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Abstract: Lead-free halide double perovskites with diverse electronic structures and optical responses, as well as superior material stability show great promise for a range of optoelectronic applications. However, their large bandgaps (generally above 2 eV) limit their applications in visible light range such as solar cells. In this work, we demonstrate an efficient temperature-derived band gap modulation, i.e., an exotic fully reversible thermochromism in both single crystals and thin films of Cs₂AgBiBr₆ double perovskites. Along with the thermochromism, we observe temperature dependent changes of bond lengths of Ag-Br ($R_{\text{Ag-Br}}$) and Bi-Br ($R_{\text{Bi-Br}}$). Our first-principle molecular dynamics simulations reveal substantial anharmonic fluctuations of the $R_{\text{Ag-Br}}$ and $R_{\text{Bi-Br}}$ at high temperatures. The synergy of

anharmonic fluctuations and associated electron-phonon coupling, and the peculiar spin-orbit coupling effect, is responsible for the thermochromism. In addition, the intrinsic bandgap of $\text{Cs}_2\text{AgBiBr}_6$ shows negligible changes after repeated heating/cooling cycles under ambient conditions, indicating excellent thermal and environmental stability. Our work demonstrates a stable thermochromic lead-free double perovskite which has great potential in the applications of smart windows and temperature sensors. Moreover, our findings on the structure modulation-induced bandgap narrowing of $\text{Cs}_2\text{AgBiBr}_6$ provide new insights for the further development of optoelectronic devices based on the lead-free halide double perovskites.

1. Introduction

Low-cost solution-processed lead (Pb) halide perovskites with superior electronic and optical properties have shown great promise on the applications of various devices, including solar cells,^[1-3] light-emitting diodes,^[4,5] photodetectors,^[6] lasers,^[7] memories,^[8] transistors,^[9] and piezoelectric energy generators.^[10] By applying external control knobs such as chemical doping,^[11] alloying,^[12] dimensional reduction,^[13] pressure,^[14] etc., their electronic and optical properties exhibit a wide range of tunability, providing new opportunities to further broaden their application field and improve the device performance. Among the control knobs, temperature, as a basic variable in material science, is relatively less explored for Pb halide perovskites. Temperature is known to cause lattice thermal expansion and modify carrier-phonon and phonon-phonon interactions, which may lead to electronic structure renormalization and changes of optical properties. However, in Pb halide perovskites, only phase transitions (from orthorhombic, tetragonal to cubic phases) were identified with increasing temperature, with the corresponding changes in optical spectra reported.^[15-17] The fact that temperature is less explored in this case may partially be ascribed to thermal instability of the organic-inorganic hybrid halide perovskites.^[18] Quite recently, based on all-inorganic caesium Pb halide perovskites with enhanced thermal stability, the temperature-

induced phase transition was exploited to realize smart photovoltaic windows with switchable states between transparent (for light transmission) and highly absorbing dark films (for light absorption).^[19]

To remedy the Pb toxicity and material instability issues of Pb halide perovskites, the halide perovskites community has expanded research interest to Pb-free halide double perovskites formed through hetero-substitution of Pb^{2+} .^[20-22] This new family of Pb-free halide perovskites (represented by $\text{Cs}_2\text{AgBiBr}_6$) demonstrate diverse electronic structures and optical responses, superior material stability, and large combinatorial space of candidate materials.^[20-25] Compared with the Pb halide perovskites, Pb-free halide double perovskites usually exhibit relatively large bandgaps (above 2 eV).^[22,23] As a result, their optoelectronic applications in visible light range such as solar cells are limited so far. It is thus desired to reduce their band gaps through proper structural modulation, making them feasible for visible-light applications. Along this direction, suitable impurities doping has been employed to achieve visible-light response in $\text{Cs}_2\text{AgBiBr}_6$ ^[26] and $\text{Cs}_2\text{AgInCl}_6$.^[27] In addition, by applying high pressure, a bandgap narrowing phenomenon (from original 2.3 eV down to 1.7 eV) was reported in $\text{Cs}_2\text{AgBiBr}_6$ single crystal.^[28]

