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Phase transitions and dielectric properties of perovskite-type oxyfluorides (1-x)$KNbO_3$-$xKMgF_3$

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ABSTRACT

(1-x)$KNbO_3$-$xKMgF_3$ was synthesized using a sealed silica tube with an oxygen generator (KNMOF-O_2) or a high-pressure and high-temperature apparatus (KNMOF-hp). The variations in phase transition temperature and dielectric properties were investigated. The temperatures of a tetragonal-to-cubic phase transition and an orthorhombic-to-tetragonal phase transition decreased with x, whereas the temperature of a rhombohedral-to-orthorhombic phase transition increased with it. The temperature variation, however, became constant for $x \geq 0.05$ and did not merge into one. In the temperature dependence of dielectric permittivity for $x = 0.05$ (KNMOF-hp), a broad maximum was observed in the vicinity of 400 K and its value reached approximately 2200 which is higher than that of a $KNbO_3$ dense ceramic. Considering the variation of phase transition temperatures and dielectric measurements, it is concluded that the relaxor-like behavior was realized for $x = 0.05$ (KNMOF-hp).

1. Introduction

To date, many oxides with a perovskite-type structure have already been synthesized and investigated, because they are very interesting in terms of industrial applications and fundamental research. In the case of the perovskite-type compounds (ABX_3), various combinations of A and B ions allow for a wide variety. In other words, the variability in this family of compounds can be enhanced when a perovskite-type compound containing two different anions is synthesized. The perovskite-type oxyfluoride is considered to be one of the best candidates.

Perovskite-type oxyfluorides can be categorized into two groups: compounds with the formula ABO_2F or $ABOF_2$ and solid solution between perovskite-type oxides and fluorides. In the former group, the compounds were synthesized using high-pressure and high-temperature synthesis method or topotactic-reaction method. Oxyfluorides containing Pb^{2+} ion as A ion, $PbMO_2F$ (M = Sc, Fe, Mn), can be synthesized under high pressure and temperature [1–5]. Especially, $PbFeO_2F$ and $PbMnO_2F$ has a tetragonal perovskite-type structure at room temperature and $PbFeO_2F$ transformed into a cubic at 450 K [3]. $KTiO_2F$ and Tl_2OF_2 are also synthesized under high pressure synthesis [6,7]. In addition, $SrMO_2F$ (M = Fe and Mn) [8–11], $BaFeO_2F$ [12], $La_{1-x}Sr_xFeO_{3-x}F$ [13], $Sr_{1-x}Ba_xFeO_2F$ [14] and $Ba_3Fe_3O_7F$ [15] have been synthesized via topotactic-reaction method from oxides using XeF_2 or poly(vinylidene fluoride) as sources of fluorine.

Solid solutions between perovskite-type oxides and fluorides were also synthesized because of the attracted interest as a potential ferroelectric relaxor. For perovskite-type oxides, ferroelectric-relaxor behavior is realized by ion substitution in ferroelectric perovskites. $BaTiO_3$ is a well-known ferroelectric perovskite and undergoes three phase transitions with increasing temperature. The substitution of Ti ions with tetravalent cations, such as Zr ions, inducing these phase transitions to merge into one diffuse transition and induces ferroelectric-relaxor behavior [16–18]. Since it is anticipated that the anion substitution is also effective for realizing this relaxor behavior, solid solution based on ferroelectric oxide has been synthesized, such as $BaLiF_3$-$BaTiO_3$ [19], $BaTiO_3$-$BaZrO_3$-$CaLiF_3$ [20], $BaTiO_3$-$PbLiF_3$ [21], $BaTiO_3$-$BaZrO_3$-$BaLiF_3$ [22], $x$$SrLiF_3$-(1-$x$)$BaTiO_3$ ($0 \leq x \leq 0.25$) [23], and $KNbO_3$-$KMgF_3$ [24]. While ferroelectric-relaxor behavior was not observed for these solid solutions, $x$$KTiO_2F$-(1-$x$)$BaTiO_3$ solid solution shows the ferroelectric-relaxor behavior at a low temperature [25,26]. The

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ceramic sample of xKTiO$_2$F-(1-x)BaTiO$_3$ has been synthesized using high-pressure and high-temperature synthesis method and exhibits a ferroelectric-relaxor behavior at $x = 0.15$ [25]. This nature was confirmed for KF-doped BaTiO$_3$ single crystals [26]. Dielectric properties for KF-doped BaTiO$_3$ have been investigated in detail and this solid solution is expected as a lead-free piezoelectric material [27–30]. Curie temperature (T_C = 192 K) of (1-x)BaTiO$_3$-xKTiO$_2$F, however, is below the room temperature because of the low T_C of BaTiO$_3$ (406 K), which makes (1-x)BaTiO$_3$-xKTiO$_2$F not desirable for applications as ferroelectric relaxor.

