction of K and Se (with Se excess of 0.5%) in liquid NH₃ as described elsewhere.^{41, 49}

Synthesis of $K_{2.5}Bi_{8.5}Se_{14-x}$. Ingots were synthesized according to the nominal compositions of $K_{2.5}Bi_{8.5}Se_{14-x}$ (x = 0, 0.007, 0.021, 0.042, 0.063, 0.07, and 0.105) mixing the K₂Se, Bi and Se in 13 mm diameter carbon-coated quartz tubes under an N₂-filled glove box. The tubes were evacuated to $\sim 2 \times 10^{-3}$ Torr and flame-sealed.

Chemistry of Materials

Then, the sealed quartz tubes were slowly heated to 1023 K over 15 h and soaked at this temperature for one day, then quenched in water. For a typical experiment, the following amounts were used: K₂Se (0.7 g, 4.45 mmol), Bi (6.3297 g, 30.29 mmol), and Se (3.5814 g, 45.36 mmol) to prepare a ~10.6 g ingot of K_{2.5}Bi_{8.5}Se_{13.979}.

Band gap measurement. To probe the band gap of $K_{2.5}Bi_{8.5}Se_{14}$, the optical diffuse reflectance measurement was performed on finely ground powder by using a Nicolet 6700 FT-IR spectrometer. The spectra were collected in the mid-IR region of 6000 – 400 cm⁻¹ at room temperature. The optical band gap was calculated from reflectance data using Kubelka-Munk function.⁴¹

Scanning Electron Microscopy (SEM) and Transmission electron microscopy TEM. Scanning/transmission electron microscopy ((S/TEM) and STEM energy dispersive spectroscopy (EDS) experiments investigations were carried out using an aberration-corrected JEOL ARM200F microscope operated at 200 kV. The thin TEM specimens were prepared by conventional methods, including cutting, grinding, dimpling, tripod, with minimal duration of Ar-ion milling (2.8 kV for ~2 hours until a hole is formed in the specimen, followed by ion cleaning with 0.3 kV) with a liquid N_2 cooling stage.

Spark plasma sintering (SPS). The obtained ingots of $K_{2.5}Bi_{8.5}Se_{14-x}$ were hand-ground to a fine powder using agate mortar and pestle. Then, the fine powders were filled into a 12.7 mm diameter graphite die and densified by using the SPS technique (SPS-211LX, Fuji Electronic Industrial Co. Ltd.) at 773 K with an axial compressive stress of 40 MPa for 10 min under vacuum. The resulting cylindrical-shaped pellets had high theoretical density (> 97%).

Electrical transport properties measurements. The electrical conductivity and Seebeck coefficient were simultaneously determined by an Ulvac Riko ZEM-3 system under a low-pressure helium atmosphere from 300 K to 873 K. For intrinsic $K_{2.5}Bi_{8.5}Se_{14}$, two different directions: one along the primary surface of the pellets and perpendicular to the SPS pressing direction ($K_{2.5}Bi_{8.5}Se_{14}$ - \perp), and the other along the SPS pressing direction and perpendicular to the primary surface of the pellets (K_{2.5}Bi_{8.5}Se₁₄-||) were tested. For K_{2.5}Bi_{8.5}Se_{14-x} samples, the only direction of along the primary surface of the pellets and perpendicular to SPS process direction was tested. All samples have the dimensions of approximately 11 mm \times 3 mm \times 3 mm. Before the ZEM-3 measurement, a thin layer (0.1 – 0.2 mm) of boron nitride was spray coated on the surface of the bars to avoid evaporation of Se and to protect the instruments. The estimated uncertainties of the Seebeck coefficient and electrical conductivity measurements are ~3% and 5%, respectively.⁵⁰

Hall measurements. The temperature-dependent Hall effect measurement was completed with an AC 4-probe method in a homemade system with excitation fields of \pm 0.5 Tesla. The specimens were polished with the size of \sim 1 mm × 3 mm × 8 mm. The homemade system uses an air-bore, helium-cooled superconducting magnet to generate the field within a high temperature oven that surrounds the Ar-filled sample probe. The estimated error is based on the standard deviation of several data points at a single temperature. The carrier concentration (*n*) was calculated from the Hall coefficient assuming a single carrier, *i.e.* $n = 1/(e|R_{\rm H}|)$, where *e* is the electron charge and $R_{\rm H}$ is the Hall coefficient, with the error propagated from the Hall coefficient. The Hall mobility ($\mu_{\rm H}$) was determined as $\mu_{\rm H} = \sigma R_{\rm H}$.

Thermal conductivity measurements. The thermal diffusivity (*D*) was measured in the temperature range 300 K to 873 K using a Netzsch Laser Flash Analysis (LFA) 457 instrument under a continuous N₂ flow. The Cowan model with pulse correction was used for data analysis. The samples with dimensions of ~10 × 10 × 1.5 mm³ were measured in the same directions as the electrical transport properties measurement. The rectangular samples were coated with a thin layer of graphite to prevent the emissivity of the material during the measurement. The total thermal conductivity was calculated with the relationship $\kappa = D \cdot C_p \cdot \rho$, where specific heat capacity is determined according to the Dulong-Petit approximation, $C_p = 3R/\overline{M}$ (*R* is the ideal gas constant, and \overline{M} is the average molar mass of each element) and ρ is the density (calculated using the sample's geometry and mass). Considering the estimated uncertainty of measurements from *D* (5%) and ρ (5%), the combined uncertainty associated with the

measurements for the determination of ZT is about 20%.

Speed of sound measurements. The speeds of sound were measured by the pulse-echo method where a piezoelectric transducer coupled to the sample first sends the initial stress-wave pulse, and then acts as receiver measuring the echoed ultrasound reflection.⁵¹ The delay time, t_d , between subsequent reflections was determined by maximizing the cross-correlation of the two reflections as follows. If $\sigma_N(t)$ is the amplitude of reflection N, then $\sum_t \sigma_N(t) \sigma_{N+1}(t-t_d)$ is maximized by varying t_d . The corresponding value of t_d along with the sample thickness, h, were used to calculate the speed of sound, $v_{L,T} = 2h/t_d$. A longitudinal transducer (measuring v_L) with a principle frequency of 5 MHz (Olympus V1091) and a transverse transducer (measuring v_T) at 5 MHz (Olympus V157-RM) were used with a Panametrics 5072PR pulser/receiver. A Tektronix TBS 1072B-EDU oscilloscope was used to record the waveforms. A typical waveform contained around four reflections (3 delay time measurements), and the measurements from a minimum of three waveforms (corresponding to 9 individual speed of sound measurements) were averaged. A single crystal of yttrium aluminum garnet (YAG) with known properties was used to determine that measurements of the speed of sound on this home-built system have an accuracy of better than 0.6%. The values for the average speed of sound v_a , Young's modulus E, Poisson's ratio v_p , Grüneisen parameter γ , and Debye temperature Θ_D were computed using the equations given by Pei *et al.*⁴⁰

Band structure calculations. Density functional theory (DFT) calculations of pristine K_{2.5}Bi_{8.5}Se₁₄ were carried out. The calculations were performed using the generalized approximation with **PBE**⁵² functional for gradient the exchange-correlation functional and projector-augmented wave potentials as implemented in Vienna Ab initio Simulation Package (VASP).53 All structures are fully relaxed with respect to cell vectors and cell-internal positions. The total energies were numerically converged to approximately 3 meV/cation using a basis set energy cutoff of 450 eV and dense k-meshes corresponding to 4000 k-points per reciprocal atom in the Brillouin zone.