Herein, we investigate temperature dependence of structural and optical properties of halide double perovskite $\text{Cs}_2\text{AgBiBr}_6$, and discover a reversible temperature-derived band gap change, *i.e.* an exotic thermochromic behaviour. The reversible thermochromism is robustly found in both single crystals (SCs) and thin films (TFs) under thermal cycling. Combining experimental characterizations and first-principles molecular dynamics simulations, we revealed the significant changes and anharmonic fluctuations of the bond lengths of Ag-Br and Bi-Br at high temperatures. The physical mechanism underlying the thermochromism was attributed to the peculiar interplay between the strong electron-phonon coupling, the spin-orbit coupling effect, and the temperature-induced renormalization of the phonons mediating band-gap transitions.

2. Results and discussion

The $\text{Cs}_2\text{AgBiBr}_6$ double perovskite single crystals were synthesized following the reported procedure.^[29,30] To prepare high quality $\text{Cs}_2\text{AgBiBr}_6$ thin films, 0.55M of $\text{Cs}_2\text{AgBiBr}_6$ crystal solution (dimethyl sulfoxide as solvent) preheated to 50 °C was deposited onto the quartz substrate. The films were annealed at 280 °C for 5 min to obtain good crystallization. From the scanning electron microscopy (SEM) images shown in **Figure 1a** and **1b**, we observe homogeneous and smooth double perovskite films composed of closely packed crystalline grains with dimensions ranging from 200 to 600 nm. The surface roughness (R_q) derived from the atomic force microscopy (AFM) image is ~18 nm (Figure 1c). In addition, as depicted in Figure 1d, the X-ray diffraction peaks of TFs matches well with those of the SCs.

We investigate the changes of the optical properties of $\text{Cs}_2\text{AgBiBr}_6$ SCs and TFs from room-temperature (RT) to 250 °C and show the optical images at different temperatures in **Figure 2a**. We observe obvious thermochromic phenomenon of the samples under elevated temperatures. With increasing temperature from RT to 250 °C, the colour of the SCs changes from red to black and that of the thin film changes from yellow to red. The SCs and TFs return to their original colour after cooling, indicating that the thermochromic behaviour of the $\text{Cs}_2\text{AgBiBr}_6$ double perovskite is fully reversible. The absorption spectra of SCs and TFs at different temperatures are presented in Figure 2b and 2c. At RT, the SC sample exhibits an absorption edge at 650 nm and the TF sample shows an absorption edge at 550 nm, both in good agreement with the literatures on $\text{Cs}_2\text{AgBiBr}_6$ double perovskites.^[29,30] The absorption spectrum expansion from the TFs to SCs has also been observed in methylammonium lead triiodide (MAPbI_3) samples and attributed to thickness difference between SCs and TFs.³¹ With increasing the temperature from the RT to 150 °C, the absorption edge shows gradual red-shift with obvious bandgap narrowing for both SCs and TFs. This bandgap narrowing is consistent with the observed colour change at different temperatures.

In addition, the double perovskites show excellent stability, without any decomposition after storing either in the air (30–50% humidity) for 90 days or irradiated with a white LED lamp (0.75 sun) under N₂ for 30 days (Figure S1). The stability of the samples has been further confirmed by measuring the absorption spectra over repeated heating/cooling cycles (Figure S2), which show negligible degradation after repeated heating/cooling cycles for both SCs and TFs. The excellent stability is further confirmed by the temperature dependence of the XRD patterns (Figure S3), which show negligible changes after repeated five heating/cooling cycles. The excellent reversibility and superior materials stability make the double perovskites promising candidates for potential applications in long-period reversible smart windows, temperature sensors and visual thermometers. For practical smart window applications, we note that it is important to decrease the thermochromic temperature (below 100 °C) through further materials engineering.

