

Bi and Pb are main group elements but they have charge degrees of freedom that depend on the $6s^2$ (Bi³⁺, Pb²⁺) and $6s^0$ (Bi⁵⁺, Pb⁴⁺) electronic configurations. The $6s^1$ configuration is prohibited. Bi and Pb are therefore called valence skipping elements. Since the energy levels of Bi and Pb 6s, transition metal 3d and oxygen 2p are close to each other, intermetallic charge transfer is observed in perovskite oxides composed of these elements [1]. The composition-, temperature- and pressureinduced changes in local charge distributions were investigated comprehensively by synchrotron X-ray diffraction, total scattering and photoemission studies.

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The perovskite BiNiO₃ has an unusual $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ valence distribution at atmospheric pressure. Distinct Bi^{3+}/Bi^{5+} crystallographic sites exist in the $\sqrt{2}a \times \sqrt{2}a \times 2a$ unit cell, where *a* is the lattice parameter of a simple cubic perovskite. The simultaneous melting of charge disproportionation and charge transfer between Bi^{5+} and Ni^{2+} ions accompanied by a triclinic (*P*-1) to an orthorhombic GdFeO₃-type (*Pbnm*) structural transition occur under high-pressure conditions. This structural transition results in a contraction of the unit cell volume by ~3%, because of the shrinkage of the Ni–O bond owing to the oxidation of Ni from 2+ to 3+. Fe³⁺ substitution for Ni²⁺ stabilizes the Bi³⁺(Ni, Fe)³⁺O₃ phase, and a charge transfer

transition accompanied by volume shrinkage occurs in BiNi_{1-x}Fe_xO₃ upon heating at atmospheric pressure [2]. This transition is of first order, but because large low-temperature (LT) triclinic and small high-temperature (HT) orthorhombic phases coexist and their fractions change upon heating, the weighted average unit cell volume linearly decreases, leading to negative thermal expansion (NTE). The crystal structure of the LT phase investigated by powder diffraction at SPring-8 BL02B2 changed to the polar R3c BiFeO₃-type with a unique Bi site, shown in Fig. 1(d), at x = 0.3. On the other hand, hard X-ray photoemission spectroscopy at SPring-8 BL09XU indicated the presence of Bi^{3+} and $\mathsf{Bi}^{5+},$ as shown in Fig. 1(a). The PDF analysis of total scattering data collected at SPring-8 BL22XU (Figs. 1(b) and 1(c)) revealed that the local structure had R3 symmetry with two Bi sites (Fig. 1(e)). These results mean that the ordering of Bi³⁺/Bi⁵⁺ is short-ranged, probably because of the deviation from the 1:1 ratio. Since the Fe ion has a +3 charge, as confirmed by Mössbauer spectroscopy, the amounts of Bi5+ and Ni2+ contributing to the charge transfer transition decrease with increasing x. The amount of unit cell volume reduction during the NTE therefore decreases with x. However, the volume reductions of $BiNi_{1-x}Fe_xO_3$ with $x \ge 0.3$ are found to be independent of x, as shown in Fig. 2(a). It is well known that ferroelectric to the



Fig. 1. (a) Observed hard X-ray photoemission spectroscopy (HAXPES) spectra (black points), fitting results (green line), Bi^{3+} components (blue) and Bi^{5+} components (red) for $BiNi_{1,x}Fe_xO_3$ measured at 300 K. Observed (blue points) and simulated (red line) pair distribution functions (PDFs) for $BiNi_{0,7}Fe_{0,3}O_3$ using (b) *R3c* and (c) *R3* models. Lower green lines indicate the difference between the observed and simulated data. Average *R3c* (d) and local *R3* (e) structures. [3]



Fig. 2. Negative thermal expansion (NTE) induced by simultaneous charge transfer and polarnonpolar transitions in $BiN_{1,x}Fe_xO_3$. (a) Fe concentration dependence of the volume difference between low-temperature (LT) phases (triclinic or rhombohedral) and high-temperature (HT) orthorhombic phase. Blue and green triangles indicate transitions from triclinic to orthorhombic phases and from rhombohedral to orthorhombic phases, respectively. (b) Calculated P_S from structural parameters refined by Rietveld analyses of synchrotron X-ray diffraction (SXRD) patterns. [3]

paraelectric change in materials such as PbTiO₃ is accompanied by NTE. The spontaneous polarization of the polar rhombohedral LT phase of BiNi_{1-x}Fe_xO₃ increases with *x* (Fig. 2(b)). These indicate that the decrease in the amount of volume reduction due to charge transfer is compensated by the NTE induced by the polar–nonpolar transition [3].

PbCoO₃ prepared at 12 GPa has a Pb²⁺_{0.25}Pb⁴⁺_{0.75} Co²⁺_{0.5}Co³⁺_{0.5}O₃ charge distribution. Pb²⁺/Pb⁴⁺ and Co²⁺/Co³⁺ are respectively ordered at A- and B-sites of perovskite ABO₃, leading to the quadruple perovskite Pb²⁺Pb⁴⁺₃Co²⁺₂Co⁴⁺₂O₁₂ structure illustrated in Fig. 3(a) [4]. Similarly to BiNiO₃, a pressure-induced charge transfer transition leading to Pb²⁺_{0.5}Pb⁴⁺_{0.5}Co³⁺O₃ is expected to occur. Synchrotron X-ray diffraction (SXRD) data collected at BL22XU indicated 1.76 and 1.12% reductions in unit cell volume at 20 and 24 GPa (Fig. 3(b)). An X-ray emission study at SPring-8 **BL12XU** revealed that the first reduction was due to the high-spin to low-spin transition of Co²⁺. The second reduction was attributed to the charge transfer transition [5].



Fig. 3. (a) Crystal structure of $PbCoO_3$ with $Pb^{2+}Pb^{4+}_3Co^{2+}_2Co^{4+}_2O_{12}$ charge distribution. (b) Pressure evolution of unit cell volume of $PbCoO_3$. [5]

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