Multiple valence bands convergence and strong phonon scattering lead to high thermoelectric performance in p-type PbSe

Thermoelectric generators enable the conversion of waste heat to electricity, which is an effective way to alleviate the global energy crisis. However, the inefficiency of thermoelectric materials is the main obstacle for realizing their widespread applications and thus developing materials with high thermoelectric performance is urgent. Here we show that multiple valence bands and strong phonon scattering can be realized simultaneously in p-type PbSe through the incorporation of AgInSe₂. The multiple valleys enable large weighted mobility, indicating enhanced electrical properties. Abundant nano-scale precipitates and dislocations result in strong phonon scattering and thus ultralow lattice thermal conductivity. Consequently, we achieve an exceptional \( ZT \) of ~ 1.9 at 873 K in p-type PbSe. This work demonstrates that a combination of band manipulation and microstructure engineering can be realized by tuning the composition, which is expected to be a general strategy for improving the thermoelectric performance in bulk materials.
The depletion of fossil fuels and the deteriorating environment motivate the human beings to find sustainable and clean energy solutions. Thermoelectric devices can be used in energy harvesting from waste heat or be utilized in refrigeration, which is favorable for raising energy efficiency, attracting widespread attention from around the world. The efficiency of thermoelectric devices is largely determined by the figure of merit $ZT$ of their constituent thermoelectric materials, $ZT = \frac{S^2 T}{\kappa L \sigma}$, where $S$ represents the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_L$ is the lattice thermal conductivity, and $T$ is the absolute temperature, respectively. However, decoupling the interdependence between electrical and thermal transport properties is a crucial but challenging issue for improving the thermoelectric performance of materials. To achieve good electrical properties, various strategies such as band convergence, band sharpening, band alignment, carrier mobility optimization and resonant states introduction were adopted. On the other hand, materials with disordered or complex crystal structure, giant anharmonicity, metavalent bonding, and lone pair electrons often exhibit intrinsic low lattice thermal conductivity, which are promising candidates for thermoelectric applications.

Moreover, the lattice thermal conductivity can be largely suppressed by microstructural engineering, including nanoscale precipitates, dislocations, grain boundaries, and all-scale hierarchical architectures. Therefore, a synergistic combination of electronic band modulation and microstructural engineering is expected to achieve advanced thermoelectric materials.

PbTe has long been used for mid-temperature power generation, whereas the scarcity of element Te makes it expensive for materials. Lead-telluride (PbTe) matrixes was pressed by microstructural engineering, including nanoscale PbSe-Na precipitates, dislocations, grain boundaries, and all-scale hierarchical architectures. Therefore, a synergistic combination of electronic band modulation and microstructural engineering is expected to achieve advanced thermoelectric materials.

The lattice thermal conductivity is another important parameter for the thermoelectric performance indicated by the quality factor $B = \frac{\mu W/\kappa_L}{\kappa_L}$, where $\mu W/\kappa_L$ is a good descriptor for the inherent electrical performance of materials. Multiple degenerate electronic bands enable large density-of-states effective mass $m^*$ without obvious effect on the carrier mobility $\mu W$. Indeed, the interplay of multiple bands enable large effective mass factor $\mu W$ and thus ultrahigh $ZT$.

However, the two-band convergence is much difficult to realize due to the large energy offset between the valence band maximum (L) and the secondary valence band maximum (Σ) in PbSe and to date only limited works can promote band convergence in PbSe and PbTe. It is more challenging to achieve multiple bands convergence in PbSe.

The lattice thermal conductivity is another important parameter for the thermoelectric performance indicated by the quality factor $B = \frac{\mu W/\kappa_L}{\kappa_L}$. The introduction of materials with low lattice thermal conductivity in MTe (M = Pb, Ge) matrixes was proved to be an effective method to manipulate their thermal transport properties. For example, the appearance of nano-dots in AgPb$_{0.95}$SbTe$_{2.1}$ (LAST) system is considered as the origin of their low lattice thermal conductivity and thus the enhanced thermoelectric performance. Interestingly, the electrical properties of materials can also be optimized in a similar way, such as in PbTe-AgInTe$_2$ (LIST) and SnTe-AgInTe$_2$. These enhanced properties motivate us to search strategies for optimizing the $\mu W$ and $\kappa_L$ simultaneously.

