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題目(和文)	PbVO3の結晶構造、電子構造に対する元素置換効果
Title(English)	Effect of Elemental Substitution on Crystal and Electronic Structures of PbVO3
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Summary of
"Effect of Elemental Substitution on Crystal and Electronic Structures of $PbVO_3$"

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$PbVO_3$ has a $PbTiO_3$-type tetragonal perovskite structure with a giant lattice distortion (c/a = 1.23 at RT) stabilized by d_{xy} orbital ordering of V^{4+} and a calculated spontaneous polarization exceeding 100 $\mu C/cm^2$. The large structural distortion of $PbVO_3$ 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 V^{4+} by Bi^{3+} substitution for Pb^{2+} 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 $PbVO_3$ with other chemical substitutions are investigated.

In chapter 2, F^- substitution for O^{2-} was conducted as an alternative way of electron doping to V^{4+}.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 $PbV_{1-x}Cr_xO_3$ ($x \leq 0.40$) 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 $PbV_{0.75}Cr_{0.25}O_3$ with c/a = 1.07. Moreover, a temperature dependence of electrical resistivity for $V_{0.70}Cr_{0.30}O_3$ 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 $PbVO_3$ derivatives.

In chapter 4, the structural and charge distribution changes in heavily Cr substituted $PbVO_3$, that is, $PbCr_{1-x}V_xO_3$ ($x \leq 0.60$) were studied. The charge distribution change from $Pb^{2+}_{(1+x)/2}Pb^{4+}_{(1-x)/2}Cr^{3+}_{1-x}V^{4+}_xO_3$ to $Pb^{2+}(Cr_{1-x}V_x)^{4+}O_3$ accompanied with a 3.5 % volume expansion was observed. This indicates the high pressure cubic phase of $PbCrO_3$, $Pb^{2+}Cr^{4+}O_3$, 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.