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Authors

Lin, Jia
Chen, Hong
Gao, Yang
[et al.](#)

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Pressure Induced Semiconductor to Metal Phase Transition of a Charge-Ordered Indium Halide Perovskite

Jia Lin^{a,d,1}, Hong Chen^{a,b,h,1}, Yang Gao^{c,f,1}, Yao Cai^{c,f}, Jianbo Jin^a, Ahmed S. Etman^e, Jooheon Kang^{a,g,i,j,k}, Teng Lei^a, Zhenni Lin^{c,f}, Maria C. Folgueras^{c,f}, Li Na Quan^{a,f}, Qiao Kong^a, Matthew Sherburne^{a,f}, Mark Asta^{a,f}, Junliang Sun^e, Michael F. Toney^b, Junqiao Wu^{c,f,2}, and Peidong Yang^{a,c,f,g,2}

^aDepartment of Chemistry, University of California, Berkeley, CA 94720, USA;

^bStanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA; ^cDepartment of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA;

^dDepartment of Physics, Shanghai University of Electric Power, Shanghai 200090, China; ^eDepartment of Materials and Environmental Chemistry, Stockholm University, Stockholm SE - 10691, Sweden; ^fMaterials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA;

^gKavli Energy NanoScience Institute, Berkeley, CA 94720, USA; ^hSchool of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China; ⁱCenter for NanoMedicine, Institute for Basic Science, Seoul 34126, South Korea; ^jY-IBS Institute, Yonsei University, Seoul 34126, South Korea; and ^kSchool of Advanced Materials Science and Engineering, Sungkyunkwan University (SKKU), Suwon 16419, South Korea

¹J.L., H.C. and Y.G. contributed equally to this work.
²To whom correspondence may be addressed. E-mail: wuj@berkeley.edu or p_yang@berkeley.edu.

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Abstract

Phase transitions in halide perovskites triggered by external stimuli generate significantly different material properties, providing a great opportunity for broad applications. Here we demonstrate an In-based, charge-ordered ($\text{In}^+/\text{In}^{3+}$) inorganic halide perovskite with the composition of $\text{Cs}_2\text{In}(\text{I})\text{In}(\text{III})\text{Cl}_6$ in which a pressure-driven semiconductor to metal phase transition exists. The single crystals, synthesized *via* a solid-state reaction method, crystallize in a distorted perovskite structure with space group $I4/m$ with $a = 17.2604(12)$ Å, $c = 11.0113(16)$ Å if both the strong reflections and superstructures are considered. The supercell was further confirmed by rotation electron diffraction measurement. The pressure-induced semiconductor to metal phase transition was demonstrated by high-pressure Raman and absorbance spectroscopies and was consistent with theoretical modeling. This type of charge-ordered inorganic halide perovskite with a pressure-induced semiconductor to metal phase transition may inspire a range of potential applications.

Keywords: charge-ordered; inorganic; halide perovskite; phase transition; high-pressure

Significance statement

Metal halide perovskites attract great interest for a wide range of applications due to their remarkable optoelectronic properties. The development of new environmentally friendly halide perovskite materials with various crystal structures and compositions offers unprecedented opportunities to achieve desired properties and applications. In this work, we demonstrated an In-based, charge-ordered all-inorganic halide double perovskite with the composition of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ synthesized by solid-state reaction. High-pressure optical properties were studied, and a pressure-driven, fully reversible semiconductor-metal phase transition was discovered. This In-based charge-ordered structure may inspire new understanding of halide perovskite as well as provide a platform for future discovery of exotic electronic phenomena such as high- T_c superconductivity in halide perovskite compounds.