In this work, beyond the two-band convergence between the L and Σ bands, we found that a third valence band Δ with a degeneracy $N_v = 8$ could be activated (Fig. 1a) through the incorporation of AgInSe$_2$ in the PbSe matrix doped with 2% Na (LISS). This three-band convergence tendency enables large weighted mobility. Additionally, local structure analysis by the x-ray absorption fine structure (XAFS) spectra indicates that about 80% of Ag and In atoms form AgInSe$_2$ in the system.

Interestingly, AgInSe$_2$ is also a good thermoelectric material with intrinsic ultralow lattice thermal conductivity. Nanoscale AgInSe$_2$ precipitates are revealed by the transmission electron microscopy (TEM), causing strong phonon scattering and hence resulting in ultralow lattice thermal conductivity. Therefore, a synergistic optimization of $\mu W$ and $\kappa_L$ is realized. As a consequence, an exceptional high $ZT \approx 1.9$ is achieved at 873 K, which is much better than the single-band and two-band activated p-type PbSe-based materials.

Results

Crystal structure. The LISS compounds crystallize in cubic structure (Space group, Fm-3m), which is reflected by the x-ray diffraction (XRD) measurements. The diffraction patterns can be indexed on the basis of cubic PbSe and no secondary phase is observed within the instrumental detection limit. The diffraction peaks tend to shift to higher angles with increment of AgInSe$_2$. Therefore, the lattice parameter ($a$) slightly decreases with increasing AgInSe$_2$ content (Fig. 2c), which may be attributed to the smaller atomic radius of Ag and In compared with that of Pb. This phenomenon also demonstrates that the AgInSe$_2$ is incorporated in the Pb$_{0.98}$Na$_{0.02}$Se matrix.

Electrical transport properties. The continuous decrease of the electrical conductivity with increasing temperature indicates a degenerate semiconducting property for LISS samples (Fig. 3a). Additionally, the electrical conductivity is suppressed significantly after the introduction of AgInSe$_2$. The electrical conductivity of Pb$_{0.98}$Na$_{0.02}$Se is as large as 3848 S/cm at room temperature, which declines to 774 S/cm for Pb$_{0.98}$Na$_{0.02}$Se–2.15% AgInSe$_2$ sample. To uncover this behavior, room temperature Hall measurements were performed. Obviously, the carrier concentration is reduced largely with increasing AgInSe$_2$ (Supplementary Fig. 1a), explaining the depressed electrical conductivity. The reduction of carrier concentration may be due to the formation of In$_{99}$ defects. These In$_{99}$ defects are shallow donors in PbSe, which will counteract with holes.

The Seebeck coefficient increases with elevated temperature for all samples and no saturate peak appears (Fig. 3b), demonstrating that no obvious bipolar effect occurs at high temperatures. The Seebeck coefficient is largely enhanced over the whole temperature range with the increment of AgInSe$_2$. Typically, the Seebeck coefficient of Pb$_{0.98}$Na$_{0.02}$Se is only 19.2 μV/K at room temperature.
Fig. 2 Crystal structure and bandgap. a Schematic crystal structure of Pb$_{0.98}$Na$_{0.02}$Se$_{1-x}$% AgInSe$_2$ (LISS). b Powder XRD patterns of LISS. c Refined lattice constants of LISS. d Room temperature infrared spectra for PbSe$_{1-x}$% AgInSe$_2$ and Pb$_{0.98}$Na$_{0.02}$Se$_{1-x}$% AgInSe$_2$.

Fig. 3 Electrical properties as a function of temperature for Pb$_{0.98}$Na$_{0.02}$Se$_{1-x}$% AgInSe$_2$ (LISS) compounds. a Electrical conductivity. b Seebeck coefficient. c Power factor. d Weighted mobility. The hollow circles in d represent the weighted mobility of single-band and two-band PbSe-based materials.
whereas a much larger Seebeck coefficient value of 116 μV/K is achieved for Pb_{0.98}Na_{0.02}Se sample. The dramatically promoted Seebeck coefficients will facilitate the enhancement of power factor (PF). Indeed, the PF have an apparent improvement especially at the 300–600 K temperature range for all doped samples (Fig. 3c). The room temperature PF value of Pb_{0.98}Na_{0.02}Se is only ~1.4 μW cm⁻¹ K⁻². In sharp contrast, the room temperature PF increases to ~11.1 μW cm⁻¹ K⁻² when x = 2.1 and this value is continuously improved to ~15.6 μW cm⁻¹ K⁻² at 423 K (Fig. 3c).