In order to understand the mechanisms of the thermochromism in Cs₂AgBiBr₆ double perovskites, we perform temperature-dependent single-crystal X-ray diffraction (SXRD) measurements of the SCs. The crystal structures of Cs₂AgBiBr₆ were determined at eight temperatures between 25 and 200 °C (Table S1). Cs₂AgBiBr₆ crystallizes in cubic space group *Fm*-3m (No. 225) at room temperature (RT, 25 °C), and shows a typical double-perovskite structure with alternating AgBr₆ and BiBr₆ octahedra (**Figure 3a**). The counter ion Cs⁺ occupies the centre of four AgBr₆ and BiBr₆ octahedra units. Figure 3b displays a perfect three-dimensional packing structure of Cs₂AgBiBr₆, where only two different bonds exist in the crystal due to its high symmetry. Upon heating from RT to 200 °C, the Ag-Br bond length elongates obviously from 2.809 to 2.829 Å, while the Bi-Br bond length shows less change from 2.826 to 2.835 Å (schematically illustrated in Figure S4). Interestingly, extrapolating the temperature-dependent Ag-Br and Bi-Br bond lengths results in a crossing point at ~ 285 °C, which is close to the optimal annealing temperature for the fabrication of high-quality films.³⁰

At this stage, we are not sure whether it is coincidence or if there is any underlying connection between the equal bond lengths and optimised annealing temperature.

Based on the SXRD measurements, we also calculate the cell parameters and volumes of $\text{Cs}_2\text{AgBiBr}_6$ double perovskites at different temperatures (Figure 3d). A linear increase of the volume from the RT to 200 °C indicates thermal-induced lattice expansion, which is further confirmed by the temperature-dependent Powder X-ray diffraction (PXRD) measurements of SCs under various temperatures. For example, a close look at the PXRD data (Figure S5) indicates that the reflection peaks of (2 2 0) and (4 0 0) in SCs regularly shift towards the low angle side with increasing the temperature from 30 °C to 250 °C (Figure 3e and 3f). The gradual lattice expansion with increasing temperature is also consistent with differential scanning calorimeter (DSC) measurements, which show no thermal anomaly in temperature range of 25-250 °C (Figure S6). The fact that the lattice expansion alone, without any structural phase transition takes place with increasing temperature explains the excellent reversibility of the thermochromism in the double perovskites.

The changes of the bond lengths are further investigated by characterizing the Raman spectroscopy of the samples (**Figure 4** and Figure S7) under different temperatures. The stretching vibrations of octahedral BiBr_6 and AgBr_6 locate at about 178 cm^{-1} , and these vibrational bands show $\sim 3\text{ cm}^{-1}$ red shift and decreased relative intensity during the heating process. In addition, the shape of this peak changes from asymmetry to symmetrical, which can be attributed to the closer bond length of Ag-Br and Bi-Br (Figure 3c) while heating. In addition, the peak position at $\sim 178\text{ cm}^{-1}$ recovered to the origin position without any degradation after one heating/cooling cycle (Figure 4b and 4c). The good recoverability on the Raman shift of the vibrations of octahedral BiBr_6 and AgBr_6 is consistent with the reversible thermochromism (Figure 2c). At the same time, another strong and broad peak locating at around 75 cm^{-1} , which is attributed to the bending frequency of $\delta_{(\text{Br-Bi-Br})}$ and $\delta_{(\text{Br-Ag-Br})}$, shows no obvious change under different temperatures. This behavior results from the

three-dimensional high symmetry framework of $\text{Cs}_2\text{AgBiBr}_6$; the fixed framework endowing the Br-Bi-Br and Br-Ag-Br have the same bend ability under different temperatures. In the Raman measurements, we also show excellent reversibility and stability of the double perovskites under the heating/cooling cycles in the temperature range of 25-250 °C (Figure 4b).

