SPECIAL TOPIC: Dedicated to the 70th Birthday of Professor Kenneth R. Poeppelmeier

Vibration uncoupling of germanium with different valence states lowers thermal conductivity of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$

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ABSTRACT The thermal phonon transport is a key matter for heat managing in materials science which is crucial for device miniaturization and power density increase. Herein, we report the synthesis, structure and characterization of a new compound, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, with a unique anisotropic structure simultaneously containing Ge^{3+} and Ge^{2+} that adopt $(\text{Ge}1)^{3+}_2\text{Se}_6$ dimer or $(\text{Ge}2)^{2+}\text{Se}_6$ octahedron, respectively. The thermal conductivity was measured to be $0.57\text{--}0.48\text{ W m}^{-1}\text{ K}^{-1}$ from 323 to 773 K, the lowest value among all the known Ge-containing compounds, approaching its glass limit according to the Cahill's formulation. More importantly, we discover for the first time that the vibration uncoupling of Ge with different valence states hinders the effective thermal energy transport between the $(\text{Ge}1)^{3+}_2\text{Se}_6$ dimer and $(\text{Ge}2)^{2+}\text{Se}_6$ octahedron, and consequently lowers the thermal conductivity. In addition, we propose a structure factor $f_i = \sin(180 - \beta) \times d_{\text{Ge-Q}} / l_i$ ($i = \text{A, B}$), with which a structure map of the $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family is given.

Keywords: $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, mixed valence states compound, thermal conductivity, phonon transport, crystallography analyses

INTRODUCTION

Heat managing is of great importance owing to the urgent needs of the miniaturization and increasing power density in modern devices [1]. Thus, the understanding of phonon thermal transport has become a key issue in materials science for engineering efficient materials towards applications. Chalcogenides, as promising functional materials with abundant compositions, crystal structures and property diversities, have shown the im-

pressive potential applications, such as optoelectronics [2], transistors [3], and thermoelectrics [4]. In particular, the correlation between thermal property and the structure has been widely reported. For instance, studies on $\text{AgPb}_m\text{SbTe}_{2+m}$ [5], $\text{Sn}_{1-x}\text{In}_x\text{Cd}_{x/2}\text{Te}$ [6], $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ [7], and $\text{Pb}_{0.95}(\text{Sb}_{0.033}\square_{0.017})\text{Se}_{1-y}\text{Te}_y$ ($\square$ = vacancy; $y = 0\text{--}0.4$) [8] show multiple defects that involve point defects, vacancy-driven dense dislocations, and Te-induced nanoprecipitates, collectively scatter thermal phonons in a wide frequency region, making the lattice thermal conductivity as low as $0.4\text{ W m}^{-1}\text{ K}^{-1}$ and even reach its amorphous limit.

The common strategies toward low thermal conductivity mostly aim at alloying [9], hierarchical architectures [10], or nanostructuring [11], which tune the structure mechanically to scatter the phonon transport. Yet, these strategies face a challenge to ensure the repeatability and stability of the entire material system, not only in terms of structure, but also the thermal transport performance. From the chemistry point of view, the multivalent materials feature structure complexity due to various bonding nature and distinct local coordination geometries, and thus new routes should be offered to regulate the phonon propagation at atomic scale. However, related study is rare.

Germanium is a very interesting element with diverse valence states in one compound (Fig. 1). For instance, the Ge^{4+} tends to adopt a tetrahedral coordination with four nearly equidistant Ge-Q ($\text{Q} = \text{S, Se, Te}$) bonds [12–19], the Ge^{3+} usually forms a Ge-Ge metal bond to fulfill its four coordination and generate the characteristic ethane-

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Figure 1 Representative compounds constructed by building units centered by Ge with different valence states: Ge^{4+}Q_4 tetrahedron (a–c), $\text{Ge}^{3+}_2\text{Q}_6$ dimers (d–f), and Ge^{2+}Q_6 octahedron (g–i), respectively.

like $\text{Ge}^{3+}_2\text{Q}_6$ dimer [20–27], and the Ge^{2+} is often found in an octahedron with six Ge–Q bonds [27,30]. Various arrangements of these structure building units lead to great diversity of structures [13–30].