To understand the nature of the improvement of Seebeck coefficient, the relationship of Seebeck coefficient as a function of carrier concentration (Pisarenko curve) was compared at room temperature (Fig. 4a). Generally, the Seebeck coefficient increases with decreasing carrier concentration. However, the Seebeck coefficient is largely departure from the theoretical values estimated by the single parabolic band (SPB) model, which with decreasing carrier concentration (Pisarenko curve) was compared at room temperature (Fig. 4a). The solid black line is calculated assuming $m^* = 0.44 m_e$ and the purple line represents the result assuming $m^* = 0.81 m_e$ within the SPB model. The gray circles show the Pisarenko plot for Na-doped PbSe reported by Wang et al.50. Hall carrier mobility ($\mu_H$) versus Hall carrier concentration ($n_H$) at 303 K.

The electronic band structures of Ag and In doped PbSe were calculated (Supplementary Fig. 2a, b) to understand their roles in band manipulation. The Ag-doping and In-doping reflect p-type and n-type doping effect, respectively, which are consistent with previous experimental results42,43. Additionally, In-doping has a more important effect on decreasing energy offset ($\Delta E_{1-2}$) compared with the Ag-doping (Supplementary Fig. 2c), while Ag-doping plays a major role in enlarging the bandgap (Supplementary Fig. 2d). The orbital projected band structures reveal that the interaction between Pb-p and Te-p (Se-p in our case) to provide the molecular bonding mechanism (metavalent bonding). For a perfect half-filled p-band, the energy band structures resemble a metallic system. Yet, the bandgap opens due to a small Peierls distortion or charge transfer41. It is the charge transfer between Pb and Se that opens a small bandgap in PbSe given its perfect octahedral arrangements. DFT results show that the enlarged bandgap is mainly attributed to the incorporation of Ag. The electronegativity difference between Ag and Se (~0.62) is larger than that between Pb and Se (~0.22). Therefore, the substitution of Ag at Pb sites will strengthen the charge transfer between cation and anion, leading to an enlarged bandgap. Interestingly, the bandgap is further enlarged to ~0.38 eV with Na doping (Fig. 2d). In addition, the L band is flattened. The sharp peaks reflected in the density of states (DOS) for valence band also reveal the band flattening character (Fig. 5b). Simultaneously, the $\Sigma$ band is elevated and hence the energy offset ($\Delta E_{1-2}$) between L and $\Sigma$ band is shortened. Surprisingly, a third valence band at the $\Lambda$ point is activated and it remains at the same energy level compared with the $\Sigma$ band (Fig. 5a). These multiple valence bands enable large effective mass without significant affect the carrier mobility, which is the origin of enhanced Seebeck coefficient and the weighted mobility ($\mu_H$).

The lattice parameters extracted from the temperature-dependent synchrotron radiation x-ray diffraction (SR-XRD) patterns (Supplementary Fig. 4), we calculated the band structures as a function of temperature (Fig. 5c and Supplementary Fig. 5). Clearly, the bandgap increases with rising temperature, which is also verified experimentally (Fig. 5d). As revealed by Brod et al.44, there is sufficient interaction between Pb-p and Te-p (Se-p in our case) to provide the molecular bonding mechanism as PbSe.

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Fig. 4 Pisarenko plot and Hall carrier mobility. a Pisarenko plot of Seebeck coefficients as a function of Hall carrier concentration ($n_H$) for Pb_{0.98}Na_{0.02}Se sample. The solid black line is calculated assuming $m^* = 0.44 m_e$ and the purple line represents the result assuming $m^* = 0.81 m_e$ within the SPB model. The gray circles show the Pisarenko plot for Na-doped PbSe reported by Wang et al.50. Hall carrier mobility ($\mu_H$) versus Hall carrier concentration ($n_H$) at 303 K.
orbits with the proper s-type symmetry to place the VBM at L point. The weak s-p hybridization is a small addition to this effect. The thermal expansion will lead to a reduction of orbital overlap between p-orbitals as well as a weakened s-p hybridization. As a result, the energy of VBM (L point) in the electronic band structure decreases, resulting in an enlarged bandgap ($E_g$). The unobvious increase tendency of bandgap above ~500 K may be attributed to the band convergence, where the heavy valence bands dominate and the position of heavy valence bands are almost temperature independent. The theoretical bandgap is smaller than the experimental result, which may be attribute to the neglect of the effect of thermal disorder on the bandgap in our calculations. Moreover, the energy offset ($\Delta E_{1,2}$) between L and $\Sigma$ bands decreases with increasing temperature (Fig. 5e). Interestingly, the energy offset ($\Delta E_{1,3}$) between L and $\Lambda$ also shows a decline tendency with rising temperature and its value is even smaller than $\Delta E_{1,2}$ in the whole temperature range (Fig. 5e). The convergence tendency and the involvement of the third valence band is also reflected in the DOS corresponding to the valence band increases with increasing temperature (Fig. 5f). This convergence behavior is experimentally verified via Hall measurements, in which a maximum Hall coefficient ($R_H$) is observed and it is a sign of band convergence of the multi-valence bands. Consequently, the effective mass ($m^*$) of Pb$_{27}$Se$_{27}$ increases from 0.73 to 2.16$ m_e$ with rising temperature, which is much higher than the $m^*$ of single Na-doped PbSe (Supplementary Fig. 6b).