In order to reveal the physical mechanism underlying the thermochromism, we performed Ab-Initio Molecular Dynamics (AIMD) simulations that can provide atomic-scale description of temperature-dependent material structural properties. The simulations started from the $\text{Cs}_2\text{AgBiBr}_6$ structure at zero temperature and were carried out at room and high temperatures. Several sets of AIMD simulations at slightly different temperatures were performed for cross-checking. From our first set of AIMD simulations, we collect the distribution of the Bi-Br and Ag-Br bond lengths, $R_{\text{Bi-Br}}$ and $R_{\text{Ag-Br}}$. These distributions are represented using pair distribution functions (PDFs), $g(r)$, fitted by Gaussian functions (**Figure 5a**). The shape of the PDFs indicates that the Bi-Br and Ag-Br bond lengths fluctuates extensively. In particular, the Ag-Br PDF deviates substantially from a single Gaussian shape, suggesting substantial anharmonicity of the bond, even at room temperature (25 °C). This may have substantial impact on the electronic structure renormalization caused by the electron-phonon coupling, which deserves further investigation. The average Bi-Br and Ag-Br bond lengths from the AIMD simulations (Figure 5b) approach a common value with increasing temperature. This is in accord with the results from our temperature-dependent SXRD measurements (Figure 3).

From a second set of AIMD simulations we have extracted results on the temperature dependent electronic band structure of $\text{Cs}_2\text{AgBiBr}_6$, as described in the computational details section. In Figure 5c-d, we show the unfolded effective band structures,^[32] calculated at 27 °C and 227 °C including the spin-orbit coupling (SOC), , along with the zero-temperature band structure. One observes substantial broadening of the bands even at 27 °C. This implies the existence of strong electron-phonon coupling, which is consistent with the experimental

observation in Pb-based perovskites^[33] and Cs₂AgBiBr₆ double perovskites.^[34] This should be closely related to the substantial fluctuations of the metal-halide bond lengths, especially the Ag-Br bonds with significant anharmonic feature. The bands broadening effect becomes more pronounced at the high temperature of 227 °C. In particular, the conduction band edge at the Γ point is significantly broadened and shifted down, and the valence band edge at the Γ point is significantly shifted up. The similar effect occurs to the band edges at the L point. Such broadening of the bands at momentum points contributing to dipole-allowed transitions would have remarkable effect on light absorptions, although the band gap transition is indirect from the valence band maximum at X and conduction band minimum at L. This peculiarity can be predominately responsible for the observed thermochromism in Cs₂AgBiBr₆. It should be pointed out that the SOC effect plays an essential role in describing the temperature dependent electronic band structure. As shown in the density of states averaged from the AIMD simulations (Figure 5e), we observe a substantial downshift of the conduction band edge only when the SOC effect is included. Figure 5f shows the change of the averaged bandgap from 27 °C to 227 °C. There is a ~23 meV reduction of the bandgap without the SOC, while we obtain a ~66 meV reduction if the SOC is included. The mechanism underlying the crucial role of the SOC could partly be attributed to the Rashba-like band splitting as reported in Pb-based perovskites.^[35,36] Here, the Rashba-like splitting could be caused by the cooperative effect of the SOC and the temperature-induced increase of anharmonic nature of the metal-halide bonds of the double perovskite structure. Finally, we note that for the indirect-gap semiconductors such as Cs₂AgBiBr₆, the temperature-induced renormalization of the phonons that mediate the band-gap transitions may also modify the absorption profile and contribute to the observed thermochromism.

3. Conclusion

In summary, we observed a novel fully reversible thermochromism of lead-free $\text{Cs}_2\text{AgBiBr}_6$ halide double perovskites in the forms of both single crystals and thin films. Variable-temperature single-crystal X-ray diffraction, powder X-ray diffraction and Raman spectrum indicate the substantial change of bond lengths of Ag-Br and Bi-Br at different temperatures. Density functional theory finite-temperature molecular dynamics simulations indicate that the anharmonic fluctuations of the Ag-Br and Bi-Br bonds, strong electron-phonon coupling and the spin-orbit coupling effect are crucial factors for thermochromism. These properties pave the way for a new class of smart windows, temperature sensors and visual thermometers with an unprecedented working lifetime based on lead-free halide double perovskites. In addition, our result on bandgap narrowing of halide double perovskite provides new insights for broadening the optoelectronic applications based on the lead-free perovskites.