RESULTS AND DISCUSSION

Crystal structure. K_{2.5}Bi_{8.5}Se₁₄ crystallizes in the low-symmetry monoclinic space group $P2_1/m$ (No. 11) with a = 17.534(4) Å, b = 4.206(1) Å, c = 21.387(5) Å, $\beta = 109.65(2)^{\circ.34}$ K_{2.5}Bi_{8.5}Se₁₄ has a complex three-dimensional (3D) anionic framework made up of two different types of Bi/Se polyhedral building blocks, NaCl- and Bi₂Te₃-type fragments,³⁴ which are highlighted by the blue squares, Figure 1. The Bi₂Te₃-type rods are arranged one by one to form layers parallel to the *a*-axis. Then, the NaCl-type rod-like fragments connect the layers to build a 3D framework with K⁺ in the channel, Figure 1. The widths of the NaCl- and Bi₂Te₃-type blocks are three and five Bi polyhedra, respectively. In the asymmetric unit, there are 3 K sites, 10 Bi sites, and 14 Se sites that are crystallographically unique. The K(1) and K(3) sites are disordered with Bi(5) and Bi(7) at a ratio of 76%/24% and 72%/28%, respectively. The K(1) and Bi(5) have the same site, and the distances between the K(3) and Bi(7) site is 0.54 Å.

Powder X-ray diffraction (PXRD). As shown in Figure 2a, the PXRD patterns of the SPSed $K_{2.5}Bi_{8.5}Se_{14}$ samples were measured along two directions: (1) the scattering vector⁵⁴ of the X-ray is perpendicular to the primary surface of the pellets $(K_{2.5}Bi_{8.5}Se_{14}-||$, parallel to the direction of applied pressure, blue pattern) and (2) the scattering vector of the X-ray is parallel to the primary surface of the pellets $(K_{2.5}Bi_{8.5}Se_{14}-||$, perpendicular to the applied pressure, black pattern). For $K_{2.5}Bi_{8.5}Se_{14-x}$ samples, the only direction tested was the scattering vector of the X-ray parallel to the primary surface of the pellets. All Bragg peaks can be indexed to the $K_{2.5}Bi_{8.5}Se_{14}$ phase (ICSD 84269), Figure 2a. Moreover, the PXRD patterns as shown in Figure 2a indicate the anisotropic structure of $K_{2.5}Bi_{8.5}Se_{14}$, which is consistent with the needle shaped $K_{2.5}Bi_{8.5}Se_{14}$ crystals with their long axis along the monoclinic *b*-axis, Figure S1 (Supporting information). The needle shaped samples also show the orientation and alignment features after the SPS process as shown in Figure S2 (Supporting information).

Thermal analysis and electronic energy band gap. The differential thermal analysis (DTA) of $K_{2.5}Bi_{8.5}Se_{14}$ is shown in Figure S3 (Supporting Information). There is an endothermic peak at 974 K corresponding to the melting during the heating cycle and an exothermic peak at 949 K of recrystallization. PXRD patterns show that the DTA product is $K_{2.5}Bi_{8.5}Se_{14}$ after heating to 1073 K for two consecutive heating-cooling cycles, Figure S4 (Supporting Information), indicating congruent melting. The optical absorption spectrum in Figure 2c reveals that the electronic energy band gap of $K_{2.5}Bi_{8.5}Se_{14}$ is about 0.55 eV, in agreement with previous reports.³⁴

TEM results analysis. $K_{2.5}Bi_{8.5}Se_{14}$ and $K_2Bi_8Se_{13}$ have the same space group $(P2_1/m)$, similar unit cells (a = 17.534(4) Å, b = 4.206(1) Å, c = 21.387(5) Å, $\beta = 109.65(2)^{\circ}$ for $K_{2.5}Bi_{8.5}Se_{14}$ and a = 17.492(3) Å, b = 4.205(1) Å, c = 18.461(4) Å, $\beta = 90.49(2)$ for $K_2Bi_8Se_{13}$), and share the same Bi_2Te_3 and NaCl type blocks.³⁴ Therefore, the possibility of intergrowth between the two structures is high. It was confirmed by the previous study of $K_2Bi_8Se_{13}$ sample via PXRD and TEM measurements.⁴⁰ Although there is no observable diffraction peaks from $K_2Bi_8Se_{13}$ in the PXRD pattern, it is necessary to verify the purity by high-resolution transmission electron microscopy.

The highly anisotropic nature of the synthesized ingot as well as SPS sample was characterized by scanning electron microscopy (SEM), as shown in Figure S1 (Supporting Information). Typically, the ingot consists of grains and crystals of needle-like morphology, where the width of the needles is around 10 microns. Similar results are also observed in the sample after SPS, where the preferred growth orientation during crystallization is observed, Figure S2 (Supporting Information). As shown in Figure S2a (Supporting Information), the needle-like grains tend to orient in layers along the plane normal to SPS pressure (in-plane). The preferred growth direction, *b*-axis, is labeled with red arrows in the figure, indicating that *b*-axis is randomly oriented within the plane. On the contrary, along the plane parallel to SPS pressure, many voids are observed between stacked layers. The differences between these two directions account for the fact that the electrical and thermal transport

 properties along SPS pressure ($K_{2.5}Bi_{8.5}Se_{14}$ -||) are lower than that along perpendicular to SPS pressure ($K_{2.5}Bi_{8.5}Se_{14}$ - \perp) since electron/heat flow needs to occur through stacked layers as well as many pores.

We also performed atomic-resolution micro-analysis with an aberration (probe) corrected scanning/transmission electron microscope under 200 kV. Figure 3a is typical high angle annular dark field STEM (HAADF-STEM) image of $K_{2.5}Bi_{8.5}Se_{14}$ specimen, showing mainly z-contrast. The selected area electron diffraction pattern (SAED) in the inset matches with monoclinic $K_{2.5}Bi_{8.5}Se_{14}$ (space group: $P2_1/m$) along [010] direction. No extra spots, spot splitting, streaking are observed, indicating that the $K_{2.5}Bi_{8.5}Se_{14}$ sample is a single phase, and with no $K_2Bi_8Se_{13}$ second phase intergrown. The magnified image in Figure 3b indicates the good agreement with the superimposed model of the crystal structure.

Thermoelectric transport properties of undoped sample. The thermoelectric performance of as made undoped samples along two different directions, $K_{2.5}Bi_{8.5}Se_{14}-\perp$ and $K_{2.5}Bi_{8.5}Se_{14}-\parallel$, is shown in Figure 4. As discussed above the SPSed samples exhibit preferential orientation because of the monoclinic anisotropic crystal structure and the preferred growth direction along the *b*-axis. The electrical conductivities for both $K_{2.5}Bi_{8.5}Se_{14}-\perp$ and $K_{2.5}Bi_{8.5}Se_{14}-\parallel$ increase with rising temperature, as would be expected from an intrinsic semiconductor, Figure 4a, although the Seebeck coefficient is characteristic of a heavily doped semiconductor up to 700K. Because the *b*-axis is the best transport direction, the electrical conductivity of $K_{2.5}Bi_{8.5}Se_{14}-\perp$ is higher than that of $K_{2.5}Bi_{8.5}Se_{14}-\parallel$. Because $K_{2.5}Bi_{8.5}Se_{14}$ has low carrier concertation at 300 K and increased carrier concertation via thermal activation at high temperature, Figure 6c, the electrical conductivity gradually increases from ~9.7 and ~6.3 S cm⁻¹ at 300 K to ~99 and ~76 S cm⁻¹ at 873 K for $K_{2.5}Bi_{8.5}Se_{14}-\perp$ and $K_{2.5}Bi_{8.5}Se_{14}-\parallel$, respectively.

The negative Seebeck coefficient as shown in Figure 4b indicates that $K_{2.5}Bi_{8.5}Se_{14}$ is an n-type semiconductor. The absolute values of the Seebeck

 coefficient for both $K_{2.5}Bi_{8.5}Se_{14}-\perp$ and $K_{2.5}Bi_{8.5}Se_{14}-\parallel$ increase with the rise of temperature and reach their maximum values at 723 K, suggesting the onset of intrinsic excitation conduction that is also seen in the enhanced σ values above 723 K. From the Goldsmid-Sharp rule, the band gap can be estimated as $E_g = 2eS_{max}T_{max}$, where *e* is the electronic charge, yielding a result of ~0.34 eV, in agreement with the optically measured band gap.⁵⁵⁻⁵⁶ Although the Seebeck coefficient of $K_{2.5}Bi_{8.5}Se_{14}-\parallel$ is superior to that of $K_{2.5}Bi_{8.5}Se_{14}-\perp$ in the entire tested temperature range, a higher power factor was obtained for $K_{2.5}Bi_{8.5}Se_{14}-\perp$ above 523 K as shown in Figure 4c, because of the higher electrical conductivity.