Introduction

Halide perovskites with ABX_3 structure (where A are the alkali elements, such as Cs^+ , Rb^+ , K^+ , $CH_3NH_3^+$ (MA^+), $HC(NH_2)_2^+$ (FA^+); B are Pb^{2+} , Sn^{2+} ; X = I^- , Br^- , Cl^-) are of great interest for a wide range of applications, such as photovoltaics, light-emitting diodes, photodetectors, and lasers, due to their remarkable optoelectronic properties (1-7). In addition, their ionic bonding nature with soft metal halide lattices allows abundant phase transition behaviors including lattice distortion, expansion, compression, and rearrangement under various external environmental conditions such as temperature, light, pressure, and electric/magnetic fields (8-13). This type of structural flexibility can lead to significant changes in their optical and electronic properties, and thus further potential opportunities including sensor, memory, and functional window applications (9, 14, 15).

Among the perovskite-type structure materials, spatially charge-ordered (or charge-disproportioned) oxide compounds at A or B site show unique properties, including high- T_c superconducting behaviors, magnetic-field induced colossal magnetoresistance, and metal-insulator transition (16-20). A few charge-ordered materials have also been explored in halide perovskites, such as Au^+/Au^{3+} , and Tl^+/Tl^{3+} -based compounds. $CsAuX_3$ (X = Cl, Br, I) was demonstrated to show both structural and semiconductor-metal transition at high pressures (21-24). Tl-based compounds ($CsTlF_3$ and $CsTlCl_3$) have been predicted to show high- T_c (~ 20 K) superconductivity under **reasonably** high pressures (25, 26). A theory was proposed to interpret the phase transitions in charge-ordered perovskites where the two B-site ions with different valence states became indistinguishable under hydrostatic pressures, and a non-charge-ordered state was achieved (27-29).

In this work, we report an In^+/In^{3+} -based charge-ordered halide perovskite compound $Cs_2In(I)In(III)Cl_6$, which shows a semiconductor to metal phase

transition under high pressures. Although both mono-valent In^+ and tri-valent In^{3+} based halide precursors are found to be unstable under ambient conditions, air-stable $\text{Cs}_2\text{In(I)In(III)Cl}_6$ single crystals can be successfully synthesized through a solid-state reaction method. Optical properties of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ under a hydrostatic pressure applied by a diamond anvil cell (DAC) were studied. The pressure-induced semiconductor-metal phase transition was observed in both Raman and absorption measurements.

Results and discussion

The charge-ordered $\text{Cs}_2\text{In(I)In(III)Cl}_6$ ($\text{In}^+:\text{In}^{3+} = 1:1$) single crystals were synthesized using a traditional solid-state reaction method. For a typical synthesis, an equivalent molar ratio of InCl_3 and InCl was mixed together with two equivalent amounts of CsCl , all of which were ground carefully in an Ar glovebox. Afterwards, the fine powder was loaded into an evacuated quartz tube. The sealed ampoule was heated at 650°C for 60 hours in a furnace and then slowly cooled down to room temperature. Colorless block-like crystals were harvested as shown in *SI Appendix*, Fig. S1.

Similar to other charge-ordered perovskites such as CsTiCl_3 (26), the crystal structure of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ is very complicated which requires a comprehensive suite of structural characterization techniques to obtain its accurate crystal structure model. Synchrotron-based single crystal X-ray diffraction (SCXRD) data obtained at 100 K indicates that there are a set of strong reflection data with weak super reflections **in the unwrapped images** (*SI Appendix*, Fig. S2). **If only considering the strong reflections**, we can deduce a tetragonal cell with space group $P4/m$ and $a = 5.3915(4) \text{ \AA}$, $c = 5.5123(6) \text{ \AA}$. Based on this analysis, a structure model with a typical perovskite framework with disordered In positions was obtained. **However, the simulated powder X-ray diffraction (PXR) based on this structure model only matches the strongest reflections in the experimental PXR data,**

indicating further work is necessary to model the weaker reflections among the strong reflections. Considering the weaker reflections together, a tetragonal supercell with space group $I4/m$ and $a = 17.2604(12) \text{ \AA}$, $c = 11.0113(16) \text{ \AA}$ can be obtained. Further analysis using rotation electron diffraction (RED) collected from a small piece of nano-sized crystal crushed from the bulk crystal also confirmed that this supercell is more suitable for describing the crystal structure of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ (*SI Appendix*, Fig. S3) (30, 31). As a result, we used this unit cell for data reduction, structure determination and refinement based on our best SCXRD dataset. The detailed structure parameters are listed in *SI Appendix*, Table S1, S2. The final structure refinement turned out to converge successfully with a low R value. The simulated PXRD pattern based on this model well matched the experimental PXRD data (see below for detailed discussion). Energy dispersive spectroscopy (EDX) shown in *SI Appendix*, Fig. S4 determined the atomic ratio of Cs:In:Cl to be around 1:0.95:2.99, which was consistent with the double perovskite structure chemical formula.