Herein, we report a new compound of the $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ ($\text{M} = \text{Ga}, \text{In}; \text{Q} = \text{Se}, \text{Te}$) family, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, in which Ge^{3+} and Ge^{2+} coexist. Single crystal diffraction data reveal that Ge with different valence states adopt $(\text{Ge}^{3+})_2\text{Se}_6$ dimer or $(\text{Ge}^{2+})_2\text{Se}_6$ octahedron coordination, respectively. Importantly, we discover for the first time that the weak coupling of the vibrations of Ge atoms with different valence states hinders the effective thermal energy transport between the $(\text{Ge}^{3+})_2\text{Se}_6$ dimer and $(\text{Ge}^{2+})_2\text{Se}_6$ octahedron which lowers the thermal conductivity. Consequently, the title compound exhibits thermal conductivity of $0.57\text{--}0.48 \text{ W m}^{-1} \text{ K}^{-1}$ from 323 to 773 K, the lowest value among all the known Ge-containing compounds, approaching its glass limit according to the Cahill's formulation. In addition, we propose a structure factor $f_i = \frac{\sin(180-\beta) \times d_{\text{Ge-Q}}}{l_i}$ ($i = \text{A}, \text{B}$), with which a structure map of the $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family is

given.

EXPERIMENTAL SECTION

Synthesis of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$

The compound was synthesized by a solid-state reaction of CsCl, Ge, Ga and Se with a molar ratio of 4:4:6:14 with slightly extra Ge and CsCl as reactive fluxes. After flame-sealing inside a silica tubing, the reactant assembly was heated to 1173 K and kept at this temperature for 7500 min, then slowly cooled to 573 K before shutting down the furnace. The yield was about 96%. The lamellar dark-red crystals of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ are stable in air and insoluble in water.

Thermal stabilities

Simultaneous thermal analysis (STA) data were measured on a NETZSCH STA 449 F3 analyzer. Fig. S1d demonstrates the $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ has good thermal stability with no evident weight loss up to 780°C. Above 800°C, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ decomposes to give Ga_2Se_3 (Fig. S1) (see

more in Supplementary information).

Single-crystal X-ray diffraction (XRD)

The single crystal structure data of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ were collected on a Bruker APEX-II CCD diffractometer equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Full-matrix least-squares refinement on F^2 was carried out by using the SHELXTL program package [31]. Structure determination was based on the direct method and absorption correction was done by using multi-scan method, and then the structure was checked with PLATON [32] eventually.

X-ray photoelectron spectroscopy (XPS)

XPS (ESCSLAB 250Xi, USA) was used to investigate the surface properties. Fig. S1c indicates the bonding energies of 30.1 and 31.0 eV are attributed to Ge^{2+} and Ge^{3+} , respectively. An atomic ratio of $\text{Ge}^{2+}:\text{Ge}^{3+} = 0.5:1$ was calculated from the area of the XPS peak, in good agreement with the single crystal diffraction refinement results.

Raman spectroscopy

The Raman spectrum was collected on a RENISHAW RM 2000 spectrometer equipped with CCD detector using 532 nm laser.

UV-vis diffuse reflectance spectra

Diffuse-reflectance spectra were measured on a SHIMADZU UV-2600 Spectrometer in the range of 220 to 1400 nm at 293 K. The UV-vis diffuse reflectance spectrum indicates an $E_g = 2.41 \text{ eV}$ (Fig. S1f).

Ultrasonic pulse echo measurement

The longitudinal and shear acoustic velocities were measured with a commercial equipment (Ultrasonic Pulser/Receiver Model 5058 PR, Olympus, USA) by counting the thickness of the sample d and the traveling time Δt .

Theoretical calculations

The Vienna *ab initio* simulation package VASP [33] was performed to calculate the band structures and density of states (DOS). The generalized gradient approximation (GGA) was chosen as the exchange-correlation function and a plane wave basis with projector augmented wave (PAW) potentials was used [34–36]. Phonon calculation was carried out using Phonopy package [37] coded with VASP to estimate the lattice vibration, phonon dispersion and projected phonon density of states.

Thermal transport measurement

Single crystals of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ were ground into fine powder and densified by spark plasma sintering (SPS-211LX). The obtained pellet has a density of ~93 % of the theoretical value. The total thermal conductivity was calculated by $\kappa = D \times C_p \times d$, where the thermal diffusivity (D) was measured with a Netzsch LFA-457 and the specific heat (C_p) was indirectly measured with a reference of pyroceram 9606.

