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Title(English)	Effect of Elemental Substitution on Crystal and Electronic Structures of PbVO ₃
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Summary of “Effect of Elemental Substitution on Crystal and Electronic Structures of PbVO₃”

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PbVO₃ has a PbTiO₃-type tetragonal perovskite structure with a giant lattice distortion ($c/a = 1.23$ at RT) stabilized by d_{xy} orbital ordering of V⁴⁺ and a calculated spontaneous polarization exceeding 100 $\mu\text{C}/\text{cm}^2$. The large structural distortion of PbVO₃ hinders polarization reversal by an external field and a tetragonal-to-cubic (T-to-C) phase transition upon heating leading to negative thermal expansion (NTE). It is recently reported that electron doping to V⁴⁺ by Bi³⁺ substitution for Pb²⁺ suppresses the large distortion and enables a temperature induced T-to-C transition accompanied by colossal NTE to occur. In this thesis, the structural evolution and the physical properties, especially NTE, of PbVO₃ with other chemical substitutions are investigated.

In chapter 2, F⁻ substitution for O²⁻ was conducted as an alternative way of electron doping to V⁴⁺. The c/a ratio gradually decreased with increasing F substitution and structural change from tetragonal to cubic was observed at PbVO_{2.79}F_{0.21}. A temperature induced T-to-C transition was observed for this composition, giving rise to the shrinkage of average unit cell volume by 4.0 %. The dilatometric volume shrinkage of 13.5 % is the largest in the existing NTE materials most probably because of the anisotropic thermal expansion: c -axis shrunk by 14 % while a -axis expanded by 2 % at the T-to-C transition.

In chapter 3, the structural evolution and the physical properties of PbV_{1-x}Cr_xO₃ ($x \leq 0.40$) were studied. The smallest c/a ratios for Bi and F substitution were respectively 1.09 and 1.18 because of the solubility limit. On the other hand, Cr substitution enabled even smaller c/a ratio. The ferroelastic domain switching was observed for PbV_{0.75}Cr_{0.25}O₃ with $c/a = 1.07$. Moreover, a temperature dependence of electrical resistivity for V_{0.70}Cr_{0.30}O₃ with $c/a = 1.04$ demonstrates a semiconductor to metal transition during the T-to-C transition giving a direct evidence of the melting of d_{xy} orbital ordering. The ferroelasticity and the temperature induced metallization were observed for the first time in PbVO₃ derivatives.

In chapter 4, the structural and charge distribution changes in heavily Cr substituted PbVO_3 , that is, $\text{PbCr}_{1-x}\text{V}_x\text{O}_3$ ($x \leq 0.60$) were studied. The charge distribution change from $\text{Pb}^{2+}_{(1+x)/2}\text{Pb}^{4+}_{(1-x)/2}\text{Cr}^{3+}_{1-x}\text{V}^{4+}_x\text{O}_3$ to $\text{Pb}^{2+}(\text{Cr}_{1-x}\text{V}_x)^{4+}\text{O}_3$ accompanied with a 3.5 % volume expansion was observed. This indicates the high pressure cubic phase of PbCrO_3 , $\text{Pb}^{2+}\text{Cr}^{4+}\text{O}_3$, is stabilized by V substitution for Cr.

From these studies, it is indicated that electron doping and substitution of non-Jahn Teller ion have crucial effects on the crystal and electronic structures of PbVO_3 and induce various physical properties. Comprehensive understanding of the elemental substitution in PbVO_3 will help the realizing of the ferroelectric, piezoelectric, and NTE in Pb-free giant tetragonal materials.