As shown in Figure 4d, the κ_{tot} values are lower than 0.6 Wm⁻¹K⁻¹ for K_{2.5}Bi_{8.5}Se₁₄- \perp and K_{2.5}Bi_{8.5}Se₁₄- \parallel over the entire temperature range, with K_{2.5}Bi_{8.5}Se₁₄- \perp possessing comparatively higher values. The κ_{tot} values for both samples increase from T > 723 K because of the enhanced minority charge carrier contribution. For the κ_{lat} , K_{2.5}Bi_{8.5}Se₁₄- \parallel has lower values than K_{2.5}Bi_{8.5}Se₁₄- \perp in the entire temperature range, Figure 4e. κ_{lat} drops rapidly with rising temperature and reaches the ultralow value of ~0.33 Wm⁻¹K⁻¹ at 773 K for K_{2.5}Bi_{8.5}Se₁₄- \parallel . Finally, the two samples have nearly identical *ZT* values, with K_{2.5}Bi_{8.5}Se₁₄- \parallel at 873K, Figure 4f.

N-type doping via Se vacancies

Charge transport properties. Because the $K_{2.5}Bi_{8.5}Se_{14}$ - \perp sample exhibited better performance we focused on optimizing its thermoelectric properties using Se deficiency as the doping strategy. Se deficiency is expected to introduce additional electron carriers corresponding to two electrons per Se atom removed.

The electrical conductivities of $K_{2.5}Bi_{8.5}Se_{14-x}$ samples, $K_{2.5}Bi_{8.5}Se_{14-x}$, exhibit a significant enhancement in electrical conductivity compared to $K_{2.5}Bi_{8.5}Se_{14-}\perp$, Figure 5a. Specifically, the electrical conductivities markedly increase from 9.6 S cm⁻¹ for $K_{2.5}Bi_{8.5}Se_{14-}\perp$ to 372.2 S cm⁻¹ for x = 0.105 sample at 300 K. For samples with x = 0.07, the electrical conductivity has a sigmoidal temperature dependence. It increases gradually from 300 K to ~500 K, then levels off and decreases slightly from 500 K to

750 K before increasing again at T > 750 K, an overall semiconducting trend, Figure 5a. In contrast, the more heavily Se deficiencies samples (x = 0.07 and 0.105), exhibit a decreasing electrical conductivity decreases from 300 K to ~800 K indicating a metal-like (degenerate semiconductor) behavior from 300 K to ~800 K, Figure 5a. The sharp increase of electrical conductivity at T > 800 K for all samples is attributed to the thermal excitation of minority charge carriers (bipolar conduction).

All samples exhibit negative Seebeck coefficients. Figure 5b displays the Seebeck coefficients as a function of temperature for $K_{2.5}Bi_{8.5}Se_{14-x}$ and $K_{2.5}Bi_{8.5}Se_{14-x}$ samples. The coefficients for $K_{2.5}Bi_{8.5}Se_{14-x}$ samples decrease with increasing Se deficiencies consistent with the electron donor nature of the deficiency. Similar to the as-made undoped sample, the absolute values of the Seebeck coefficients for all $K_{2.5}Bi_{8.5}Se_{14-x}$ samples rise with temperature, then reach their peak values at ~700 – 800 K, before declining. The peak in the Seebeck coefficient reflects the onset of hole carrier excitation at high temperature (bipolar conduction), with a corresponding sharp increase of electrical conductivity. The power factor improves to ~4.53 µWcm⁻¹K⁻² at 873 K, obtained for x = 0.021 sample, see Figure S5 (Supporting Information). Compared with its sister compound $K_2Bi_8Se_{13}$ (~6 µWcm⁻¹K⁻² at 873 K),⁴⁰ $K_{2.5}Bi_{8.5}Se_{14}$ has a relatively lower value. This is mainly attributed to the decrease of Seebeck coefficient caused by bipolar conduction at T > 750 K.

The carrier concentrations in the samples were estimated from temperature dependent Hall effect measurements, with the room temperature results shown in Figure 6a. For all samples, $R_{\rm H} < 0$ is consistent with the n-type conduction observed in the Seebeck coefficient data. A low number of Se vacanices seem to have a minor impact on the carrier concentration *n*, showing a slight decrease in *n* from ~1.2 × 10²⁰ cm⁻³ for undoped sample to ~1.1 × 10²⁰ cm⁻³ for x = 0.021 sample at room temperature, Figure 6a. At higher Se deficiencies (e.g. x = 0.042 and above), however, the *n* is enhanced, such as ~1.5 × 10²⁰ cm⁻³ for x = 0.042 sample, ~2.0 × 10²⁰ cm⁻³ for x = 0.07 sample, and ~2.9 × 10²⁰ cm⁻³ for x = 0.105 sample at room temperature.

Chemistry of Materials

Figure 6b displays the Seebeck coefficient as a function of *n* (based on the Pisarenko relation) for $K_{2.5}Bi_{8.5}Se_{14}$ and $K_{2.5}Bi_{8.5}Se_{14-x}$ samples. The dotted curves are the theoretically calculated values based on the single parabolic band (SPB) model at 300 K (black), 573 K (red) and 773 K (blue) with an effective mass of 1.2 m_e . At 300 K, all samples fit the electron effective mass of ~1.2 m_e . With rising temperature, the effective mass of electrons increases for the K_{2.5}Bi_{8.5}Se₁₄, x = 0.021 and 0.07 samples, as indicated by the position of the data points above the theoretical curves.

As a function of temperature, the *n* of the undoped, x = 0.021 and 0.07 samples, Figure 6c, is essentially flat until *T* ~623 K when minority carriers begin to short the Hall signal at elevated temperatures, Figure S6 (Supporting Information). According to Figure 6d, the charge carrier mobility is significantly improved with the introduction of Se deficiencies from ~0.50 cm²V⁻¹s⁻¹ in the undoped sample to ~7.73 cm²V⁻¹s⁻¹ in the x = 0.07 sample at room temperature. This plays a large part in enhancing the power factor. Also the mobility is increasing with rising temperature for the undoped (from ~0.50 cm²V⁻¹s⁻¹ at room temperature to 3.03 cm²V⁻¹s⁻¹ at 623 K) and x = 0.021 samples (from 2.37 cm²V⁻¹s⁻¹ at room temperature to 5.13 cm²V⁻¹s⁻¹ at 573 K) indicating that the charge carrier scattering is dominated by grain boundaries.⁵⁷ For the x= 0.07 sample we observed $\mu_{\rm H}/dT < 0$, which indicate strong acoustic phonon-charge carrier interactions. We can see that, intrinsic and K_{2.5}Bi_{8.5}Se_{14-x} samples show lower mobilities compared to the Cl-doped K₂Bi₈Se₁₃ samples (~31.57 cm²V⁻¹s⁻¹ at *n* ~8.8 × 10¹⁹ cm⁻³) at room temperature.⁴⁰

Thermal conductivity. The temperature-dependent thermal conductivity values κ_{tot} of K_{2.5}Bi_{8.5}Se₁₄- \perp and K_{2.5}Bi_{8.5}Se_{14-x} samples are shown in Figure 7a. In general, the thermal conductivity drops with rising temperature as expected. The κ_{tot} raises with increasing Se deficiencies content. For instance, the κ_{tot} values significantly increase from ~0.57 Wm⁻¹K⁻¹ for K_{2.5}Bi_{8.5}Se₁₄- \perp to ~0.86 Wm⁻¹K⁻¹ for x = 0.105 sample at room temperature. Moreover, the x = 0.021 sample possesses an ultralow κ_{tot} ~0.38 Wm⁻¹K⁻¹ at 823 K.