RESULTS AND DISCUSSION

Synthesis and crystal growth of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$

The $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ was successfully synthesized *via* a modified solid-state reaction. In the procedure, not only extra CsCl as a reactive flux, but also extra Ge (one of the reactants) with high melting point was purposely introduced, which successfully increased the heterogeneity and promoted the reaction with relatively high surface diffusion to significantly facilitate the single crystal growth [38–40]. The melting points of the reactants, CsCl, Ge, Ga and Se, are 918, 1211, 302 and 494 K, respectively. Actually, the difficulty in the synthesis of the multinary alkali metal chalcogenide $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ lies in not only the low reaction capacity with a low product yield about 10%, but also the high stability of the by-product Ga_2Se_3 that cannot be simply removed by distilled water or ethanol. To solve such problems, we first introduced extra amount of CsCl that served as a reactive flux in the reaction, which also helped to generate plenty of tiny single crystals with average sizes of $0.2 \times 0.2 \times 0.1 \text{ mm}^3$ (Fig. S2a). Secondly, we further investigated the crystal growth process to increase the crystal size. Fig. S2b implies that prolonging the annealing time to 7500 min results in a single crystal size of $0.3 \times 0.3 \times 0.2 \text{ mm}^3$. Significantly, the introduction of extra Ge with high melting point leads to a remarkable enhancement of the single crystal sizes up to $3 \times 3 \times 0.5 \text{ mm}^3$ (Fig. S2c), almost 10 times larger than the first attempt. Since the complexity and particularity of solid state reaction and crystal growth, this approach may shed some useful light on other systems with similar crystal habit and crystal structure. The purity of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ was checked by the powder XRD patterns shown in Fig. S1a. Furthermore, the semi-quantitative element analyses (Fig. S3) confirm the stoichiometry with an average formula of $\text{Cs}_2\text{Ge}_{3.5(8)}\text{-Ga}_{6.4(1)}\text{Se}_{14.8(0)}$.

Crystal structure and structure relationship

$\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ crystallizes in space group $P\bar{3}m1$ (No. 164)

with unit cell parameters of $a = b = 7.6396(3) \text{ \AA}$, $c = 13.5866(6) \text{ \AA}$, $V = 686.72(6) \text{ \AA}^3$, and $Z = 1$. Crystallographic data and refinement details are displayed in Tables S1–S3. The Ga atom locates at the Wyckoff site $6i$ with a GaSe_4 tetrahedron geometry to form a $\text{Ga}_6\text{Se}_{14}$ layer that further alternatively connects $\text{Ge}^{3+}_2\text{Se}_6$ dimer and $\text{Ge}^{2+}\text{Se}_6$ octahedron generating a 3D structure with Cs atoms filling in the vacancies.

The Ge–Q bonding nature determines the structure distribution of $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family, $\text{Cs}_2\text{Ge}_3\text{In}_6\text{Te}_{14}$, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Te}_{14}$, and $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ take the $P\bar{3}m1$ -type structure, while $\text{Cs}_2\text{Ge}_3\text{In}_6\text{Se}_{14}$ crystallizes in the space

group $R\bar{3}m$. There are two crystallographically different sites A and B, confined by the Q–Q–Q triangle (Fig. 2c). When the $\text{Ge}^{3+}_2\text{Se}_6$ dimer occupies the site A, the compound adopts the $P\bar{3}m1$ structure, otherwise the $R\bar{3}m$ -type structure is taken. The Ge–Q bond distance, Ge–Ge–Q bond angle in the $\text{Ge}^{3+}_2\text{Q}_6$ dimer, and the size of the site A or B mainly drives the site preference, which determines the structure type. The size of site A or B is defined as the equivalent Q–Q distance of Q–Q–Q triangle in the M_6Q_{14} layer as listed in Table S4.