**Thermal transport properties and the dimensionless figure-of-merit (ZT).** Thermal conductivity is another important parameter for thermoelectric performance. The total thermal conductivity ($\kappa_{tot}$) decreases significantly with increasing AgInSe$_2$ (Fig. 6a). The $\kappa_{tot}$ is a sum of lattice thermal conductivity ($\kappa_L$) and electronic thermal conductivity ($\kappa_e$). The $\kappa_L$ was calculated by the Wiedemann-Franz relation, $\kappa_L = L \rho T$, where $L$ (Supplementary Fig. 7a) is estimated by SPB model assuming acoustic phonon
scattering dominates (Supplementary Fig. 6c). The $\kappa_L$ decreases remarkably with doping due to largely depressed electrical conductivity (Supplementary Fig. 7b). Furthermore, the $\kappa_L$ is obtained by subtracting the electronic contribution from the total thermal conductivity (Fig. 6b). Similarly, the $\kappa_L$ is largely suppressed with doping and the room temperature $\kappa_L$ values are much lower than the theoretical estimation by the Callaway model (Fig. 6b, inset). In addition, the $\kappa_L$ decreases with rising temperature and a clear departure from $T^{-1}$ relation is observed, demonstrating that the strong phonon scattering occurs. To further uncover the mechanism of the reduction of $\kappa_L$, sound velocities were measured for all the samples at room temperature (Supplementary Table 1). Interestingly, the average sound velocity ($v_{avg}$) slightly increases after doping (Fig. 6c). The deduced Grüneisen parameters ($\gamma$) and bulk modulus ($K$) of LISS have no obvious change (Supplementary Table 1). The lattice thermal conductivity can be expressed as $\kappa_L = \frac{1}{2} C v_{avg}^2 \tau$ based on the simple kinetic theory51, where $C$ is the specific heat, $\tau$ is the phonon lifetime. Here, the $v_{avg}$ increases upon doping and thus the reduction of lattice thermal conductivity should be derived from the decrease of phonon lifetime. In another word, enhanced phonon scattering is the main origin of the largely suppressed lattice thermal conductivity.

Thanks to the complex band structure behavior and strong phonon scattering with the introduction of AgInSe$_2$, the ZT is largely enhanced in the whole temperature range and a maximum ZT value of ~1.9 is achieved at 873 K for Pb$_{0.98}$Na$_{0.02}$Se$_{1-x}$% AgInSe$_2$ (LISS) compounds (Fig. 6d). The high thermoelectric properties of LISS samples are reproducible (Supplementary Fig. 8).

**Microstructure and local structure analysis.** The TEM images of LISS sample display that abundant nanoscale precipitates are embedded in PbSe matrix (Fig. 7a, b). In addition, strip-like dislocations are also observed (circled regions in Fig. 7a). Both nanoscale precipitates and multi-scale dislocations are effective phonon scattering centers52. The annular dark-field scanning transmission electron microscopy (STEM) image and the energy dispersive x-ray spectroscopy (EDS) elemental mappings exhibit obvious Ag-rich and In-rich patterns for the precipitates (Supplementary Fig. 9). Accordingly, the elemental distributions of Se and Na are relatively homogeneous in the entire area, whereas Pb-poor regions are observed within the precipitates (Supplementary Fig. 9). A clearer microstructural feature of the precipitate is revealed by performing HRTEM (Fig. 7c). The corresponding selected area electron diffraction pattern indicate a main cubic structure along [111], whereas the precipitates shows a different crystal structure from the PbSe matrix as another series of diffraction spots are exhibited which can be indexed to AgInSe$_2$ (Fig. 7d). The high angle annular dark field (HAADF) patterns show that the tetragonal AgInSe$_2$ is perfectly inserted in the cubic PbSe matrix as a nine-atom grid (Fig. 7e). We can also observe lattice dislocation in the HAADF (Fig. 7f). The lattice mismatch induced by precipitates and dislocations will introduce large strain fluctuations and thus enhance the phonon scattering53. Therefore, the lattice thermal conductivity of LISS was largely reduced to its amorphous limit of 0.31 Wm$^{-1}$K$^{-1}$ at 873 K arising from the strong phonon scattering.