The κ_{lat} was determined by subtracting κ_{ele} from κ_{tot} . According to the Wiedemann–Franz law, the κ_{ele} can be estimated by following equation:

$$\kappa_{\rm ele} = L\sigma T \tag{1}$$

where *L* is the Lorenz number (See Supporting Information, with Figure S9) displaying the *L* and κ_{ele} values).⁵⁸ All K_{2.5}Bi_{8.5}Se_{14-x} samples exhibit remarkable low κ_{lat} between ~0.51–0.61 Wm⁻¹K⁻¹ at 300 K, Figure 7b. Meanwhile, κ_{lat} values for all samples decrease with temperature. Surprisingly, the κ_{lat} of ~0.31 Wm⁻¹K⁻¹ at ~723 K is ultralow for x = 0.021 sample. Because it is difficult to precisely estimate the Lorenz number and heat capacity in the intrinsic excitation regime, the calculated κ_{lat} values may be underestimated for T > 723 K. Although the κ_{lat} of x = 0.021 sample is slightly higher than the ~0.21 Wm⁻¹K⁻¹ at 873 K of Cl-doped K₂Bi₈Se₁₃, the value is still ultralow as compared with other state-of-the-art thermoelectric materials.^{19, 31, 40, 48, 59-64}

Figure 7c displays the *ZT* values only along the perpendicular to SPS pressing direction. For all samples, the values increase with temperatures and the peak *ZT* values are enhanced from ~0.67 for K_{2.5}Bi_{8.5}Se₁₄- \perp to ~1.0 for the x = 0.021 sample at 873 K. The simultaneous improvement of the power factor and reduction of κ_{lat} demonstrates that the Se deficiencies doping is effective for enhancing the thermoelectric performance of this system.

Phonon velocity. To uncover the origin of the ultralow κ_{lat} , we performed phonon velocity measurements and theoretical calculations of phonon dispersions in the lattice of K_{2.5}Bi_{8.5}Se₁₄. The phonon velocities were obtained by ultrasonic pulse echo measurements along the primary surface of the pellets (perpendicular to SPS pressure) at room temperature. The longitudinal (v_l), shear (v_s) and average (v_a) phonon velocity, Young's modulus (*E*), Poisson ratio (v_p), Grüneisen parameter (γ , obtained by using the formula, $\gamma = \frac{3}{2}(\frac{1+v_p}{2-3v_p})$, and Debye temperature (Θ_D) are shown in Table 1. A comparison of the room temperature elastic properties of K_{2.5}Bi_{8.5}Se₁₄ with those of several other Bi-chalcogenide based thermoelectric materials with low thermal conductivity is also shown in Table 1.

Chemistry of Materials

The Young's modulus of 35.8 GPa for $K_{2.5}Bi_{8.5}Se_{14}$ is lower than other Bi-chalcogenide based thermoelectric materials (*e.g.* 37.1 GPa for $K_2Bi_8Se_{13}^{40}$, 76.5 GPa for BiCuSeO⁶⁵ and 70.6 GPa Bi₂YO₄Cu₂Se₂⁶⁶). Also, the small Young's modulus leads to a low average phonon velocity of 1610 ms⁻¹ for $K_{2.5}Bi_{8.5}Se_{14}$. Generally, the Young's modulus reflects the material's stiffness and chemical bond strength.⁶⁷ The low Young's modulus is attributed to weak individual atomic bonds, which often result in low κ_{lat} .¹⁹⁻²⁰

The Grüneisen parameter (γ), a measure of the lattice anharmonicity is another means of understanding the thermal conductivity.¹⁹ The experimental Grüneisen parameter value of ~1.96 for K_{2.5}Bi_{8.5}Se₁₄ is larger than other Bi-chalcogenide based thermoelectric materials (*e.g.* 1.71 for K₂Bi₈Se₁₃⁴⁰, 1.5 for BiCuSeO⁶⁵ and 1.71 for Bi₂YO₄Cu₂Se₂⁶⁶). The higher value suggests a larger anharmonicity in K_{2.5}Bi_{8.5}Se₁₄. The substantial Grüneisen parameter likely originates from the presence of the stereochemically active] Bi.⁶⁸ In addition, the different coordination environments (3and 6-fold coordinated with Se atoms) and mixed occupancy of Bi and K atoms lead to a more asymmetric structure, which results in stronger lattice anharmonic vibrations.

The Debye temperature is related to the mean sound velocity and is typically < 300 K in low thermal conductivity materials.⁶⁷ The value of ~126 K for K_{2.5}Bi_{8.5}Se₁₄ was obtained by using the formula, $\Theta_D = \frac{h}{k_B} [\frac{3N}{4\pi V}]^{1/3} v_a$, where *h*, *k*_B, *N*, *V*, and *v*_a are Planck's constant, Boltzmann constant, number of atoms in a unit cell, unit-cell volume and average phonon velocity, respectively. This result is lower than other Bi-chalcogenide based thermoelectric materials (*e.g.* 154 K for K₂Bi₈Se₁₃ with~30% second phase K_{2.5}Bi_{8.5}Se₁₄,⁴⁰ 243 K for BiCuSeO⁶⁵ and 280 K Bi₂YO₄Cu₂Se₂⁶⁶), consistent with the low average phonon velocity (1610 ms⁻¹) and thermal conductivity of K_{2.5}Bi_{8.5}Se₁₄.

DFT electronic band structure and phonon dispersion calculations. Electronic band structure calculations on $K_{2.5}Bi_{8.5}Se_{14}$ indicate that it is an indirect band gap semiconductor with multiple conduction bands close to the Fermi level, Figure 8. The

calculated band gap of 0.03 eV, is underestimated however relative to the experimental value 0.55 eV, Figure 2c. Moreover, the partial electronic density of states plots show that the conduction band bottom within 0.2 to 0 eV of the CBM is mainly contributed by Bi 6p orbitals. The contribution of K orbital states in the conduction band minimum and valence band maximum is negligible suggesting electron transport in this material is through Bi based 6p orbitals in the [Bi_{8.5}Se₁₄]^{2.5-} framework.

The phonon dispersions along the Γ -Z and Γ -Y directions are much lower in energy than in the Γ -X direction, which is determined by the significantly shorter lattice parameter *b* (4.206(1) Å) compared to *a* (17.534(4) Å) and *c* (21.387(5) Å), Figure 9a. The lower energy vibrations along the Γ -Z and Γ -Y directions also indicates that the Debye temperatures in the *a* and *c* directions are much smaller than in the *b* direction and point to lower lattice thermal conductivity along *a* and *c*. As shown in Figure 9b, the theoretically calculated κ_{lat} of K₅Bi₁₇Se₂₈ in the *a* and *c* directions are as low as 0.4 Wm⁻¹K⁻¹ and 0.3 Wm⁻¹K⁻¹ at 300 K, respectively. The larger Debye temperature in the *b* direction, together with relatively lower calculated Grüneisen parameters, result in a higher κ_{lat} of 1.3 Wm⁻¹K⁻¹ at 300 K along the *b* direction, Figure 9c.

To compare with the experimental results from the polycrystalline SPSed samples, we consider the average of the calculated κ_{lat} over the three lattice directions, as shown in black squares in Figure 9b. The calculated value of 0.68 Wm⁻¹K⁻¹ at 300 K gradually decreases to 0.3 Wm⁻¹K⁻¹ at 900 K. The higher average values than the experimental lattice thermal conductivity near room temperature can be attributed to the fact that we consider an ordered crystalline structure of K₅Bi₁₇Se₂₈ in the DFT calculation without taking into account the partial occupancy of both K and Bi species. In addition, we only include normal and Umklapp scattering processes of acoustic phonons in a pure single crystal without including other phonon scattering mechanisms present in real samples, such as point defects and grain boundary contributions. Thus, the calculated thermal conductivities are ideally larger than the experimental ones.

Page 17 of 34

Chemistry of Materials

The ultralow κ_{lat} is consistent with the very low calculated phonon velocities as shown in the Table 2. The low velocities primarily originate from low frequency acoustic vibrations because of the heavier Bi atoms with minimal contribution from K atoms, Figure 9d. Indeed, more than half of the PDOS for the acoustic phonons (< 40 cm⁻¹) stems from Bi atoms. Of course, accounting for the site occupancy disorder of K and Bi atoms³⁴ within the calculations may affect these results. Lastly, the highly anisotropic structure induces relatively large Grüneisen parameters in the Γ -Y and Γ -Z directions, Figure 9c, hence very low κ_{lat} in the *a* and *c* directions.