And a factor is defined as $f_i = \sin(180 - \beta) \times d_{\text{Ge-Q}} / l_i$ ($i = \text{A, B}$), clearly showing how the two structure types distribute among the $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family, where

Figure 2 Crystal structure of $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family. (a) The views of the packing along the b axis for the $P\bar{3}m1$ -type and $R\bar{3}m$ -type structures. Red octahedron: $\text{Ge}^{2+}\text{Se}_6$, blue tetrahedron: GaSe_4 , ball and stick: $\text{Ge}^{3+}_2\text{Se}_6$ dimer; (b) a single M_6Q_{14} layer viewed on the ab plane, site A or B is marked; (c) the Q–Q–Q triangle confines the site A and B, with the edge marked as l_i ($i = \text{A, B}$), the $\text{Ge}^{3+}_2\text{Q}_6$ dimer with the Ge–Q bond length ($d_{\text{Ge-Q}}$) and the Ge–Ge–Q angle (β) labeled; (d) the definition of the factor of f_i ; and (e) the structure map classified by the f_i factor.

$d_{\text{Ge-Q}}$ represents the Ge-Q bond distance, β is the bond angle of Ge-Ge-Q, l_i represents the distance of Q-Q. The factor $f_i = \frac{\sqrt{3}}{3}$ indicates the projection of three Ge-Q bonds of the $\text{Ge}^{3+}_2\text{Q}_6$ dimer rightly crosses in the center of site A or B. When $f_A = \frac{\sqrt{3}}{3} < f_B$, the $\text{Ge}^{3+}_2\text{Q}_6$ dimer will choose the larger site A instead of the smaller site B, and the compound will adopt the $P\bar{3}m1$ -type structure, when $f_A < f_B = \frac{\sqrt{3}}{3}$, the site A is too large to accommodate the $\text{Ge}^{3+}_2\text{Q}_6$ dimer, which will occupy the site B instead and then generates the $R\bar{3}m$ -type structure (Fig. 2d). For $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, the site A is more tolerable for the $\text{Ge}^{3+}_2\text{Se}_6$ dimer, with a l_A of 3.9571 Å about 7% larger than that of site B. As a result, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ adopts the space group $P\bar{3}m1$.

Thermal transport property

The density of SPS-densified $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ pellet reaches 4.5 g cm^{-3} , about ~93% of the theoretical value. The thermal conductivity was obtained by the formula $\kappa = D \times C_p \times d$, where thermal diffusivity (D) measured in the temperature range of 323–773 K and the specific heat (C_p) was indirectly counted by the reference of pyroceram 9606. Fig. 3d depicts the thermal conductivity (κ) of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, the very low value of $0.57\text{--}0.48 \text{ W m}^{-1} \text{ K}^{-1}$ from 323 to 773 K is striking. This value is competitive to those Ge-containing thermal conductive dense solids, such as two representatives of the mid-IR nonlinear optical material ZnGeP_2 [41] and short-period superlattice Ge [42], respectively, showing large thermal conductivities of 35 and $70 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K, which are at least 70 times larger than that of the title compound. Moreover, compared with other Ge-based thermoelectric materials, such as GeSe ($1.6\text{--}0.8 \text{ W m}^{-1} \text{ K}^{-1}$, 300–570 K) [43], $\text{Cu}_2\text{ZnGeSe}_4$ ($1.0\text{--}0.8 \text{ W m}^{-1} \text{ K}^{-1}$, 300–723 K) [44], $\text{K}_8\text{Ga}_8\text{Ge}_{38}$ ($0.9\text{--}1.3 \text{ W m}^{-1} \text{ K}^{-1}$, 100–300 K) [45], $\text{Cu}_{22}\text{Fe}_8\text{Ge}_4\text{Se}_{32}$ ($1.7\text{--}1.2 \text{ W m}^{-1} \text{ K}^{-1}$, 300–570 K) [46], $\text{Ag}_{10}\text{Ge}_{10}\text{P}_{12}$ ($1.2\text{--}1.0 \text{ W m}^{-1} \text{ K}^{-1}$, 300–700 K) [47], $\text{Ba}_{24}\text{Ge}_{100}$ ($2.8\text{--}3.8 \text{ W m}^{-1} \text{ K}^{-1}$, 300–750 K) [48], $\text{Cu}_2\text{ZnGeSe}_4$ ($3.2\text{--}1.0 \text{ W m}^{-1} \text{ K}^{-1}$, 300–670 K) [49], $\text{Cu}_2\text{ZnGeS}_4$ ($3.8\text{--}1.2 \text{ W m}^{-1} \text{ K}^{-1}$, 300–670 K) [49], $\text{Ba}_2\text{Cr}_4\text{GeSe}_{10}$ ($0.8\text{--}0.6 \text{ W m}^{-1} \text{ K}^{-1}$, 300–770 K) [50], $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ possesses an extreme lower thermal conductivity which makes it stand out. Note that the majority of the Ge-based compounds only contain Ge with single valence state. Differently, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ owns structural complexity with mixed valence states (Ge^{2+} , Ge^{3+}). The room temperature ultrasonic measurement was carried out to ex-