KNbO$_3$ has an orthorhombic perovskite-type structure and is ferroelectric at room temperature. Identically to BaTiO$_3$, this compound undergoes successive phase transitions from low to high temperatures. A rhombohedral-to-orthorhombic phase transition at $T_{R\text{-}O} \sim 263$ K, an orthorhombic-to-tetragonal phase transition at $T_{O\text{-}T} \sim 498$ K, and a tetragonal-to-cubic phase transition at temperature $T_{T\text{-}C} \sim 708$ K occur sequentially with increasing temperature [31,32]. $T_{T\text{-}C}$ is considered to be T_C for KNbO$_3$ because the compound becomes paraelectric above it. Accordingly, KNbO$_3$-based solid solutions are expected to be ferroelectric relaxors with a higher T_C than that of (1-x)BaTiO$_3$-xKTiO$_2$F solid solution. However, the effect of anion substitution has not been elucidated precisely for KNbO$_3$-based solid solutions. Ladjeroud et al. synthesized the KNbO$_3$-KMgF$_3$ solid solution using a conventional solid-state reaction method under an ambient atmosphere [24]. For this solid solution, only a slight change in the lattice parameter and phase transition temperatures was observed with increasing KMgF$_3$ content, indicating that this solid solution was hardly synthesized using this method and KNbO$_3$ was doped with only a small amount of Mg^{2+} and F^- ions. In this study, the (1-x)KNbO$_3$-xKMgF$_3$ solid solution was synthesized using a sealed silica tube with an oxygen generator or using a high-pressure and high-temperature apparatus. Subsequently, the variation in crystal structure, phase transition temperatures, and dielectric properties of the resulting samples were investigated.

2. Experimental

(1-x)KNbO$_3$-xKMgF$_3$ solid solution was synthesized via a solid-state reaction method using a sealed silica tube with an oxygen generator or using a high-pressure and high-temperature apparatus. The starting materials were K$_2$CO$_3$, Nb$_2$O$_5$, KF and MgF$_2$. A stoichiometric mixture of K$_2$CO$_3$ and Nb$_2$O$_5$ was calcined at 1073 K for 5 h to obtain KNbO$_3$ powder.

The obtained KNbO$_3$ powder, KF, and MgF$_2$ were weighted and mixed in an Ar-filled glove box. The mixture was then dried by evacuating at approximately 500 K for 2 h. For $x \leq 0.03$ and KNbO$_3$, the mixture was pressed into a disk form which was covered with a Pt foil before sealed in a silica tube with the oxygen generator, Ag$_2$O which decomposes and generates O$_2$ gas at a high temperature. The silica tube was heated at 1123 K for 48 h. The oxygen partial pressure in the tube reached approximately 500 kPa at this temperature. The samples synthesized using this method are abbreviated as KNMOF-O$_2$ in this study.

When the samples were synthesized using the high-pressure and high-temperature apparatus, KNbO$_3$ powder, KF, and MgF$_2$ mixture was sealed in a gold capsule in a glove box. The capsule was placed in a pyrophyllite cube block with a NaCl sleeve and a carbon heater. This cube block was placed in a cubic multianvil-type high pressure apparatus (TRY Engineering NAMO2001). The sample was allowed to react at 3 GPa and 1373 K for 1 h. The samples as synthesized were usually reduced. Thus, they were annealed under an oxygen atmosphere at 823 K for 10 h. These samples are denoted as KNMOF-hp.

