論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Development of Novel Ferroelectrics Utilizing Distortions of Non-Lead Cations
著者(和文)	福田真幸
Author(English)	Masayuki Fukuda
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第11708号, 授与年月日:2022年3月26日, 学位の種別:課程博士, 審査員:東 正樹,舟窪 浩,川路 均,笹川 崇男,山本 隆文
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第11708号, Conferred date:2022/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 系 材料 コース	申請学位（専攻分野）： Academic Degree Requested	博士 （理学） Doctor of
学生氏名： Student's Name	福田 真幸	指導教員（主）： Academic Supervisor(main)	東 正樹
		指導教員（副）： Academic Supervisor(sub)	山本 隆文

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Because of ion displacements with respect to the nonpolar references, ferroelectric materials exhibit spontaneous polarization, P_s. The direction of P_s can be reversed by an external electric field. Such switchable polarization provides electromechanical properties such as piezoelectricity. Ferroelectrics, therefore, find various applications, such as actuators and sensors. Since the first report of ferroelectricity in Rochelle salts 100 years ago, numerous ferroelectric materials have been developed. Lead-based perovskite ferroelectrics, Pb(Zr, Ti)O_3 solid solutions are the most commonly used because of their superior piezoelectric effects and higher operating temperature. $PbVO_3$ is also one of the excellent lead-based perovskites with a large spontaneous polarization derived from the stereochemical effect of Pb^{2+} and the first-order Jahn-Teller effect of V^{4+}, providing $PbVO_3$-based colossal negative thermal expansion materials. However, in recent years, demand for the development of lead-free ferroelectric materials has been increasing due to environmental concerns. As lead-free ferroelectric materials, perovskite ferroelectrics containing the second-order Jahn-Teller active Ti^{4+} and Nb^{5+}, such as $BaTiO_3$ and $KNbO_3$ have been studied most intensively.

In this thesis, by using the high-pressure synthesis technique, I have developed novel compounds with the distortion of non-lead cations, i.e., first- or second-order Jahn-Teller distortions of V^{4+} and Nb^{5+}. I synthesized two novel polar materials, $CaMn(Ti_{1-x}V_x)_2O_6$ which combine the first-order Jahn-Teller distortion of V^{4+} and an order-disorder type ferroelectric mechanism, and $CuNbO_3$, where the coexistence of the second-order Jahn-Teller distortion of Nb^{5+} with the covalent nature of Cu-O bonding leads to an unusual ferrielectric dipole ordering. I also found the latter compound shows a novel topochemical reaction with cation-deinsertion, forming a novel colossal permittivity material, $CuNb_2O_6$.

First, I investigated the structural evolution and physical properties of $CaMn(Ti_{1-x}V_x)_2O_6$ ($0 \leq x \leq 0.6$). I successfully found enhanced spontaneous polarization of an order-disorder type ferroelectric $CaMnTi_2O_6$ by introducing the first-order Jahn-Teller active V^{4+} ion. The maximum P_s value was observed for $x = 0.4$, and was 1.7 times larger than that for $x = 0$. On the other hand, the presence of antisite disorder between Ca^{2+} and Mn^{2+} associated with Mn−V inter-metallic charge transfer hindered

such a V^{4+} displacement in V^{4+}-rich composition as clarified by our magnetic and hard X-ray photoemission spectroscopy studies, leading to the decrease in P_s ($x \geq 0.5$). These findings indicate that introduction of V^{4+} which favors polar pyramidal coordination is efficient to enhance the P_s of order−disorder type ferroelectrics.

Next, I observed a temperature-induced ferrielectric-ferroelectric phase transition in the perovskite-type $CuNbO_3$. The high-temperature phase adopts a "collinear ferroelectric" *R*3*c* $LiNbO_3$-type structure. It transforms into the low-temperature "noncollinear ferrielectric" *Pc* structure at 470 K, accompanied by an antiparallel off-center Nb^{5+} displacement. Such a monoclinically distorted $LiNbO_3$-type structure has not been reported ever. By DFT calculation, I found the monoclinic distortion originates from the coexistence of Cu-O and Nb-O covalencies. This highlights that the bonding nature of both cations, as well as the tolerance factor, has a great impact on electric dipole order in perovskites.

Finally, I investigated a novel topochemical reaction in $CuNbO_3$, the combination of the high-pressure synthesis and subsequent ambient-pressure post-annealing. This reaction represents a rare example of cation-deinsertion, forming a novel perovskite-type $CuNb_2O_6$. I found this compound crystallizes in an A-site deficient quadruple perovskite structure and exhibits colossal dielectric constant up to 10^4. This colossal value can be attributed to an extrinsic effect, i.e., space charge, as previously reported in related quadruple perovskite-type compounds, $CaCu_3Ti_4O_{12}$ and $CuTa_2O_6$.

The conclusion of the whole thesis is that we can design ferroelectric materials exhibiting fascinating behaviors by not only introducing first- or second-order Jahn-Teller active V^{4+} or Nb^{5+} in B-sites of perovskites but combining these cations with other distortions, i.e., the order-disorder type ferroelectric mechanism or A-O covalency. In such ways, I synthesized a polar material with colossal displacement of V^{4+} in lead-free compounds for the first time and found unusual cation dipole ordering in a noncollinear ferrielectric manner, which will provide a new design concept for high-performance ferroelectrics. In addition, I successfully observed a novel topochemical reaction accompanied by cation-deinsertion. This type of reactions will provide novel metastable functional materials.