Synthesis of the novel perovskite-type oxyfluoride PbScO₂F under high pressure and high temperature

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ABSTRACT

We synthesized a novel perovskite-type oxyfluoride, $PbScO_2F$, and investigated its crystal structure, thermal stability and dielectric properties. $PbScO_2F$ has a cubic perovskite-type structure with Pb ions displaced from the ideal A-site positions along the $\langle 110 \rangle$ direction. By thermal gravity and differential thermal analyses, we found that this compound is stable up to 963 K (690 °C) under ambient atmosphere. The dielectric permittivity of $PbScO_2F$ is approximately 80, at room temperature, which is almost the same as $KTiO_2F$ and smaller than that of $PbFeO_2F$. Furthermore, an anomaly in the dielectric permittivity was observed in the vicinity of 100 K that seems to be related to the displacement of the Pb ions.

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1. Introduction

Many studies on perovskite-type oxides have been performed because these compounds are very interesting in terms of industrial applications and fundamental research. However, many oxides with a perovskite-type structure have already been synthesized, and thus a novel functional material is rarely found in this family of compounds. In the case of the perovskite-type compounds (ABX_3), various combinations of A and B ions allow for a wide variety in these compounds. In an analogous manner, the variability in this family of compounds can be enhanced when we synthesize a perovskite-type compound containing two different anions in which the anion content is precisely controlled. A perovskite-type oxyfluoride is considered to be one of the best candidates.

Perovskite-type oxyfluoride can be categorized into two groups: compounds synthesized under ambient pressure and compounds with the formula ABO_2F or $ABOF_2$ which is generally synthesized under high pressure and temperature. In the former group, the syntheses of $BaLiF_3$–$BaTiO_3$ [1], $BaTiO_3$–$BaZrO_3$–$CaLiF_3$ [2], $BaTiO_3$–$PbLiF_3$ [3], $BaTiO_3$–$BaZrO_3$–$BaLiF_3$ [4], $xSrLiF_3$–$(1-x)$ $BaTiO_3$ $(0 \leqslant x \leqslant 0.25)$ [5], and $xKTiO_2F$–$(1-x)BaTiO_3$ $(x \leqslant 0.1)$ single crystal [6] have been reported. While these compounds can be synthesized by a conventional solid-state reaction method or a flux method, it is difficult to synthesize the compounds containing a large concentration of F ions. On the other hand, the compounds in the latter group are considered good candidates for anion-complex perovskites because of their large F ion content. Nevertheless, only a few compounds, such as $KNbO_2F$, $NaNbO_2F$ [7], $KTiO_2F$ [8], $TlTlOF_2$ [9], $BaFeO_2F$, and $PbFeO_2F$ [10], have been synthesized up until now. Therefore, the systematic research must be carried out to realize the possibility of the perovskite-type oxyfluorides, and we are attempting to synthesize novel or high-purity oxyfluorides in order to characterize these compounds [11,12].

In this study, we synthesize a novel perovskite-type oxyfluoride, $PbScO_2F$, under high pressure and temperature. Furthermore, we investigate its crystal structure and dielectric properties.

2. Experimental

$PbScO_2F$ was synthesized under high pressure and temperature. PbF_2(5N), Sc_2O_3(3N), and PbO(3N) were used as starting materials. The metal content of Sc_2O_3 was determined volumetrically with ethylenediaminetetraacetic acid (EDTA) because Sc_2O_3 easily adsorbs CO_2 and H_2O. A well-grounded stoichiometric mixture of these materials was dried by evacuating at approximately 250 °C for one night. The dried powder was packed in an Au capsule (0.2 mm in thickness, 3.1 mm in inner diameter and 3.2 mm in depth). The capsule was placed in a pyrophyllite cube block with a NaCl sleeve and a carbon heater, and the block was then set in a cubic multi-anvil-type high-pressure apparatus (TRY Engineering NAMO2001). The reaction was carried out at