Phase identification was performed with a powder X-ray diffractometer (BrukerAXS D8 ADVANCE). For KNMOF-O$_2$, high- and low-temperature X-ray diffraction measurements were carried out additionally using this X-ray diffractometer. The lattice parameters were determined with the program TOPAS (BrukerAXS). For KNMOF-hp, synchrotron X-ray diffraction (SXRD) measurements at high and low temperatures were performed. The SXRD data were collected using a Debye-Scherrer camera with an imaging-plate-type detector at the BL02B2 beamline at SPring-8. The wavelength of used to collect data was 0.77506 Å. The annealed powder samples were held in a Lindemann glass capillary tube with an inner diameter of 0.2 mm. During the measurement, the glass capillary was rotated. The data were collected in the temperature range of 200–600 K. The wavelength of the incident synchrotron radiation was determined using a lattice parameter of a CeO$_2$ standard. The Rietveld refinements were performed using a program RIETAN-FP [33].

The dielectric permittivity and dielectric loss were measured in the temperature range of 100–800 K with a handmade probe and precision LCR meter (Agilent Technology precision LCR meter E4980A). For the dielectric permittivity measurement, the bulk samples of KNMOF-hp were annealed at 823 K for 120 h under an oxygen atmosphere. No structural change was confirmed by X-ray diffraction (Fig. A1) after annealing. The obtained sample was a disk-shaped ceramic with about 4 mm in diameter and about 0.5 mm in thickness. Au electrodes were applied on both surfaces of a polished sample using Au sputtering. For $x = 0.05$ (KNMOF-hp), the D–E hysteresis loop was measured using an electroceramic analyzer (aixACT TF analyzer 2000E) at room temperature with a measurement frequency of 100 Hz. It was confirmed by X-ray photoelectron spectroscopy that F^- and Mg^{2+} ions remained in the sample before and after D–E hysteresis loop measurement (Fig. A2).

3. Results and discussion

3.1. Synthesis of KNMOF-O$_2$ and KNMOF-hp

Fig. 1(a) and (b) shows the X-ray diffraction patterns for $x = 0.005$–0.03 (KNMOF-O$_2$) and $x = 0.01$–0.07 (KNMOF-hp), respectively. SEM images of $x = 0.04$ (KNMOF-hp) are also shown in Fig A3. Perovskite-type compounds were obtained with a single phase for all samples. In addition, the structure varied from orthorhombic to rhombohedral for both types of samples with increasing x. The rhombohedral structure was stable at room temperature above $x = 0.01$ and $x = 0.03$ for KNMOF-O$_2$ and KNMOF-hp, respectively. Table 1 is a list of lattice parameters and cell volumes of the perovskite unit cell. Fig. 2 shows the variation in the cell volume for the perovskite-unit cell, V_p, with x. The volume per formula unit of KMgF$_3$ is 64.14 Å^3 [34], which is smaller than that of KNbO$_3$. Therefore, V_p, was predicted to decrease continuously with increasing x. For KNMOF-O$_2$, V_p decreased with increasing x and changed abruptly at the phase boundary. For KNMOF-hp, the variation of V_p was not consistent with the KNMOF-O$_2$ below $x = 0.03$. Above $x = 0.04$, however, the variation of V_p was similar to KNMOF-O$_2$. Hence, the phase transition temperatures, thus, were investigated for KNMOF-O$_2$ with $x \leq 0.03$ and KNMOF-hp with $x \geq 0.04$.

3.2. High- and low-temperature X-ray diffraction for KNMOF-O$_2$ and KNMOF-hp

To determine the phase transition temperature, we focused on 310 and 222 diffraction peaks for a cubic phase because their shape and intensity vary significantly with phase transition. Fig. 3 shows high- and low-temperature X-ray diffraction patterns for $x = 0.005$, 0.01, and 0.02 (KNMOF-O$_2$). For $x = 0.005$, at 648 K, the peaks corresponding to 310 and 222 reflections in a cubic perovskite-type structure were observed at $2\theta = 75^\circ$ and 83.5°, respectively. Below 598 K, the diffraction peak at $2\theta = 75^\circ$ diminished and two peaks corresponding to the 103 reflection and a near overlap of 130 and 031 reflections in the tetragonal phase appeared. Hence, $T_{T\text{-}C}$ could be determined to be between 598–648 K. Below 448 K, the intensities of these peaks changed and three peaks appeared at $2\theta = 83^\circ$. The two peaks around $2\theta = 75^\circ$ were assigned to the near overlap of 024 and 133 reflections and the 311 reflection in the orthorhombic phase. The three peaks around $2\theta = 83^\circ$ were also assigned to the overlap of 204 and 240 reflections in the