The final structure model of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ turns out to be heavily disordered. The structure model shows common structure features as the reported charge-ordered structure of CsTiCl_3 and $\text{Cs}_{1.17}\text{In}_{0.81}\text{Cl}_3$ (26, 32), but with its own signature. In our structure model, the In, Cl and Cs ions are found to be located at disordered positions with various occupancies. Among all the four individual In positions, In(I)3 and In(I)4 are refined to be at a few disordered positions with different occupancies as shown in Fig. 1A and Fig. 1B. The exact coordinational polyhedra are hard to be concluded here due to the disorder complexity, as the ionic radius of In(I) is very similar to Cs^+ , and significantly different from In(III). The coordination sphere of In(I) with Cl might be more similar to Cs^+ instead of being located as octahedra like In(III)Cl₆. As there lacks enough accurate statistic experimental data on In(I)-Cl coordinational sphere in both CCDC and ICSD database, here we prefer not

to make an absolute conclusion on the In(I)-Cl coordinational sphere, but just use a red ball to represent In(I) position when illustrating our structure model. Unlike the disordered location of In(I), both of the two independent In(III) atoms are refined to be located at the ordered positions, while the coordinated Cl atoms around the equatorial plane of the octahedra are all disordered into two positions. These disorders introduce the 45° rotation of the In(III)Cl₆ octahedra as highlighted in green and yellow in Fig. 1C. The partial occupancies of Cl2A/Cl2B, Cl5A/Cl5B and Cl7A/Cl7B equal to 0.79/0.21, 0.79/0.21 and 0.77/0.23, respectively. The rotation of the In(III)Cl₆ results in two disordered structural components as shown in Fig. 1D-F and Fig. 1G-I, with a ratio around 0.78/0.22 as determined by the ratio of disordered Cl atom components. The general crystal structure model of component 1 shown in Fig. 1D-F is very much the same as a double perovskite, while the rotation of the In(III)Cl₆ octahedra as highlighted in blue introduces the supercell feature which is very similar to the reported Cs_{1.17}In_{0.81}Cl₃. The small difference between component 1 and Cs_{1.17}In_{0.81}Cl₃ is the atomicity of In(I) position as illustrated with a red ball in the figure. In our structure, based on the comprehensive elemental analysis and refinement results, In(I) positions should be fully occupied with In, while mixed occupancies of Cs⁺ and In⁺ have been observed in Cs_{1.17}In_{0.81}Cl₃. The other 22 % of the single crystal is contributed by component 2 resulting from the 45° rotation of the In(III)Cl₆ octahedra as shown in Fig. 1G-I. In component 2, the structure model is deviated far away from a typical perovskite structure. Although it is not fully understood why the In(III)Cl₆ octahedra preferred to be partially disordered with a rotation feature, it should be the reason for the eight-fold like extra reflection circles in the unwrapped image of the SCXRD pattern (*SI Appendix*, Fig. S2). Moreover, as compared with Cs_{1.17}In_{0.81}Cl₃, this structure difference actually contributes to the different physical and chemical properties of our material and results in significant differences in the PXR patterns.