plore the origin of the low thermal conductivity. The lattice vibration, coupled with the long wavelengths and the acoustic phonons propagation speeds, mainly governs the thermal conduction in materials. The acoustic phonons velocity therefore is a key measure of the lattice thermal conduction behavior. The ultrasonic pulse echo measurements show the longitudinal and transverse sound velocities of $v_l = 2811 \text{ ms}^{-1}$ and $v_s = 1680 \text{ ms}^{-1}$, respectively. Theoretical elastic property calculations of the average sound velocity v_a , Young's modulus E , shear modulus G , Poisson ratio ν_p , and Grüneisen parameter γ are obtained according to the following equations [51,52]:

$$v_a = \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_s^3} \right) \right]^{-1/3}, \quad (1)$$

$$E = \frac{\rho v_s^2 (3v_l^2 - 4v_s^2)}{v_l^2 - v_s^2}, \quad (2)$$

$$G = \frac{E}{2(1 + \nu_p)}, \quad (3)$$

$$\nu_p = \frac{1 - 2(v_s/v_l)^2}{2 - 2(v_s/v_l)^2}, \quad (4)$$

$$\gamma = \frac{3}{2} \left(\frac{1 + \nu_p}{2 - 3\nu_p} \right). \quad (5)$$

As listed in Table 1, all the positive elastic constants reveal the mechanical stability of this compound. The low transverse sound velocity of 1680 ms^{-1} , indicates the soft shear modes scarcely propagate through the lattice, which gives rise to the low κ in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$. In addition, the longitudinal sound velocity of 2811 ms^{-1} also features a distinct low value in comparison with the general reported materials with low thermal conductivity [53–55]. And the relatively low average sound velocity of 1859 ms^{-1} leads to the low Young's modulus (33.48 GPa) and Shear modulus (13.69 GPa). Besides, the Debye temperature θ_D is calculated [52]:

$$\theta_D = \frac{h}{k_B} \left[\frac{3N}{4\pi V} \right]^{1/3} v_a, \quad (6)$$

where V represents the volume of unit cell, N is the number of atoms in the unit cell, and v_a indicates the average sound velocity. The low Debye temperature 183.49 K and the relatively large Grüneisen parameter γ 1.37, which is comparable to majority of the state-of-the-art thermoelectric materials with $\gamma = 1.0\text{--}2.6$ [56], illustrate the thermal transport behavior in a way. All these results support the low thermal conductivity κ observed in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$. The strong temperature-dependence of

Figure 3 Thermal transport properties of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$. (a) Theoretically calculated phonon dispersion. Red, blue: the transverse acoustic phonon scattering branches TA and TA', green: the longitudinal acoustic phonon models (LA). (b) The projected partial phonon density of states. (c) The calculated lattice thermal conductivity along three crystal axes. (d) The measured temperature-dependent thermal conductivity. Some Ge-containing binary and multinary materials are also listed. The black dotted line: the glass limit of the lattice thermal conductivity in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ according to the Cahill's formulation.

the thermal conductivity in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ indicates a typical crystal behavior (Fig. 3). Since the $E_g = 2.41$ eV (Fig. S1f), the carriers thermal conductivity is negligible in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, and the measured thermal conductivity can be roughly treated as the lattice thermal conductivity.

