

De Novo Photovoltaic Paramagnetic Copper-doped Double Perovskite: Deducing Atomic Structure with Ultrahigh Field Solid-state NMR and EPR

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Lead halide perovskites (LHP) with general formula $APbX_3$ (A and X are organic/inorganic monovalent cation and halide anion, respectively) have attracted worldwide scientific attention for highly-efficient semiconducting materials in perovskite-based solar cell devices with an extraordinary power conversion efficiency of 28% within a decade.¹ Unfortunately, lower thermal and moisture stability along with lead-toxicity due to the high water solubility of Pb^{2+} hinder these materials for the long-term applications.^{2,3} On the other hand, halide double perovskites with general formula $A_2B'(III)B''(I)X_6$ (A and B are cations) are leading candidates being explored as a lead-free, high-thermal and moisture stable alternative of LHPs.⁴ However, most of the double perovskites reported to date are less suitable as they are commonly higher bandgap materials (i.e., over 2 eV).⁵ One such material is $Cs_2SbAgCl_6$ double perovskite with an indirect bandgap of 2.6 eV, reported by Deng *et al.* in 2017.⁶ Here, we present a new heterovalent Cu^{2+} doped $Cs_2SbAgCl_6$ double perovskite material with a stark change of bandgap to ca. 1 eV, which is ideal for solar cell absorbers. To decode the atomic-level, short- and medium-range structural evolution upon doping with paramagnetic Cu(II) in $Cs_2SbAgCl_6$, a suite of complementary magnetic resonance spectroscopic techniques, namely, solid-state NMR and EPR have been used. Subsequently, variable-temperature ^{133}Cs MAS NMR revealed more structural information that Cu^{2+} incorporated within $Cs_2SbAgCl_6$ lattice is situated in the B''-site impacting the ^{133}Cs NMR through a Fermi contact interaction. Powder X-ray diffraction confirms the phase-purity and long-range crystallinity with non-uniform microstrain upon Cu^{2+} incorporation within $Cs_2SbAgCl_6$ crystal lattice. Finally, stability test experiments indicate an ideal long-term environmental stability towards heat and moisture for photovoltaic applications.⁷

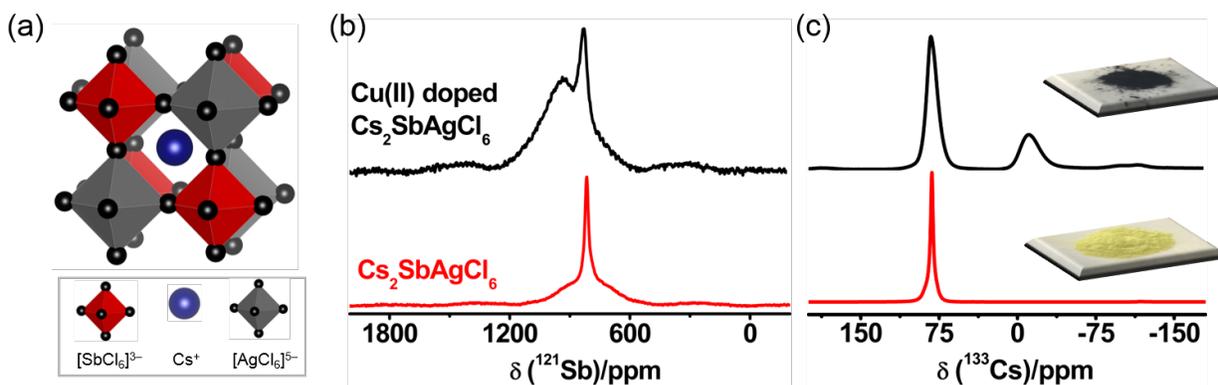


Figure 1. Schematic representation of $Cs_2SbAgCl_6$ lattice (a). Room temperature solid-state ^{121}Sb (b) and ^{133}Cs (c) NMR spectra for $Cs_2SbAgCl_6$ and its Cu(II) doped material; non-spinning ^{121}Sb NMR were acquired at 21.1 T, and ^{133}Cs MAS NMR were acquired at 11.7 T. The inserts in (c) represent photographs of polycrystalline $Cs_2SbAgCl_6$ (yellow) and its Cu(II) doped (black) material.

References:

- (1) <https://www.nrel.gov/pv/assets/pdfs/pv-efficiencychart.20181214.pdf>
- (2) Needleman, H. *Annu. Rev. Med.* **2004**, *55*, 209–222.
- (3) Askar, A. M.; *et al.* *J. Phys. Chem. C* **2017**, *121*, 1013–1024.
- (4) Slavney, A. H.; *et al.* *J. Am. Chem. Soc.* **2016**, *138*, 2138–2141.
- (5) Filip, M. R.; *et al.* *J. Phys. Chem. C* **2018**, *122*, 158–170.
- (6) Deng, W.; *et al.* *Appl. Phys. Lett.* **2017**, *111*, 151602.
- (7) Karmakar, A.; *et al.* *Chem. Mater.* **2018**, *30*, 8280–8290.