PXRD collected with lab source Cu K α radiation in Fig. 2A shows that the experimental result is well consistent with the simulated pattern, indicating that the sample is in a single pure phase. Also, we reproduced the crystal of the reported Cs_{1.17}In_{0.81}Cl₃ and find the experimental and simulated PXRD patterns are significantly different from ours (see *SI Appendix*, Fig. S5). As most of the In(I) based halides materials are susceptible to oxidation (33), the structure stability of the as-synthesized Cs₂In(I)In(III)Cl₆ was investigated under ambient condition with PXRD, as shown in Fig. 2B. The framework of Cs₂In(I)In(III)Cl₆ is stable in dry air (relative humidity of 35 %) even over 18 days. The air stability is further confirmed by Raman and absorption spectra (*SI Appendix*, Fig. S6, S7). The air stability is significantly enhanced as compared with the reported Cs_{1.17}In_{0.81}Cl₃. We have confirmed the stability difference by tracking the PXRD, absorption, and appearance evolution in the same condition as shown in *SI Appendix*, Fig. S8, S9. Since In⁺ can be easily oxidized, and InCl₃ is highly hygroscopic, the formation of the charge-ordered perovskite structure could significantly enhance the stability. To investigate the In⁺ charge stability, ex-situ synchrotron-based soft X-ray photoelectron spectroscopy (SXPS) has been conducted (Fig. 2C, D). The results indicate that the surface of the as-synthesized fresh Cs₂In(I)In(III)Cl₆ crystal has an In⁺/In³⁺ ratio of about 0.55:1, while the sample after exposure in air shows only pure In³⁺, suggesting that the valence state of In⁺ is not stable against oxidation. Although the PXRD peaks indicate that the crystallographic crystalline phase remains the Cs₂In(I)In(III)Cl₆ charge-ordered phase, In⁺ might have already been oxidized to In³⁺ on the surface, and prevents the framework from collapsing through self-limiting surface oxidation of the crystals (34, 35). This is also consistent with the weaker peak intensity and peak broadening of the PXRD pattern after a few days of air exposure.

Previous studies on the charge-ordered halide perovskites such as

CsAuCl₃ and CsTlCl₃ claimed that the wide bandgap semiconducting properties in these crystals originated from the strong coupling of the charge carriers (25, 29). Herein, we utilize optical and electrical measurements to explore the properties of our Cs₂In(I)In(III)Cl₆ crystals. *SI Appendix*, Fig. S10 shows the absorbance spectrum at room temperature, indicating that the material has an optical bandgap of **around 3.0 eV**. From photoluminescence (PL) measurement (*SI Appendix*, Fig. S11), a broad emission peak centered at about 500 nm with very low intensity appears at room temperature. Further lowering the temperature down to 4 K, the emission intensity is increased two-fold of its original intensity, but still quite broad and weak, indicating poor light emitting property of the material. Furthermore, electrical characteristics of this crystal were studied *via* current (*I*) - voltage (*V*) measurements. Symmetric and linear *I-V* output characteristics in the dark (*I*_{dark}), under white-light illumination (*I*_{light}), and the photocurrent (*I*_{ph} = *I*_{light} - *I*_{dark}) are shown in *SI Appendix*, Fig. S12, respectively, indicating the semiconducting behavior of this material without external stress.

To test possible semiconductor to metal phase transition of this crystal at high pressures, we explored its optical properties under pressure using a four-post symmetric DAC coupled with a hydrostatic pressure medium. DAC has been widely used to investigate the structural and electronic properties of halide perovskites under high pressures (10, 36-41). Raman measurement of Cs₂In(I)In(III)Cl₆ at ambient pressure (0 GPa) and room temperature (295 K) **showed one prominent peak at 279 cm⁻¹ which could be assigned to the In(I)-Cl-In(III) mode (26, 32) and two other minor peaks at 143 cm⁻¹ and 189 cm⁻¹** (*SI Appendix*, Fig. S6). The Raman spectra did not show any significant temperature dependence from 295 K down to 77 K (*SI Appendix*, Fig. S13). We then performed pressure-dependent Raman spectroscopy at room temperature. The main Raman peak at 279 cm⁻¹ gradually shifts to higher wavenumber with the increase of pressure (Fig. 3A and *SI Appendix*, Fig.

