

## DOUBLE PEROVSKITES

## Equally charged with orderly conduct

“  
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Double perovskite oxides are valued for their versatile cation arrangements, which impart notable physical properties such as ferrimagnetism and large magnetoresistance. B' and B'' cation arrangements in such A<sub>2</sub>B'B''O<sub>6</sub> materials span from entirely disordered to impeccably ordered. Cation ordering usually occurs when the oxidation states and radii of the ions are substantially different. A difference in oxidation state of two or more is generally required to achieve B'/B'' cation-ordered double perovskites. There are approximately 650 known ordered double perovskites, but all cases to date featuring isovalent cations (A<sup>3+</sup><sub>2</sub>B'<sup>3+</sup>B''<sup>3+</sup>O<sub>6</sub>) are disordered. Now, writing in *Angewandte Chemie*, Athinarayanan Sundaresan and co-workers describe unusual ordering of Fe<sup>3+</sup> and Al<sup>3+</sup> in the double perovskite Bi<sub>2</sub>FeAlO<sub>6</sub>.

The bismuth-based perovskite oxide BiAlO<sub>3</sub> is ferroelectric at room temperature, whereas its iron counterpart — BiFeO<sub>3</sub> — is multiferroic with weakly coupled magnetism and ferroelectricity. A polar phase in which half of the B sites in BiFeO<sub>3</sub> are replaced with non-magnetic Al<sup>3+</sup> ions may exhibit a spontaneous magnetization that in turn may enhance magnetoelectric

coupling. Since both BiAlO<sub>3</sub> and BiFeO<sub>3</sub> have similar crystalline phases, it is reasonable to expect that a BiFe<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> solid solution is accessible. However, previous exploration of this composition space showed that the BiFe<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> solid solution was limited to  $x = 0.1$  in bulk and  $x = 0.4$  in thin film. Attempts to stabilize a BiFe<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> phase at ambient pressure were unsuccessful.

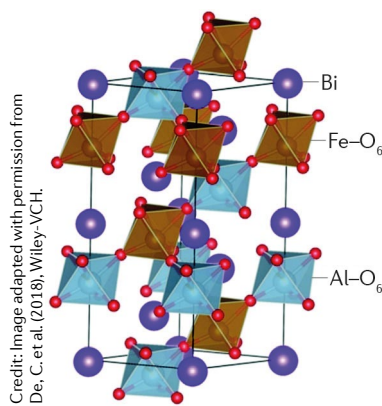
A previous similar experience with the polar oxide AlFeO<sub>3</sub> inspired the group to persevere. Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> also have similar crystalline phases, but again an isostructural solid solution could not be formed. Instead, a 1:1 mixture unexpectedly crystallizes as AlFeO<sub>3</sub> in a different space group. The isovalent cations in AlFeO<sub>3</sub> are largely ordered, albeit with some partial anti-site disorder in which Al<sup>3+</sup> and Fe<sup>3+</sup> exchange sites. Although unprecedented, a 1:1 mixture of BiAlO<sub>3</sub> and BiFeO<sub>3</sub> may also yield ordered Al<sup>3+</sup> and Fe<sup>3+</sup> ions in a polar structure. Polar materials, or those with permanent dipoles, are required for ferroelectricity and other interesting behaviours.

Considering that high pressure stabilizes BiAlO<sub>3</sub> as well as perovskite oxides with ordering of multiple cations (for example, double double perovskites), the group turned to a technique described earlier by collaborator and co-author Attfield. Polycrystalline samples of BiFe<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> with  $x = 0.2-0.5$  were prepared by pressing metal oxides at 6 GPa (~59,200 atm) and 1,000 °C. Rietveld refinement of the expected polar rhombohedral R3c model, with disordered Fe<sup>3+</sup> and Al<sup>3+</sup> ions, fitted X-ray powder diffraction data for several Fe<sup>3+</sup>:Al<sup>3+</sup> ratios, but not for BiFe<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub>. Instead, rock salt ordering of the Fe<sup>3+</sup> and Al<sup>3+</sup> cations on B'/B'' sites occurs in the BiFe<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub>, or Bi<sub>2</sub>FeAlO<sub>6</sub> double

perovskite, in the R3 space group, which is supported by time-of-flight neutron powder diffraction.

By replacing half of the Fe<sup>3+</sup> ions in BiFeO<sub>3</sub> with non-magnetic Al<sup>3+</sup>, the magnetic transition temperature from paramagnetic to an antiferromagnetic phase is decreased from 640 K to 280 K. The dielectric constant exhibits conventional temperature dependence with a magnitude similar to that of BiFeO<sub>3</sub>, and lower conductivity that is dominated by a *d*-electron hopping mechanism. Piezoelectric measurements confirm that Bi<sub>2</sub>FeAlO<sub>6</sub> exhibits a polar structure and ferroelectric properties at room temperature. The size difference between the Al<sup>3+</sup> and Fe<sup>3+</sup> cations as well as the nature of Al–O and Fe–O bonding may partly account for the cation ordering. However, there must be another factor at play because cation ordering is not observed in another similar compound, LaAl<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub>. Distortions around the Bi<sup>3+</sup> cations may accommodate the difference in isovalent cation radii, facilitating order. Although it is not well understood, the electron lone pair on Bi<sup>3+</sup> might be key in achieving ordering. “The cation ordering itself is highly surprising as ordering of two 3<sup>+</sup> cations at perovskite B-sites is unprecedented,” explains Sundaresan. “With appropriate selection of B'/B'' cations, many polar materials of the type Bi<sub>2</sub>B'B''O<sub>6</sub> may be accessible by the same high pressure methods.”

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**ORIGINAL ARTICLE** De, C. et al. Isovalent cation ordering in the polar rhombohedral perovskite Bi<sub>2</sub>FeAlO<sub>6</sub>. *Angew. Chem. Int. Ed.* <https://doi.org/10.1002/anie.201810122> (2018)

**FURTHER READING** De, C. et al. Nonswitchable polarization and magnetoelectric coupling in the high-pressure synthesized doubly ordered perovskites NaYmWO<sub>6</sub> and NaHoCoWO<sub>6</sub>. *Phys. Rev. B* **97**, 214418 (2018)