CONCLUSIONS

The as-made undoped $K_{2.5}Bi_{8.5}Se_{14}$ samples exhibit ultralow lattice thermal conductivity of 0.34 Wm⁻¹K⁻¹ at 873 K and a peak *ZT* value of 0.67 at 873 K. Introducing Se deficiencies is an efficient way to control the n-type doping behavior of the mateirals and can be used to increase the *ZT* value to ~1 at 873 K. Phonon velocity measurements and phonon dispersion calculations suggest that the physical origins of such low thermal conductivity in $K_{2.5}Bi_{8.5}Se_{14}$ mainly derive from the very strong anharmonicity in the structure and low phonon velocities imposed by the complex low-symmetry, heavy atom crystal structure and large unit cell.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the Department of Energy, Office of Science Basic Energy Sciences under grant DE-SC0014520, DOE Office of Science (sample preparation, synthesis, XRD, TE measurements, TEM measurements, DFT calculations). ZZL and QY gratefully acknowledge the National Natural Science Foundation of China (61728401). This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF

ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. User Facilities are supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357 and DE-AC02-05CH11231. Access to facilities of high performance computational resources at the Northwestern University is acknowledged. The authors also acknowledge Singapore MOE AcRF Tier 2 under Grant Nos. 2018-T2-1-010 and MOE2017-T2-2-069, Singapore A*STAR Pharos Program SERC 1527200022, the support from FACTs of Nanyang Technological University for sample analysis.

Supporting Information

 PXRD and DTA characterizations, DFT for phonon dispersion calculations, SEM images, DTA results, PXRD before and after DTA of $K_{2.5}Bi_{8.5}Se_{14}$, power factor and electronic thermal conductivity of $K_{2.5}Bi_{8.5}Se_{14}$ - \perp and $K_{2.5}Bi_{8.5}Se_{14-x}$ samples, temperature-dependent $R_{\rm H}$ for $K_{2.5}Bi_{8.5}Se_{14}$ - \perp , x = 0.021 and 0.07 samples, temperature-dependent Lorenz numbers, thermal diffusivity, room temperature densities of $K_{2.5}Bi_{8.5}Se_{14-x}$ (x = 0, 0.007, 0.021, 0.042, 0.063, 0.07, and 0.105), HAADF-STEM EDS mapping of $K_{2.5}Bi_{8.5}Se_{14}$. The Supporting Information is available free of charge on the ACS Publications website.

References

Biswas, K.; He, J.; Blum, I. D.; Wu, C.-I.; Hogan, T. P.; Seidman, D. N.; Dravid,
 V. P.; Kanatzidis, M. G. High-performance bulk thermoelectrics with all-scale hierarchical architectures. *Nature* 2012, *489*, 414.

2. Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G. Cubic $AgPb_mSbTe_{2+m}$: Bulk Thermoelectric Materials with High Figure of Merit. *Science* **2004**, *303* (5659), 818-821.

3. Tang, Y.; Gibbs, Z. M.; Agapito, L. A.; Li, G.; Kim, H.-S.; Nardelli, M. B.; Curtarolo, S.; Snyder, G. J. Convergence of multi-valley bands as the electronic origin of high thermoelectric performance in CoSb₃ skutterudites. *Nat. Mater.* **2015**, *14* (12), 1223-1228.

4. Heremans, J. P.; Jovovic, V.; Toberer, E. S.; Saramat, A.; Kurosaki, K.; Charoenphakdee, A.; Yamanaka, S.; Snyder, G. J. Enhancement of Thermoelectric

Page 19 of 34

Efficiency in PbTe by Distortion of the Electronic Density of States. *Science* 2008, *321* (5888), 554-557.

5. Su, X.; Hao, S.; Bailey, T. P.; Wang, S.; Hadar, I.; Tan, G.; Song, T.-B.; Zhang, Q.; Uher, C.; Wolverton, C.; Tang, X.; Kanatzidis, M. G. Weak Electron Phonon Coupling and Deep Level Impurity for High Thermoelectric Performance $Pb_{1-x}Ga_xTe$. *Adv. Energy Mater.* **2018**, *8* (21), 1800659.

6. Luo, Z.-Z.; Hao, S.; Cai, S.; Bailey, T. P.; Tan, G.; Luo, Y.; Spanopoulos, I.; Uher, C.; Wolverton, C.; Dravid, V. P.; Yan, Q.; Kanatzidis, M. G. Enhancement of Thermoelectric Performance for n-Type PbS through Synergy of Gap State and Fermi Level Pinning. *J. Am. Chem. Soc.* **2019**, *141* (15), 6403-6412.

7. Ahn, K.; Biswas, K.; He, J.; Chung, I.; Dravid, V.; Kanatzidis, M. G. Enhanced thermoelectric properties of p-type nanostructured PbTe-MTe (M = Cd, Hg) materials. *Energy Environ. Sci.* **2013**, *6* (5), 1529-1537.

8. Biswas, K.; He, J.; Zhang, Q.; Wang, G.; Uher, C.; Dravid, V. P.; Kanatzidis, M. G. Strained endotaxial nanostructures with high thermoelectric figure of merit. *Nat. Chem.* **2011**, *3* (2), 160-166.

9. Schröder, T.; Rosenthal, T.; Giesbrecht, N.; Maier, S.; Scheidt, E.-W.; Scherer, W.; Snyder, G. J.; Schnick, W.; Oeckler, O. TAGS-related indium compounds and their thermoelectric properties - the solid solution series $(GeTe)_xAgIn_ySb_{1-y}Te_2$ (x = 1-12; y = 0.5 and 1). *J. Mater. Chem. A* **2014**, *2* (18), 6384-6395.

10. Luo, Z.-Z.; Zhang, X.; Hua, X.; Tan, G.; Bailey, T. P.; Xu, J.; Uher, C.; Wolverton, C.; Dravid, V. P.; Yan, Q.; Kanatzidis, M. G. High Thermoelectric Performance in Supersaturated Solid Solutions and Nanostructured n-Type PbTe–GeTe. *Adv. Funct. Mater.* **2018**, *0* (0), 1801617.

11. Luo, Y.; Yang, J.; Jiang, Q.; Li, W.; Xiao, Y.; Fu, L.; Zhang, D.; Zhou, Z.; Cheng, Y., Large enhancement of thermoelectric performance of CuInTe₂ via a synergistic strategy of point defects and microstructure engineering. *Nano Energy* **2015**, *18*, 37-46.

12. Zhou, Z.; Yang, J.; Jiang, Q.; Lin, X.; Xin, J.; Basit, A.; Hou, J.; Sun, B., Enhanced thermoelectric performance of SnTe: High efficient cation - anion Co-doping, hierarchical microstructure and electro-acoustic decoupling. *Nano Energy* **2018**, *47*, 81-88.

13. Meng, X.; Liu, Z.; Cui, B.; Qin, D.; Geng, H.; Cai, W.; Fu, L.; He, J.; Ren, Z.; Sui, J. Grain Boundary Engineering for Achieving High Thermoelectric Performance in n-Type Skutterudites. *Adv. Energy Mater.* **2017**, *7* (13), 1602582.

14. Luo, Z.-Z.; Hao, S.; Zhang, X.; Hua, X.; Cai, S.; Tan, G.; Bailey, T. P.; Ma, R.; Uher, C.; Wolverton, C.; Dravid, V. P.; Yan, Q.; Kanatzidis, M. G. Soft phonon modes from off-center Ge atoms lead to ultralow thermal conductivity and superior thermoelectric performance in n-type PbSe–GeSe. *Energy Environ. Sci.* **2018**, *11* (11), 3220-3230.

15. Zhou, C.; Yu, Y.; Lee, Y. K.; Cojocaru-Mirédin, O.; Yoo, B.; Cho, S.-P.; Im, J.; Wuttig, M.; Hyeon, T.; Chung, I. High-Performance n-Type PbSe–Cu2Se Thermoelectrics through Conduction Band Engineering and Phonon Softening. *J. Am. Chem. Soc.* **2018**, *140* (45), 15535-15545.