Understanding the atomic occupation of doping elements in the crystal lattice allow us elucidate their roles on manipulating the thermal or electrical transport properties. The XAFS spectroscopy is a powerful tool to investigate the local structure in materials54–59. Here, we performed XAFS measurements for PbSe, AgInSe$_2$ and LISS, respectively. The x-ray absorption near-edge structure (XANES) of Se K-edge and Pb L$_3$-edge do not show any change after the introduction of AgInSe$_2$ in PbSe.
Supplementary Fig. 10), demonstrating a steady PbSe cubic matrix, which is well consistent with the XRD patterns. There are four main features in the XANES of In K-edge of LISS (Fig. 7g), in which 1, 3, 4 features can well reflected in the In K-edge of AgInSe2, indicating that the most of In atoms may form AgInSe2 in the system. Furthermore, we calculated the XANES spectra of In K-edge for Pb0.98Na0.02Se assuming that In occupies the Pb site, in which the peak B is well corresponding with the feature 2 of In K-edge of LISS. Moreover, after adding the second shell (12 Pb atoms) as shown by the 19-atoms cluster calculation (Fig. 7h), the feature B is well reflected and the calculation is almost convergent. Therefore, the origin of feature 2 is mainly arising from the multiple scattering of the photoelectrons by the second shell of Pb atoms in the PbSe matrix. The linear combination fitting (LCF) was used to evaluate the atomic occupied ratio of In atoms in each standards (Supplementary Table 2), causing strong phonon scattering.

Discussion
In summary, a combined effect of three activated valence bands and strong phonon scattering is realized via introducing AgInSe2 in Pb0.98Na0.02Se matrix. These multiple valence bands convergence enable the enhancement of thermoelectric power factor at low temperature region and maintain at a high level at elevated temperature. Interestingly, local structure studies by XANES reveal that most of Ag or In atoms form AgInSe2 secondary phase. The numerous nanoscale AgInSe2 precipitates and multi-scale dislocations observed in the TEM will cause strong phonon scattering. Therefore, the lattice thermal conductivity is largely depressed. As a consequence, a distinguished dimensionless figure-of-merit ZT of ~1.9 is achieved at 873 K, which is among the best bulk thermoelectric materials. This work proves that multiple valence bands could be activated in p-type PbSe and highlights the strong phonon scattering effect through the introduction of secondary phase with ultralow thermal conductivity, which guide a promising route to achieve excellent thermoelectric performance in bulk materials. The quantitative atomic occupation of doping elements provides a microscopic perspective to understand their role on manipulating transport properties. It is expected that more advanced thermoelectric materials can be achieved by employing the present strategy.

Methods
Synthesis. High-purity starting materials, Pb (99.999%), Se (99.999%), Na (99.9%), Ag (99.99%), In (99.9%) were weighted in stoichiometric ratio (Pb0.98Na0.02Se−x% AgInSe2) and loaded in carbon coating silica tubes under a N2-filled glove box. The silica tubes were sealed under vacuum and then slowly heated to 1423 K in 24 h, soaked at this temperature for 10 h and followed by furnace cooling down to room temperature. The obtained ingots were grounded into powders and then
Thermoelectric property measurements. The bulk samples were cut into rectangular solids (3 × 3 × 10 mm³) and square pieces (10 × 10 × 1 mm³) for electrical transport properties measurements, respectively. The Seebeck coefficients and electrical conductivities were measured using the Uvacc Riko ZEM-3 instrument. We calculated the thermal conductivity using the equation of

\[ \kappa_T = D \cdot \tau \cdot \rho, \]

where the thermal diffusivity (D) was determined using a laser flash method by the Netzsch LFA 457 facility, the heat capacity (Cp) was estimated using an empirical equation (Cp/\text{atom} = 1.306 \times 4.7 \times 10^{-4} (\text{JK}^{-1} \cdot \text{mol}^{-1}), and the sample density is calculated by the dimensions and mass of the samples. The combined uncertainty of all measurements for determining the ZT is less than 20%.