4. Experimental Section

Chemicals and Materials: All the chemicals used were purchased from Sigma-Aldrich without any further purification.

Preparation of $\text{Cs}_2\text{AgBiBr}_6$ crystals: Solid CsBr (213 mg, 1.00 mmol) and BiBr_3 (225 mg, 0.5 mmol) were dissolved in 3 mL of 47% HBr. Solid AgBr (94 mg, 0.5 mmol) was then added to the solution and transfer the mixture into a 25 cm³ Teflon-lined digestion bomb. The bomb was sealed and placed in the oven where it was heated to 120 °C for 24 h. After being slowly cooled to room temperature, red octahedral single crystals were achieved (yield ca. 79% based on Ag).

Double perovskite film fabrication: The perovskite solution was prepared by dissolving 292.0 mg $\text{Cs}_2\text{AgBiBr}_6$ crystals in dimethyl sulfoxide (0.5 mL, DMSO, 99.9 %, Sigma-Aldrich). After complete dissolution of the crystals, preheat the solution to 50 °C in case of using. 20 μL of the solution was spin-coated onto quartz at 3000 rpm for 60 s. The substrates were

subsequently annealed at 280 °C for 5 min in order to achieve high-quality films, both the spin-coating process and annealing temperature have been optimized.

Characterization: The general morphologies of the films were characterized by scanning electron microscopy (SEM, LEO 1550). The Atomic force microscope measurement was carried out using a Dimension 3100/NanoScope IV system equipped with a C-AFM module (Veeco, Bruker). The XRD patterns of the products were recorded with a X'Pert PRO X-ray diffractometer using Cu K α 1 irradiation ($\lambda = 1.5406 \text{ \AA}$). Variable temperature power X-ray diffraction (PXRD) data were collected using a Bruker D8 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the temperature ranges 25-250 °C. The temperature dependent optical images were taken at selected temperatures using a Leica DMRX polarizing optical microscope equipped with a hot stage. Variable temperature ultraviolet-visible spectroscopy was recorded using a PE Lambda 950 UV-vis spectrophotometer equipped with a heating ring in diffuse reflectance mode. Thermogravimetric (TG) experiments were performed with a STA449 F3 thermogravimetric analyzer in the range 30-700 °C at a warming rate of 10 °C min⁻¹ under a nitrogen atmosphere and the crystal samples were placed in an Al₂O₃ crucible. Differential scanning calorimetry (DSC) were carried out on a Q2000 V24.9 Build 121 instrumental in the temperature range of 60-280 °C with a rate of 20 °C·min⁻¹. Temperature dependent Raman spectra were conducted using a SPEX-1403 laser Raman spectrometer with a 532 nm laser line as an excitation source.

X-ray single crystallography: The single-crystal X-ray diffraction data for Cs₂AgBiBr₆ were collected at 298, 323, 348, 373, 398, 423, 448 and 473 K with graphite monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) on a CCD area detector (Bruker-SMART), respectively. Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. Structures were solved by a direct method using the SHELXL-97 software package.^[37] The non-hydrogen atoms were anisotropically refined using the full-matrix least-

squares method on F^2 . The details about data collection, structure refinement and crystallography are summarized in Table S1.