16. Chen, Z.; Ge, B.; Li, W.; Lin, S.; Shen, J.; Chang, Y.; Hanus, R.; Snyder, G. J.; Pei, Y. Vacancy-induced dislocations within grains for high-performance PbSe thermoelectrics. *Nat. Commun.* **2017**, *8*, 13828.

17. Jana, M. K.; Pal, K.; Waghmare, U. V.; Biswas, K. The Origin of Ultralow Thermal Conductivity in InTe: Lone-Pair-Induced Anharmonic Rattling. *Angew. Chem. Int. Ed.* **2016**, *128* (27), 7923-7927.

18. Lin, H.; Tan, G.; Shen, J.-N.; Hao, S.; Wu, L.-M.; Calta, N.; Malliakas, C.; Wang, S.; Uher, C.; Wolverton, C.; Kanatzidis, M. G. Concerted Rattling in CsAg₅Te₃ Leading to Ultralow Thermal Conductivity and High Thermoelectric Performance. *Angew. Chem. Int. Ed.* **2016**, *55* (38), 11431-11436.

19. Zhao, L.-D.; Lo, S.-H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* **2014**, *508*, 373.

20. Morelli, D. T.; Jovovic, V.; Heremans, J. P. Intrinsically Minimal Thermal Conductivity in Cubic I–V–VI₂ Semiconductors. *Phys. Rev. Lett.* **2008**, *101* (3), 035901.

21. Jana, M. K.; Pal, K.; Waghmare, U. V.; Biswas, K. The Origin of Ultralow Thermal Conductivity in InTe: Lone-Pair-Induced Anharmonic Rattling. *Angew. Chem. Int. Ed.* **2016**, *55* (27), 7792-7796.

22. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. CsBi₄Te₆: A High-Performance Thermoelectric Material for Low-Temperature Applications. *Science* **2000**, *287* (5455), 1024-1027.

23. Toberer, E. S.; May, A. F.; Snyder, G. J. Zintl Chemistry for Designing High Efficiency Thermoelectric Materials. *Chem. Mater.* **2010**, *22* (3), 624-634.

24. Kim, S.-J.; Hu, S.; Uher, C.; Kanatzidis, M. G. Ba₄In₈Sb₁₆: Thermoelectric Properties of a New Layered Zintl Phase with Infinite Zigzag Sb Chains and Pentagonal Tubes. *Chem. Mater.* **1999**, *11* (11), 3154-3159.

25. Chung, D.-Y.; Hogan, T. P.; Rocci-Lane, M.; Brazis, P.; Ireland, J. R.; Kannewurf, C. R.; Bastea, M.; Uher, C.; Kanatzidis, M. G. A New Thermoelectric Material: CsBi₄Te₆. *J. Am. Chem. Soc.* **2004**, *126* (20), 6414-6428.

26. Choi, K.-S.; Chung, D.-Y.; Mrotzek, A.; Brazis, P.; Kannewurf, C. R.; Uher, C.; Chen, W.; Hogan, T.; Kanatzidis, M. G. Modular Construction of $A_{1+x}M_{4-2x}M_{7+x}^{*}Se_{15}$ (A = K, Rb; M = Pb, Sn; M^{*} = Bi, Sb): A New Class of Solid State Quaternary Thermoelectric Compounds. *Chem. Mater.* **2001**, *13* (3), 756-764.

27. Liu, H.; Shi, X.; Xu, F.; Zhang, L.; Zhang, W.; Chen, L.; Li, Q.; Uher, C.; Day, T.; Snyder, G. J. Copper ion liquid-like thermoelectrics. *Nat. Mater.* **2012**, *11*, 422.

28. Nielsen, M. D.; Ozolins, V.; Heremans, J. P. Lone pair electrons minimize lattice thermal conductivity. *Energy Environ. Sci.* **2013**, *6* (2), 570-578.

29. Lai, W.; Wang, Y.; Morelli, D. T.; Lu, X. From Bonding Asymmetry to Anharmonic Rattling in $Cu_{12}Sb_4S_{13}$ Tetrahedrites: When Lone-Pair Electrons Are Not So Lonely. *Adv. Funct. Mater.* **2015**, *25* (24), 3648-3657.

30. Pei, Y.-L.; Wu, H.; Sui, J.; Li, J.; Berardan, D.; Barreteau, C.; Pan, L.; Dragoe, N.; Liu, W.-S.; He, J.; Zhao, L.-D. High thermoelectric performance in n-type BiAgSeS due to intrinsically low thermal conductivity. *Energy Environ. Sci.* **2013**, *6*

(6), 1750-1755.

31. Guin, S. N.; Biswas, K. Cation Disorder and Bond Anharmonicity Optimize the Thermoelectric Properties in Kinetically Stabilized Rocksalt AgBiS₂ Nanocrystals. *Chem. Mater.* **2013**, *25* (15), 3225-3231.

32. Xiao, C.; Qin, X.; Zhang, J.; An, R.; Xu, J.; Li, K.; Cao, B.; Yang, J.; Ye, B.; Xie, Y. High Thermoelectric and Reversible p-n-p Conduction Type Switching Integrated in Dimetal Chalcogenide. *J. Am. Chem. Soc.* **2012**, *134* (44), 18460-18466.

33. Qiu, W.; Xi, L.; Wei, P.; Ke, X.; Yang, J.; Zhang, W. Part-crystalline part-liquid state and rattling-like thermal damping in materials with chemical-bond hierarchy. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111* (42), 15031-15035.

34. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. High Thermopower and Low Thermal Conductivity in Semiconducting Ternary K–Bi–Se Compounds. Synthesis and Properties of β -K₂Bi₈Se₁₃ and K_{2.5}Bi_{8.5}Se₁₄ and Their Sb Analogues. *Chem. Mater.* **1997**, *9* (12), 3060-3071.

35. Meng, J. F.; Shekar, N. V. C.; Chung, D.-Y.; Kanatzidis, M.; Badding, J. V. Improvement in the thermoelectric properties of pressure-tuned β -K₂Bi₈Se₁₃. *J. Appl. Phys.* **2003**, *94* (7), 4485-4488.

36. Kyratsi, T.; Kanatzidis, M. G. Synthesis, Crystallographic Studies, and Characterization of $K_2Bi_8Se_{13-x}S_x$ Solid Solutions. *Z. Anorg. Allg. Chem.* **2003**, *629* (12-13), 2222-2228.

37. Kyratsi, T.; Hatzikraniotis, E.; Paraskevopoulous, M.; Dyck, J. S.; Shin, H. K.; Uher, C.; Kanatzidis, M. G. Lattice thermal conductivity of K₂(Bi_{1-z}Sb_z)₈Se₁₃ solid solutions. *J. Appl. Phys.* **2004**, *95* (8), 4140-4146.

38. Bilc, D. I.; Mahanti, S. D.; Kyratsi, T.; Chung, D. Y.; Kanatzidis, M. G.; Larson, P. Electronic structure of K₂Bi₈Se₁₃. *Phys. Rev. B* **2005**, *71* (8), 085116.

39. Hoang, K.; Tomic, A.; Mahanti, S. D.; Kyratsi, T.; Chung, D.-Y.; Tessmer, S. H.; Kanatzidis, M. G. Role of K/Bi disorder in the electronic structure of β -K₂Bi₈Se₁₃. *Phys. Rev. B* **2009**, *80* (12), 125112.

40. Pei, Y.; Chang, C.; Wang, Z.; Yin, M.; Wu, M.; Tan, G.; Wu, H.; Chen, Y.; Zheng, L.; Gong, S.; Zhu, T.; Zhao, X.; Huang, L.; He, J.; Kanatzidis, M. G.; Zhao, L.-D. Multiple Converged Conduction Bands in K₂Bi₈Se₁₃: A Promising Thermoelectric Material with Extremely Low Thermal Conductivity. *J. Am. Chem. Soc.* **2016**, *138* (50), 16364-16371.

41. McCarthy, T. J.; Ngeyi, S. P.; Liao, J. H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. Molten salt synthesis and properties of three new solid-state ternary bismuth chalcogenides, .beta.-CsBiS₂, .gamma.-CsBiS₂, and K₂Bi₈Se₁₃. *Chem. Mater.* **1993**, *5* (3), 331-340.

