Systematic charge distribution changes in Bi, Pb-3d transition metal perovskite oxides

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Bi and Pb have a unique $6s^0$ and $6s^2$ electron configuration that creates charge degrees of freedom. Due to the lack of this $6s^1$ electron configuration, a property called valence skipper, Bi takes 3+ and 5+ and Pb takes 2+ and 4+. In particular, for perovskite compounds containing Bi or Pb at the A site, the valence state changes according to the depth of the d-orbitals of the transition metal ions corresponding to the order in the periodic table of the elements due to the close relationship between the 6s level of Pb or Bi and the 3d level of the 3d transition metal ions. For example, for $BiMO_3$, M= Cr, Mn, Fe, Co, the state is $Bi^{3+}M^{3+}O_3$, while $BiNiO_3$ has a specific valence state of $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$. $PbMO_3$ has $Pb^{2+}_{0.5}Pb^{4+}_{0.5}MO_3$ for M= Ti and V, $Pb^{2+}_{0.5}Pb^{4+}_{0.5}M^{3+}O_3$ for M= Cr and Fe, $PbCoO_3$ has $Pb^{2+}_{0.25}Pb^{4+}_{0.75}Co^{2+}_{0.5}Co^{3+}_{0.5}O_3$, $PbNiO_3$ has $Pb^{4+}Ni^{2+}O_3$. In $BiNiO_3$ and $PbMO_3$ (M = Cr, Fe and Co), Bi and Pb become charge disproportionated in the $6s^0$ and $6s^2$ states, and temperature- and pressure-induced elimination of charge disproportionation and charge transfer phase transitions occur. The valence of the transition metal M is changed in this process, which leads to unique properties such as metal-insulator transition and negative thermal expansion. In this study, we evaluated the electronic states of these materials by HAXPES, and the crystal structure distortions caused by these electronic states were investigated by crystal structure analysis using synchrotron radiation X-ray diffraction and local structure analysis using atomic pair distribution function (PDF) obtained from synchrotron radiation X-ray total scattering patterns.

[1] Azuma, M.; Sakai, Y.; Nishikubo, T.; Mizumaki, M.; Watanuki, T.; Mizokawa, T.; Oka, K.; Hojo, H.; Naka, M. *Dalton Transactions* **2018**, *47* (5), 1371–1377