

A-site and B-site charge ordering in perovskite-type PbCoO_3

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Charge degree of freedom in transition metals gives rise to various fascinating properties such as charge ordering associated with metal–insulator transition, high-temperature superconductivity, colossal magnetoresistance and high thermopower. Metal ions with half-integer valence tend to split into two integer valence ions and these get spatially ordered as typically observed in $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}^{3.5+}\text{O}_3$.¹ To realize a half-integer valence state and charge ordering in the B site of a perovskite ABO_3 , it is generally necessary to mix two or more elements with different valences in the A site. Perovskite PbCoO_3 synthesized at 12 GPa was found to have an unusual average charge distribution of $\text{Pb}^{3.5+}\text{Co}^{2.5+}\text{O}_3$ with half-integer valences in both of A and B sites in spite of the simple chemical composition of Pb, Co, and O. Comprehensive studies using electron diffraction, synchrotron X-ray diffraction (SXR), neutron powder diffraction (NPD), Hard X-ray photoemission spectroscopy, soft X-ray absorption spectroscopy and measurements of magnetic and electrical properties provide evidence of lead ion and cobalt ion charge ordering leading to $\text{Pb}^{2+}\text{Pb}^{4+}_3\text{Co}^{2+}_2\text{Co}^{3+}_2\text{O}_{12}$ quadruple perovskite structure.² Moreover, a series of *in situ* high-pressure measurements including electrical transport, NPD, SXR, emission, and absorption spectroscopies revealed the pressure-induced sequential spin state transition and intermetallic charge transfer in PbCoO_3 .³ Here we show that half-integer valence states in both the A and B sites can be stabilized by tuning the energy levels of Pb 6s and transition metal 3d orbitals.

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[2] Y. Sakai et al., *J. Am. Chem. Soc.*, **139**, 4574–4581 (2017).

[3] Z. Liu, Y. Sakai et al., *J. Am. Chem. Soc.*, **142**, 5731–5741 (2020).