42. Chung, D.-Y.; Iordanidis, L.; Choi, K.-S.; Kanatzidis, M. G. Complex chalcogenides as thermoelectric materials: a solid state chemistry approach. *Bull. Korean Chem. Soc.* **1998**, *19*, 1283-1293.

43. Mrotzek, A.; Iordanidis, L.; Kanatzidis, M. G. New Members of the Homologous Series $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$: The Quaternary Phases $A_{1-x}M'_{3-x}Bi_{11+x}Se_{20}$ and $A_{1+x}M'_{3-2x}Bi_{7+x}Se_{14}$ (A = K, Rb, Cs; M' = Sn, Pb). *Inorg. Chem.* **2001**, 40 (24),

6204-6211.

44. Samanta, M.; Pal, K.; Pal, P.; Waghmare, U. V.; Biswas, K. Localized Vibrations of Bi Bilayer Leading to Ultralow Lattice Thermal Conductivity and High Thermoelectric Performance in Weak Topological Insulator n-Type BiSe. J. Am. Chem. Soc. 2018, 140 (17), 5866-5872.

45. Kim, J.-H.; Chung, D.-Y.; Bilc, D.; Loo, S.; Short, J.; Mahanti, S. D.; Hogan, T.; Kanatzidis, M. G. Crystal Growth, Thermoelectric Properties, and Electronic Structure of $AgBi_3S_5$ and $AgSb_xBi_{3-x}S_5$ (x = 0.3). *Chem. Mater.* **2005**, *17* (14), 3606-3614.

46. Pan, L.; Bérardan, D.; Dragoe, N. High Thermoelectric Properties of n-Type AgBiSe₂. J. Am. Chem. Soc. **2013**, 135 (13), 4914-4917.

47. Zhao, L. D.; Lo, S. H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* **2014**, *508* (7496), 373-7.

48. Zhao, L.-D.; Tan, G.; Hao, S.; He, J.; Pei, Y.; Chi, H.; Wang, H.; Gong, S.; Xu, H.; Dravid, V. P.; Uher, C.; Snyder, G. J.; Wolverton, C.; Kanatzidis, M. G. Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe. *Science* **2016**, *351*, 141–144.

49. Hanko, J. A.; Sayettat, J.; Jobic, S.; Brec, R.; Kanatzidis, M. G. $A_2CuP_3S_9$ (A = K, Rb), $Cs_2Cu_2P_2S_6$, and $K_3CuP_2S_7$: New Phases from the Dissolution of Copper in Molten Polythiophosphate Fluxes. *Chem. Mater.* **1998**, *10* (10), 3040-3049.

50. Borup, K. A.; de Boor, J.; Wang, H.; Drymiotis, F.; Gascoin, F.; Shi, X.; Chen, L.; Fedorov, M. I.; Muller, E.; Iversen, B. B.; Snyder, G. J. Measuring thermoelectric transport properties of materials. *Energy Environ. Sci.* **2015**, *8* (2), 423-435.

51. Subject Index. In *Ultrasonic Methods in Solid State Physics*, Truell, R.; Elbaum, C.; Chick, B. B. Eds. Academic Press: 1969; pp 450-464.

52. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865-3868.

53. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54* (16), 11169-11186.

54. Yan, X.; Poudel, B.; Ma, Y.; Liu, W. S.; Joshi, G.; Wang, H.; Lan, Y.; Wang, D.; Chen, G.; Ren, Z. F. Experimental Studies on Anisotropic Thermoelectric Properties and Structures of n-Type Bi₂Te_{2.7}Se_{0.3}. *Nano Lett.* **2010**, *10* (9), 3373-3378.

55. Goldsmid, H. J.; Sharp, J. W. Estimation of the thermal band gap of a semiconductor from seebeck measurements. *J. Electron. Mater.* **1999**, *28* (7), 869-872.

56. Gibbs, Z. M.; Kim, H.-S.; Wang, H.; Snyder, G. J. Band gap estimation from temperature dependent Seebeck measurement—Deviations from the 2e|S|maxTmax relation. *Appl. Phys. Lett.* **2015**, 106 (2), 022112.

57. Kuo, J. J.; Kang, S. D.; Imasato, K.; Tamaki, H.; Ohno, S.; Kanno, T.; Snyder, G. J. Grain boundary dominated charge transport in Mg3Sb2-based compounds. *Energy Environ. Sci.* **2018**, 11 (2), 429-434.

58. Kim, H.-S.; Gibbs, Z. M.; Tang, Y.; Wang, H.; Snyder, G. J. Characterization of Lorenz number with Seebeck coefficient measurement. *APL Materials* **2015**, *3* (4),

P	a
1	
2	
3	
4	
5	
6	
7	
8	
9	
1	0
1	1
1	2
1	3
1	4
1	5
1	6
1	7
1	8
1	9
2	0
2	1
2	2
2	3
2	4
2	5
2	6
2	7
2	8
2	9
3	0
3	1
3	2
3	3
3	4
3	5
3	6
3	7
3	8
3	9
4	0
4	1
4	2
4	3
4	4
4	5

041506.

59. Chang, C.; Wu, M.; He, D.; Pei, Y.; Wu, C.-F.; Wu, X.; Yu, H.; Zhu, F.; Wang, K.; Chen, Y.; Huang, L.; Li, J.-F.; He, J.; Zhao, L.-D. 3D charge and 2D phonon transports leading to high out-of-plane ZT in n-type SnSe crystals. *Science* **2018**, *360* (6390), 778-783.

60. Zhao, L.-D.; Lo, S.-H.; He, J.; Li, H.; Biswas, K.; Androulakis, J.; Wu, C.-I.; Hogan, T. P.; Chung, D.-Y.; Dravid, V. P.; Kanatzidis, M. G. High Performance Thermoelectrics from Earth-Abundant Materials: Enhanced Figure of Merit in PbS by Second Phase Nanostructures. *J. Am. Chem. Soc.* **2011**, *133* (50), 20476-20487.

61. Biswas, K.; Zhao, L.-D.; Kanatzidis, M. G. Tellurium-Free Thermoelectric: The Anisotropic n-Type Semiconductor Bi₂S₃. *Adv. Energy Mater.* **2012**, *2* (6), 634-638.

62. Xie, H. Y., Su, X. L., Zheng, G., Zhu, T., Yin, K., Yan, Y. G., Uher, C., Kanatzidis, M. G., Tang, X. F. The Role of Zn in Chalcopyrite CuFeS₂: Enhanced Thermoelectric Properties of Cu1–xZnxFeS2 with In Situ Nanoprecipitates. *Adv. Energy Mater.* **2017**, *7* (3), 1601299.

63. Luo, Y.; Zheng, Y.; Luo, Z.; Hao, S.; Du, C.; Liang, Q.; Li, Z.; Khor, K. A.; Hippalgaonkar, K.; Xu, J.; Yan, Q.; Wolverton, C.; Kanatzidis, M. G. n-Type SnSe₂ Oriented-Nanoplate-Based Pellets for High Thermoelectric Performance. *Adv. Energy Mater.* **2017**, *8*, 1702167.

64. Ahn, J. Y.; Hwang, J.-Y.; Ryu, B. K.; Oh, M.-W.; Lee, K. H.; Kim, S. W. Importance of crystal chemistry with interstitial site determining thermoelectric transport properties in pavonite homologue Cu-Bi-S compounds. *CrystEngComm* **2016**, *18* (8), 1453-1461.

65. Zhao, L.-D.; He, J.; Berardan, D.; Lin, Y.; Li, J.-F.; Nan, C.-W.; Dragoe, N. BiCuSeO oxyselenides: new promising thermoelectric materials. *Energy Environ. Sci.* **2014**, *7* (9), 2900-2924.

66. Xiao, Y.; Pei, Y.; Chang, C.; Zhang, X.; Tan, X.; Ye, X.; Gong, S.; Lin, Y.; He, J.; Zhao, L.-D. Electrical and thermal transport properties of layered Bi₂YO₄Cu₂Se₂. *J. Solid State Chem.* **2016**, *239*, 178-183.