S14), and experiences an abrupt intensity drop at 13.2 GPa and finally disappears at 21.9 GPa, suggesting a metallic phase at and beyond this pressure. Meanwhile, the two minor Raman peaks at lower frequencies were too weak to be detected under high pressure. The Raman peaks fully recover after the pressure is released, hence the phase transition is reversible. As shown in Fig. 3B, the Raman peak shifts almost linearly with pressure at a rate of $d\omega/dP = 3.7 \text{ cm}^{-1}/\text{GPa}$ before it collapses at about 22 GPa. The integrated area also shows a drastic drop at $\sim 10 \text{ GPa}$ and becomes non-detectable at $> 22 \text{ GPa}$ (10). The Raman vibration modes softening can be regarded as an important evidence of a charge-ordering to non-charge-ordering phase transition (23, 28, 29). To better demonstrate the pressure-induced semiconductor-metal phase transition, pressure-dependent optical absorbance measurement at room temperature has been performed. As shown in Fig. 3C, the absorbance spectrum of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ redshifts with pressure up to 13.9 GPa, above which absorption increases abruptly with a broad-band metallic feature. In the raw transmittance spectra (SI Appendix, Fig. S15), the transmitted light intensity abruptly drops at 13.9 GPa and remains low up to 34.7 GPa. The pressure-dependent bandgap evolution of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ is shown in Fig. 3D. The bandgap starts at about 2.9 eV under ambient pressure, and then gradually decreases to about 2.0-2.1 eV until 13.9 GPa and closes completely under higher pressures. A strong absorption was also observed in MAPbI_3 and charge-ordered CsAuI_3 at the transition pressure, consistent with the simultaneous electrical conductivity change near the same pressure, suggesting a semiconductor-metal phase transition (10, 27, 28). The good agreement between optical bandgap closure and electrical conductivity change detected in these two similar materials implies that experimentally the optical band gap closure is a reliable and robust clue of a metallic phase, especially when combined with Raman spectra change.

The pressure-induced bandgap changes and semiconductor-metal

transition of the charge-ordered $\text{Cs}_2\text{In(I)In(III)Cl}_6$ were further interpreted by density functional theory (DFT) calculations. We built a 5-atom unit cell of perovskite structure with space group $P4/m$ and a 10-atom unit cell of double perovskite structure with space group $I4/m$ for the **hypothesized** non-charge-ordered CsInCl_3 (purely In^{2+}) and charge-ordered $\text{Cs}_2\text{In(I)In(III)Cl}_6$, respectively. The calculated band structure and density of states are shown in *SI Appendix*, Fig. S16. The results show that without external stress, the charge-ordered perovskite possesses an electronic bandgap of about 2.3 eV, while the non-charge-ordered system lies in a metallic state of 0 eV bandgap. Particularly, under ambient pressure, the charge-ordered semiconducting phase possesses a lower energy than the non-charge-ordered state, suggesting that the charge-ordered phase is the ground state. The calculated bandgap of the charge-ordered phase gets narrower with the increase of pressure and decreases smoothly to 0 eV at around 13 GPa (Fig. 4A). As pressure increases, the energies of both non-charge-ordered and charge-ordered phases increase, and the difference between the energies of the two phases decreases (Fig. 4B). We further analyzed the In-Cl bond length in the two phases under increasing pressure (*SI Appendix*, Fig. S17). The length difference between the two types of In-Cl bonds in the charge-ordered phase becomes smaller with the increase of pressure and their values approach the In-Cl bond length in the non-charge-ordered phase. The electronic delocalization of the In^+ and In^{3+} centers contributes to the bandgap change and semiconductor to metal transition. To summarize, by combining the Raman peaks disappearance, bandgap closure and DFT simulations, we conclude that the charge-ordered perovskite undergoes a gradual and reversible semiconductor-metal phase transition within the pressure range of 14-22 GPa.