On the basis of density function theory (DFT) phonon calculation of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, lattice dynamical properties trigger better understanding of its ultralow thermal conductivity. Various chemical bonding interactions and diverse geometries in a solid crystalline material cause

Table 1 The measured sound velocity v_l , v_s , v_a , elastic properties (E , G , ν_p), Grüneisen parameter (γ) and Debye temperature (θ_D) for $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ at room temperature

Parameters	$\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$
Longitudinal sound velocity, v_l (m s^{-1})	2811
Transverse sound velocity, v_s (m s^{-1})	1680
Average sound velocity, v_a (m s^{-1})	1859
Young's modulus, E (GPa)	33.48
Shear modulus, G (GPa)	13.69
Poisson ratio, ν_p	0.22
Grüneisen parameter, γ	1.37
Debye temperature, θ_D (K)	183.49

quite flat phonon dispersion as shown in Fig. 3a, demonstrating its thermodynamic stability with no imaginary eigenvalue observed. Indeed, the various structure geometries and bonding natures of $(\text{Ge}2)^{2+}\text{Se}_6$ octahedron, $(\text{Ge}1)^{3+}_2\text{Se}_6$ dimer, and GaSe_4 tetrahedron in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, contribute quite differently to the heat propagation. The $(\text{Ge}2)^{2+}\text{Se}_6$ octahedron exhibits high symmetry with six equivalent Ge–Se bonds of 2.86 Å, and the long interatomic distance between $(\text{Ge}2)^{2+}$ and Se illustrates the weak chemical bonding, which coupled with its discrete inter-octahedron arrangement motif in the structure (Fig. 2a) give rise to the strong disruption of the heat propagation. Differently, the four-fold coordinated $(\text{Ge}1)^{3+}$ shows a dimeric structure with three Ge–Se bonds of 2.35 Å and a Ge–Ge metallic bond of 2.41 Å. In addition, Ga^{3+} is four coordinated in the GaSe_4 tetrahedron with Ga–Se bond length range from 2.39 to 2.40 Å, and shares the tetrahedral vertexes to generate the $\text{Ga}_6\text{Se}_{14}$ layer that is parallel to the ab plane. Owing to the similar bonding nature, same valence state, same coordination geometry, comparable bond length, and reduced mass, the $(\text{Ge}1)^{3+}_2\text{Se}_6$ dimer and the $\text{Ga}^{3+}\text{Se}_4$ tetrahedron exhibit strong coupling interaction as shown in Fig. 3b with similar curve shape at the lower frequencies region that contributes more to the heat transport. Thus, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ features a $(\text{Ga}^{3+})_6(\text{Ge}1^{3+})_2\text{Se}_{14}$ double layer motif that runs parallel to the ab plane. On the other hand, the inter-atomic $(\text{Ge}1)^{3+}/(\text{Ga}^{3+})$ –Se distance of 2.35–2.41 Å is much shorter than the distance of $(\text{Ge}2)^{2+}$ –Se = 2.86 Å between adjacent double layers, convincing that the heat propagation is strongly restrained along the c axis direction perpendicular to the $(\text{Ga}^{3+})_6(\text{Ge}1^{3+})_2\text{Se}_{14}$ double layers. And $(\text{Ge}2)^{2+}$ transports less heat supported by the phonon density of states shown in Fig. 3b, where the phonon frequencies of $(\text{Ge}2)^{2+}$ locate at the higher frequency region than that of Ga^{3+} and

$(\text{Ge}1)^{3+}$. The isolated Cs atoms are strongly rattling within the spacious vacancies (with size up to 4.04 Å) evidenced by the lower lying Cs^+ phonon states. The Cs^+ highly localized at the lower frequency (Fig. 3b), greatly contributes to the ultralow lattice thermal conductivity of the compound. According to all analyses above, the structure complicity in $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ leads to the large lattice anharmonicity and the ultralow lattice thermal conductivity. The heat anisotropically propagates with much lower lattice thermal conductivity along the c direction that is perpendicular to the $(\text{Ga}^{3+})_6(\text{Ge}1^{3+})_2\text{Se}_{14}$ double layer. This is supported by the Slack model DFT thermodynamics calculations [57], κ_l (along c) < κ_l (along b) $\approx \kappa_l$ (along a) (Fig. 3c). Furthermore, the phonon mean free path l is roughly estimated according to the relationship $\kappa_l = C_v v_a l / 3$ by using the calculated lattice thermal conductivity κ_l along the a axis, the observed average sound velocity v_a , and the heat capacity at constant volume. The estimated small phonon mean free path (l) of 2.40 Å at 300 K is quite close to the bond length of $(\text{Ge}1)^{3+}$ –Se = 2.35 Å, and Ga–Se = 2.39 Å, indicating the $(\text{Ge}1)^{3+}_2\text{Se}_6$ dimer and $\text{Ga}^{3+}\text{Se}_4$ tetrahedron mainly contribute to the low lattice thermal conductivity in the ab plane. In short, the relatively large number of atoms in unit cell of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ (25 atoms per unit), small volume of the first Brillouin zone coupled with the unique rattling modes, large lattice anharmonicity, and structure complexity, are all responsible for the extremely low lattice thermal conductivity of the compound. Usually, glass exhibits the minimum thermal conductivity because the heat propagates by a random pathway through the sublattice of phonons rather than a smooth transport behavior as in a crystalline media. And the glass limit $\kappa_{\min}$ for the lattice thermal conductivity of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ can be estimated by using the measured longitudinal and transverse sound velocities based on the Cahill's formula [58],