Characterizations. Room temperature powder XRD measurements were conducted using a D/MAX 2500 PC system with Cu Kα radiation. High-temperature SR-XRD patterns were performed for Pb0.87Na0.13Se–2% AglnSe2 at the BL14B1 beamline of Shanghai synchrotron radiation facility. The wavelength of the x-ray is 0.6887 Å. The sample was heated from 300 K to 875 K at a rate of 5 K min⁻¹. The bandgap was measured using the Shimadzu Model UV-3600 Plus instrument and was estimated by the Kubelka-Munk equation. Pulse-echo method was used to measure the speed of sound and the waveforms were recorded using a Tektronix TBS 1102 oscilloscope. The Hall coefficient (R_H) was conducted by the Van der Pauw method using the Lake Shore 8400 Series. STEM and TEM were performed using a JEOL ARM200F equipped with cold field emission gun and ASCOR probe corrector. More details can be found in the Supporting Information.

First-principles calculations. Density functional theory calculations were performed using the projector-augmented wave method, as implemented in the Vienna Ab initio Simulation Package. We utilized the revised Perdew-Burke-Ernzerhof generalized gradient approximation to estimate the exchange-correlation interactions. A cutoff energy was set to 450 eV for the plane-wave expansion of the electron density and the Monkhorst-Pack k-point sampling 0.1 Å⁻¹ was used within all the calculations. The atomic positions were fully relaxed when the maximum residual ionic force accumulated current during the experiment. The Si (311) double-crystal monochromator was used for tuning the monochromatic beam. We measured the XAFS of Ag K-edge and In K-edge for AglnSe2 in transmission mode. The XAFS measurements of Se K-edge and Pb L₁-edge for PbSe and Pb0.87Na0.13Se–2% AglnSe2 were conducted in transmission mode, while the measurements of Ag K-edge and In K-edge for Pb0.87Na0.13Se–2% AglnSe2 were performed in fluorescence mode using 19-element Ge solid-state detector. All experimental XAFS spectra were preprocessed using the IFEFFIT package.

XAFS calculation and analysis. The x-ray absorption near-edge structure (XANES) calculations of Ag K-edge for Ag-doped PbSe and In K-edge for In-doped PbSe were performed based on the full multiple scattering (EMS) theory using FEFF9 program. We use self-consistent field (SCF) method to estimate the atomic scattering potential. To investigate the doping site of Ag or In in PbSe, we simply replace the central Pb absorber with Ag or In atom while maintaining the coordinates. To achieve good convergence, the cluster radius for SCF and EMS was fixed as 8 and 10 Å, respectively. LCF of In K-edge for Pb0.87Na0.13Se–2% AglnSe2 was performed using the Athena software assuming that the XANES of In K-edge of AglnSe2 and In-doped PbSe as the standards. A similar LCF analysis was applied for the XANES of Ag K-edge of Pb0.87Na0.13Se–2% AglnSe2. Since we cannot ensure that the Ag or In atoms totally occupy the Pb site in PbSe matrix without formation of impurity phases, we thus used the calculated XANES as one of standards in the LCF analysis.

Reporting summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. All of the other data are available from the authors upon reasonable request.

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Acknowledgements
The authors thank BL14U at Shanghai synchrotron radiation facility (SSRF) for the SR-XRD measurements. We thank BL01B1 at Spring-8 for the XAFS experiments (Proposal Number: 2021B1109). This work was supported by National Key Research and Development Program of China (2018YFA0702100 and 2018YFB0703600), National Natural Science Foundation of China (51772012, 52002042 and 52020011), National Postdoctoral Program for Innovative Talents (BX20200028), the Beijing Natural Science Foundation (QJ18004), and 111 Project (B17002). L.-D.Z. appreciates the support of the high-performance computing (HPC) resources at Beihang University, the National Science Fund for Distinguished Young Scholars (51925101), and center for High Pressure Science and Technology Advanced Research (HPSTAR) for TEM measurements.

Author contributions
Y.Z. and L.-D.Z. prepared the samples, carried out the experiments, analyzed the results and wrote the paper. T.H. and X.G. performed the TEM experiments. D.W. carried out the DFT calculations. Y.Z., L.H. and T.I. conducted the XAFS measurements and analyzed the data. S.Z., B.Q., H.S. and L.S. performed the SR-XRD experiments. All authors coedited the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-31939-4.

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Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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