Conclusions

In this work, we have successfully synthesized charge-ordered In-based halide perovskite $\text{Cs}_2\text{In(I)In(III)Cl}_6$ single crystals by a solid-state reaction method. The structure was characterized by synchrotron-based SCXRD and RED techniques. Although the surface mono-valent In^+ ions tend to oxidize in ambient conditions, the bulk single crystals show high structural stability. The intrinsic semiconducting properties were explored *via* optical and electrical measurements. We further studied high-pressure optical properties and discovered a pressure-driven semiconductor-metal phase transition. The characteristic Raman peak blueshifts with the increase of pressure and disappears completely after about 22 GPa. Its optical bandgap gradually shrinks, and a broad-band metallic absorption feature appears after about 14 GPa. Based on the Raman and absorbance spectra, the semiconductor-metal phase transition starts at about 14 GPa and ends completely at about 22 GPa, in agreement with the DFT calculations. Our findings show the great potential of the charge-ordered $\text{Cs}_2\text{In(I)In(III)Cl}_6$ as a phase transition material with multifunctional properties and a material of high- T_c superconductivity with appropriate doping and high pressure.

Materials and Methods

Single crystals of $\text{Cs}_2\text{In(I)In(III)Cl}_6$ were synthesized by a solid-state reaction method under vacuum. Synchrotron based single crystal X-ray diffraction was performed on a tiny colorless crystal mounted on a Bruker D8 diffractometer equipped with a PHOTON 100 CCD detector with silicon (111) monochromated synchrotron radiation ($\lambda = 0.7288 \text{ \AA}$) at 100 K. Rotation electron diffraction data was collected at 200 K under cryo N_2 atmosphere to confirm the supercell. The valent states of indium atoms in the single crystals were determined by ex-situ soft X-ray photoelectron spectroscopy. Hydrostatic high pressure measurements were performed in a diamond anvil cell. The calculations were carried out employing spin-polarized DFT methods using the Projector Augmented Wave method, as implemented in the Vienna ab initio simulation package. More detailed information regarding the materials and methods are available in the *SI Appendix*.

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Author contributions

J.L., H.C. and Y.G. contributed equally to this work. P.Y. and J.W. conceived the idea and designed the study. J.L., H.C. and M.F.T. contributed to the material synthesis and structure characterization. Y.G. performed the high-pressure experiments. Y.C, M.S. and M.A. carried out the DFT modeling. A.E. and J.S. carried out the RED experiments and data analysis. J.K. and T.L. performed the transport measurement. Z.L. and L.N.Q helped with the optical characterizations. J.J., Y.G. and M.C.F measured the stability. Q.K. performed the EDX measurement. J.L., H.C., Y.G. and P.Y. wrote the manuscript. All authors discussed the results and revised the manuscript.

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Figure Legends

Fig. 1. Single crystal structure of $\text{Cs}_2\text{In(I)In(III)Cl}_6$. (A) Disordered In(I)_3 and (B) In(I)_4 positions in the In(I)Cl_6 octahedra. (C) Disordered Cl ion positions around the In(III)Cl_6 octahedra. (D-F) Disordered component 1 viewing along [001], [110], and [100] zone axis, respectively. (G-I) Disordered component 2 viewing along [001], [110], and [100] zone axis, respectively. Color scheme: red ball, In(I) atoms; green and yellow ball, Cl atoms; blue and amber, In(III) atoms; purple, Cs atoms.

Fig. 2. Structure and valence state stability. PXRD patterns of (A) as-synthesized $\text{Cs}_2\text{In(I)In(III)Cl}_6$ powder and (B) that after exposure to air for 0-18 days. (C, D) SXPS of fresh sample and that after exposure to air for 1 day.

Fig. 3. Semiconductor-metal transition under high pressures. (A, B) Raman peak blueshifts and intensity (normalized integrated area) weakens with the increase of pressure and disappears completely at about 22 GPa. (C) Absorbance spectra and (D) bandgap shrink with the increase of pressure. After about 14 GPa, a broad-band metallic absorption feature appears.

Fig. 4. DFT modelling on the pressure-induced phase transition. (A) Bandgap and (B) average energy per atom changes of the charge-ordered and non-charge-ordered states at high pressures. The charge-ordered system equilibrium energy (at 0 GPa) is lower than the non-charge-ordered case.