$$\kappa_{\min} = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} \kappa_B V^{-2/3} (2\vartheta_s + \vartheta_l). \quad (7)$$

The Cahill estimation utilizes a summation of all sound modes with the associated sound speed. And the slight lower value of the glass limit, 0.43 W m^{−1} K^{−1}, implies an ultralow lattice thermal conductivity for $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$, and also the fact that the lattice vibration is the major contribution of the total thermal transport.

CONCLUSIONS

In summary, the synthesis, single crystal structure and thermal transport properties of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ were stu-

died. Single crystal diffraction data reveal that Ge with different valence states adopts $(\text{GeI})^{3+}_2\text{Se}_6$ dimer, or $(\text{Ge2})^{2+}\text{Se}_6$ octahedron, respectively. The thermal conductivity was measured to be $0.57\text{--}0.48\text{ W m}^{-1}\text{ K}^{-1}$ from 323 to 773 K, the lowest value among all the known Ge-containing compounds, approaching its glass limit according to the Cahill's formulation. The *ab initio* phonon dispersion and single crystal structure analyses reveal for the first time that the vibration uncoupling of Ge with different valence states hinders the effective thermal energy transport between the $(\text{GeI})^{3+}_2\text{Se}_6$ dimer and $(\text{Ge2})^{2+}\text{Se}_6$ octahedron. Such a previously unknown uncoupling, together with the well-known Cs-rattling feature lead to the ultralow thermal conductivity of $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$. In addition, we propose a structure factor $f_i = \frac{\sin(180-\beta) \times d_{\text{Ge-Q}}}{l_i}$ ($i = \text{A, B}$), with which a structure map of the $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ family is given, where if $f_A = \frac{\sqrt{3}}{3}$, compound adopts the $P\bar{3}m1$ symmetry, if $f_B = \frac{\sqrt{3}}{3}$, the $R\bar{3}m$ space group will be adopted.

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Supplementary information Details of crystallography data, TG and DSC, detailed XRD patterns and calculated band structures, photographs of crystals, XPS, Raman and UV-vis diffuse-reflectance spectra, electron localization function and EDS analyses are available in the online version.

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低热导率新机制— $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$ 中异价锗离子的振动弱耦合性

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摘要 热管理是电子器件小型化和功率密度提高的关键, 因此研究材料热输运性质及声子传输机制具有非常重要的意义. 本文报道了一例含多价态锗(Ge^{3+} , Ge^{2+})的新型硒化物, $\text{Cs}_2\text{Ge}_3\text{Ga}_6\text{Se}_{14}$. 单晶结构衍射数据表明, 化合物中不同价态锗分别采用 $(\text{Ge}^{3+})_2\text{Se}_6$ 二聚体或 $(\text{Ge}^{2+})\text{Se}_6$ 八面体的配位模式, 323–773 K范围内, 其热导率测试值为 $0.57\text{--}0.48\text{ W m}^{-1}\text{ K}^{-1}$, 该值是目前已知含锗固体材料中的最低值, 接近其玻璃态极限值. 更重要的是, 我们发现由于不同价态锗离子振动模式之间存在弱耦合性, 使得热振动能量无法在两种结构单元之间有效传递, 从而降低了化合物热导率. 这种机制在材料热导率研究领域尚属首次发现. 本文还通过结构因子 $f_i = \sin(180^\circ - \beta) \times d_{\text{Ge-O}}/l_i$ ($i=A, B$)的大小, 给出了 $\text{Cs}_2\text{Ge}_3\text{M}_6\text{Q}_{14}$ 家族的晶体结构分布规律.