# Tailoring Stable Chiral Materials Without Lead

Basic Research

Chiral optical materials have attracted strong attention in multiple disciplines due to their wide application in various fields such as remote sensing, 3D display, information communication, and optical information storage. With the strong demand for stable and environmentally friendly materials, two-dimensional chiral lead-free halide double perovskites are expected to generate rich chiroptical and optoelectronic properties.

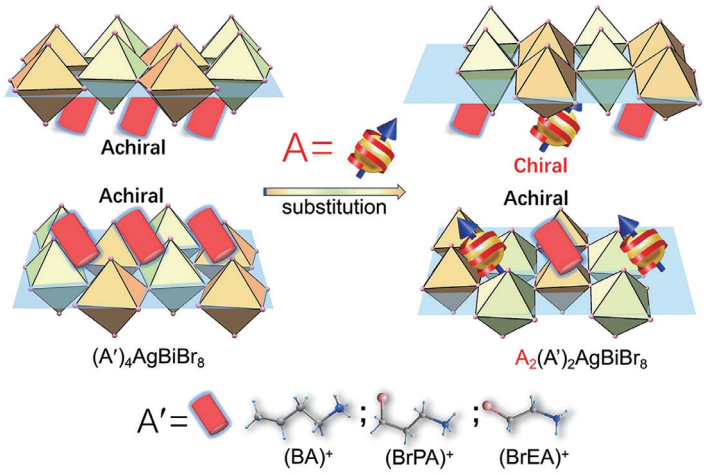
However, the reported chiral lead-free double perovskites are rare. The main challenge is that there is only one kind of organic cation A in the interlayer of double perovskites $A_4B_IB_{III}X_8$ (A is organic cation, $B_I$ and $B_{III}$ are metallic cations, X is halogen.) and the selective domain of chiral cations A in double perovskites is limited by the width of the organic interlayer.

In a study published in *Chem*, the research group led by Prof. LUO Junhua from Fujian Institute of Research on the Structure of Matter (FJIRSM) of the Chinese Academy of Sciences proposed an achiral-chiral cation intercalation strategy to rationally design a series of new enantiomeric lead-free halide double perovskites with asymmetric and chiral bifunctional features.

Through an unprecedented strategy of achiral-chiral cation intercalation, the researchers realized charge conservation and overall steric hindrance balance. The arrangement of the original intercalated cations is changed from a single cation A to diverse cations A+A′, wherein A′ represents abundant achiral cations.

The researchers synthesized a series of six new enantiomeric lead-free halide double perovskites (R/S-PPA)$_2$(BA)$_2$AgBiBr$_8$, (R/S-PPA)$_2$(BrPA)$_2$AgBiBr$_8$ and (R/S-PPA)2(Br-EA)2AgBiBr8, demonstrating the feasibility of this synthesis strategy.

Single crystal X-ray diffraction analysis showed that achiral and chiral cations arrange alternately and connect with diverse noncovalent intermolecular interactions like CH-π, π-π, CH-Br. These interactions make the chiral organic cations and achiral organic cations coexist stably and harmoniously in chiral halide double perovskites.




Schematic diagram of chiral-achiral cations intercalation strategy for designing a series of chiral lead-free halide double perovskites (Image by Prof. LUO's group)

Further analysis showed that chiral compounds may prefer to possess more distorted structure because of their natural asymmetric features. Larger structural distortions generally result in lower crystal symmetries, inducing to asymmetry breaking and thus paving the way to the generation of circular dichroism (CD) and second harmonic generation (SHG) signals.

Taking compounds (R/S-PPA)$_2$(Br-EA)$_2$AgBiBr$_8$ as examples, the researchers found that they present a nonlinear optical response up to 2 times stronger than that of state-of-the-art $KH_2PO_4$ nonlinear crystals and produce robust circular dichroism signals in the visible region.

This study provides a new approach to explore chiral lead-free halide double perovskites.

This paper can be accessed at https://www.cell.com/chem/pdfExtended/S2451-9294(23)00564-8.

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