Computational details: Density functional theory based zero-temperature static calculations and finite-temperature Ab-Initio Molecular Dynamics (AIMD) simulations were performed by using the plane-wave projector augmented wave method^[38] as implemented in the Vienna Ab initio Simulation Package.^[39-41] In order to explicitly investigate effects of thermal vibrations on the electronic properties, we have performed two sets of AIMD simulations in the NVT ensemble for cross-checking. The first set of calculations was performed for the experimental lattice constants of $\text{Cs}_2\text{AgBiBr}_6$ at 25 and 200 °C. Perdew, Burke and Ernzerh of functional^[42] was employed to treat the exchange and correlation effects, and with the kinetic energy cutoff of 400 eV. The second set of simulations was carried out at the fixed volume corresponding to its experimental value at 27 °C, using the PBEsol exchange-correlation functional^[43] and 500 eV kinetic energy cutoff. For both sets of AIMD simulations 320 atoms supercells and Γ point sampling of the Brillouin Zone were used. In the first set of AIMD simulations, an about 1 ps canonical trajectory with a time step of 1 fs was generated using the Noé-Hoover thermostat. We then sampled 30 structures around 1 ps equilibration condition to extract the pair-distribution functions. The second AIMD simulation set was run for the longer time scale of ~5-7 ps. After a 1 ps equilibration period, we extracted 20 uncorrelated samples, for which we recalculated the electronic structure self-consistently using a refined 2x2x2 k-point grid, both including the spin orbit coupling (SOC) and without it. The temperature-dependent electronic density of states and bandgap were averaged from these 20 samples. The unfolded effective band structures were obtained using the eigenvalues mapping through supercell calculations via the BandUP code,^[32,44] and averaged over 3 samples at each temperature.

CCDC 1531091, 1588117 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) Low- and (b) high-magnification SEM images for double perovskite TFs on the quartz substrate. (c) A typical AFM image of TFs. (d) PXRD pattern of the prepared SCs and TFs, where the broad peak at $2\theta \approx 21^\circ$ is assigned to the diffraction of polycrystalline SiO_2 from the quartz substrate in TFs. The simulated XRD was obtained from software (Mercury) simulation by using the CIF file of $\text{Cs}_2\text{AgBiBr}_6$.

Figure 2. (a) Optical images of SCs and TFs at different temperatures for one heating-cooling cycle. (b) Ultraviolet-vis absorption spectra of SCs and TFs (c) at room temperature, 50 °C, 100 °C, 150 °C (RT-C, cooling to room temperature).

Figure 3. (a) Molecule structure and (b) packing structure of SCs in 25 °C. (c) Variation of Ag-Br and Bi-Br bond lengths measured at different temperatures. (d) Temperature dependent cell parameters of SCs *a*-axes and cell volume *V* in the temperature range of 25-200 °C. (e) temperature dependent reflections (2 2 0) and (f) (4 0 0) at the selected temperatures for SCs.

Figure 4. Raman spectra collected at selected temperatures, (a) heating process (b) cooling process. (c) Temperature dependence of $\nu_{\text{as}}(\text{Ag-Br})$ and $\nu_{\text{as}}(\text{Bi-Br})$ in the heating and cooling modes. (d) Comparison of Raman spectra after one heating/cooling cycle (C-25 °C, cooling to 25 °C).

Figure 5. Evolution of structural parameters and electronic structure with temperature from the AIMD simulations. (a) The pair distribution function $g(r)$ (fitted by Gaussian function) of Bi-Br (red lines) and Ag-Br (blue lines) atomic pairs at 25 °C (dash lines) and 200 °C (solid lines), respectively. (b) Fluctuation of the bond lengths of $R_{\text{Ag-Br}}$ and $R_{\text{Bi-Br}}$ (top panel), and the averaged bond length (bottom panel) at 25 °C and 200 °C. (c, d) Unfolded effective band structures including spin-orbit coupling (SOC) at 27 °C and 227 °C, respectively. The band structure at zero temperature is shown in black line. The color scale represents the weights of the unfolded bands, normalized to the interval [0, 1].^[32] (e) Electronic density of states, without (upper panel) and with (lower panel) SOC, at 27 °C to 227 °C. (f) Change of the bandgap with temperature.