67. Kurosaki, K.; Kosuga, A.; Muta, H.; Uno, M.; Yamanaka, S. Ag₉TlTe₅: A high-performance thermoelectric bulk material with extremely low thermal conductivity. *Appl. Phys. Lett.* **2005**, *87* (6), 061919.

68. Dutta, M.; Pal, K.; Waghmare, U. V.; Biswas, K. Bonding heterogeneity and lone pair induced anharmonicity resulted in ultralow thermal conductivity and promising thermoelectric properties in n-type AgPbBiSe₃. *Chem. Sci.* **2019**, *10*, 4905.

69. Tan, G.; Hao, S.; Zhao, J.; Wolverton, C.; Kanatzidis, M. G. High Thermoelectric Performance in Electron-Doped AgBi₃S₅ with Ultralow Thermal Conductivity. *J. Am. Chem. Soc.* **2017**, *139* (18), 6467-6473.





Figure 1. Crystal structure of $K_{2.5}Bi_{8.5}Se_{14}$ from the approximate perspective of the *b* axis. Black, blue, red, and green spheres: Bi, K/Bi, Se, and K. $K_{2.5}Bi_{8.5}Se_{14}$ has a complex 3D anionic framework that includes two different types of Bi/Se polyhedral building blocks, NaCl- and Bi₂Te₃-type fragments, which are highlighted by the blue squares. The Bi₂Te₃-type rods are arranged one by one to form layers parallel to the *a*-axis. The NaCl-type rod fragments connect the layers to build a 3D framework with K⁺ in the channel. The unit cell is demarcated by a solid black line.³⁴





Figure 2. (a) PXRD patterns of the intrinsic $K_{2.5}Bi_{8.5}Se_{14}$ along two directions: (1) the scattering vector of the X-ray is perpendicular to the primary surface of the pellets ($K_{2.5}Bi_{8.5}Se_{14}$ -|| blue pattern), (2) the scattering vector of the X-ray is parallel to the primary surface of the pellets ($K_{2.5}Bi_{8.5}Se_{14}$ -|| blue pattern), (2) the scattering vector of the X-ray is parallel to the primary surface of the pellets ($K_{2.5}Bi_{8.5}Se_{14}$ -⊥, black pattern). The red curve is the simulated pattern of $K_{2.5}Bi_{8.5}Se_{14}$ (ICSD 84269). The PXRD patterns indicate the anisotropic feature of $K_{2.5}Bi_{8.5}Se_{14}$; (b) PXRD patterns of $K_{2.5}Bi_{8.5}Se_{14}$ and $K_{2.5}Bi_{8.5}Se_{14-x}$ samples; and (c) Electronic absorption spectra obtained from diffuse reflectance infrared spectroscopy measurement on $K_{2.5}Bi_{8.5}Se_{14}$ at room temperature.

Figure 3. (a) Typical HAADF-STEM image of $K_{2.5}Bi_{8.5}Se_{14}$ specimen viewed down the monoclinic *b*-axis [010] of the unit cell, showing mainly z-contrast. Inset is the electron diffraction pattern along [010] direction. (b) Zoom-in image with crystal direction and atom labeled.

Figure 4. Thermoelectric properties as a function of temperature for $K_{2.5}Bi_{8.5}Se_{14}$ - \perp and $K_{2.5}Bi_{8.5}Se_{14}$ - \parallel : (a) Electrical conductivity, σ ; (b) Seebeck coefficient, *S*; (c) Power factor, *PF*; (d) Total thermal conductivity, κ_{tot} ; (e) Lattice thermal conductivity, κ_{lat} ; and (f) Figure of merit, *ZT*.

Figure 5. Thermoelectric transport properties as a function of temperature for $K_{2.5}Bi_{8.5}Se_{14}$ - \perp and $K_{2.5}Bi_{8.5}Se_{14-x}$ samples: (a) electrical conductivity, σ ; (b) Seebeck coefficient, *S*.

Figure 6. (a) Hall coefficient, $R_{\rm H}$ and *n* at 300 K for K_{2.5}Bi_{8.5}Se₁₄- \perp and K_{2.5}Bi_{8.5}Se_{14-x} samples; (b) Seebeck coefficient as a function of Hall carrier concentration with an effective mass of 1.2 $m_{\rm e}$. The short dot curves are the theoretical Pisarenko plots at 300 K (black), 573 K (red) and 773 K (blue). The solid black square, red circle, blue up-triangle, dark cyan down-triangle, dark yellow right-triangle, and navy diamond are K_{2.5}Bi_{8.5}Se₁₄- \perp , x = 0.007, x = 0.021, x = 0.042, x = 0.07 and x = 0.105 samples at 300 K. The half-right black square, blue up-triangle, and dark yellow right-triangle are K_{2.5}Bi_{8.5}Se₁₄- \perp , x = 0.021 and 0.7 samples at 573 K. The half-left black square, blue up-triangle are K_{2.5}Bi_{8.5}Se₁₄- \perp , x = 0.021 and 0.7 samples at 773 K; (c) Temperature-dependent carrier concentration, *n* for K_{2.5}Bi_{8.5}Se₁₄- \perp , x = 0.021 and 0.7 samples; and (d) Temperature-dependent $\mu_{\rm H}$ for K_{2.5}Bi_{8.5}Se₁₄- \perp , x = 0.021 and 0.7 samples.

Figure 7. (a) Total thermal conductivity, κ_{tot} ; (b) Lattice thermal conductivity, κ_{lat} ; and (c) Figure of merit, *ZT*, for K_{2.5}Bi_{8.5}Se₁₄- \perp and K_{2.5}Bi_{8.5}Se_{14-x} samples.

Figure 8. The calculated electronic band structure (a) and projected density of state (b) of $K_5Bi_{17}Se_{28}$. It is shown the very small calculated band gap of 0.03 eV. The electronic density of states decomposition shows that the conduction bands bottom with 0.2 to 0 eV are mainly the hybridization of Bi 6p and Se 4s electrons. The contribution of K states in the conduction band minimum and valence band maximum is negligible.

Figure 9. (a) The phonon dispersions show compressed acoustic branches (colored curves) that lead to low phonon velocity and low thermal conductivity;^{18, 69} (b) Calculated κ_{lat} of K_{2.5}Bi_{8.5}Se₁₄ as a function of temperature along the *a*-, *b*-, and *c*-axes as well as the averaged values; (c) Grüneisen parameters across reciprocal space, and (d) the projected phonon density of states (PDOS) for K₅Bi₁₇Se₂₈.

Table 1. Comparison of measured elastic properties (speed of sound) of $K_{2.5}Bi_{8.5}Se_{14}$ at room temperature with other Bi-chalcogenide based thermoelectric materials with low thermal conductivity: $K_2Bi_8Se_{13}$,⁴⁰ BiCuSeO,⁶⁵ and Bi₂YO₄Cu₂Se₂ (Vertical direction)⁶⁶. Longitudinal (v_l , ms⁻¹), shear (v_s , ms⁻¹) and average (v_a , ms⁻¹) phonon velocities, Young's modulus (E, GPa), Poisson ratio (v_p), Grüneisen parameter (γ), Debye temperature (Θ_D , K)

	$K_{2.5}Bi_{8.5}Se_{14}$	$K_2Bi_8Se_{13}$	BiCuSeO	Bi ₂ YO ₄ Cu ₂ Se ₂
v_l	2840	2683	3290	3970
v_s	1436	1438	1900	2151
v _a	1610	1605	2107	2400
E	35.8	37.1	76.5	70.6
v_p	0.33	0.30	0.25	0.29
γ	1.96	1.71	1.5	1.71
\varTheta_D	126	154	243	280

Table 2. The calculated phonon velocities v_{TA} , $v_{TA'}$, and v_{LA} (ms⁻¹) for the *a*, *b*, and *c* directions of K_{2.5}Bi_{8.5}Se₁₄. The average value is 2054 ms⁻¹.

	v_{TA}	v_{TA} ,	$v_{ m LA}$	average
а	1370	1870	2660	1966
b	1735	2230	3640	2535
С	1160	1250	2580	1663

ToC graphic