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4 GPa and 1000 °C for 30 min. Phase identification was executed with a powder X-ray diffractometer (Rigaku RINT 2100, graphite-monochromatized Cu $K\alpha$). A Rietveld refinement was carried out using the program RIETAN 2000 [13]. The X-ray diffraction data were collected in the range of $2\theta = 20$–$120°$ at $0.02°$ intervals for the refinement. A thermogravimetric analysis/differential thermal analysis (TG/DTA) was performed with a TG-DTA2000S (BRUKERaxs). The sample was heated at a rate of 10 °C/min from room temperature to 700 °C under ambient atmosphere. The dielectric properties were measured with a precision LCR meter (Agilent technology 4284A) in the temperature range from 300 to 8 K. Au electrodes were attached on both surfaces of a pelletized sample by sputtering. The density of the sample used in this measurement and the ideal density of PbScO$_2$F are 4.497 and 7.125 g/cm^3, respectively.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern and refined pattern produced by the Rietveld method. A compound with a cubic perovskite-type structure was obtained, though the trace-amount impurities were present, as shown in the inset of Fig. 1. While PbO and AuPb$_3$ were identified as the impurities, the origins to the other weak peaks have not yet been determined. At present, the synthesis condition used in this study seems to be the most suitable (see Figs. S1 and S2 in the Supporting Information). The structure could be refined on a structure model as belonging to the space group $Pm\bar{3}m$, an ideal cubic perovskite structure. In this model, however, the isotropic atomic displacement factor of the Pb ions was abnormally large ($B(\mathrm{Pb}) = 5.22(3)\,\text{Å}^2$), which indicates a structural disorder in the Pb ions. We then investigated this disorder with three types of disorder models where the Pb ions are displaced along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. In this study, the structure models with $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ displacements are referred to as the $\langle 100 \rangle$ model, the $\langle 110 \rangle$ model, and the $\langle 111 \rangle$ model, respectively. Table 1 shows the R factors obtained for all models. While the R_{wp}s are comparable among these disorder models, both the R_{I} and the R_{F} of the $\langle 110 \rangle$ model are the smallest among the disorder models. On the other hand, the R_{wp} and R_{I} of the non-disorder model (usual $Pm\bar{3}m$) are smaller than that of the $\langle 110 \rangle$ model. In this study, however, we considered that the $\langle 110 \rangle$ model is most plausible, because the isotropic atomic displacement factor of the Pb ions in the $\langle 110 \rangle$ model is reasonable and the displacement of

the Pb ions along the $\langle 110 \rangle$ direction was observed in an analogous oxyfluoride, PbFeO$_2$F [11]. Fig. 1 and Table 2 show the X-ray diffraction pattern with the refinement using the $\langle 110 \rangle$ model and the refined structure parameters, respectively. As shown in this table, the temperature factor of the anion is abnormally large. While the structural disorder in the anion could be considered as well as that in the Pb ions, we did not investigate the disorder in the anions because of the difficulty involved in determining the anion position with powder X-ray diffraction. The crystal structure of PbScO$_2$F is shown in Fig. 2.

Fig. 3 shows the TG/DTA curve for PbScO$_2$F. A gradual decrease in the mass of the sample was observed below 300 and above 600 °C. In addition, a drastic decrease and exothermic peak were also observed at approximately 700 °C on the TG and DTA curves, respectively. To determine the cause for the mass loss below 300 °C, we annealed the sample at 400 °C for 8 h under ambient atmosphere and compared the X-ray diffraction pattern of this sample with that of the sample before annealing. No change was observed in the X-ray diffraction pattern: thus, the mass change below 300 °C is attributed to the desorption of adsorbates. On the

Table 1
R factors and isotropic atomic displacement factors for the Pb ions for all structure models

R value	Structure model			
	Non-disorder	$\langle 100 \rangle$ model	$\langle 110 \rangle$ model	$\langle 111 \rangle$ model
R_{wp} (%)	8.03	8.12	8.13	8.15
R_{I} (%)	5.47	5.40	4.81	5.04
R_{F} (%)	7.94	8.71	8.31	9.44
B (Å^2)	5.22(3)	1.7(2)	0.6(5)	1.0(3)

Table 2
Structure parameters refined using the $\langle 110 \rangle$ structure model[a]

Ion	Site	Occ.	x	y	z	B (Å^2)
Pb	12i	1/12	0.066(2)	0.066 ($= x$)	0	0.6(5)
Sc	1b	1	1/2	1/2	1/2	0.4(1)
X (O/F)	3c	1	0	1/2	1/2	2.5(2)

[a] Space group $Pm\bar{3}m$ (no. 221), formula PbScO$_2$F, $a = 4.134(2)\,\text{Å}$, $R_{\mathrm{wp}} = 8.13\%$, $R_{\mathrm{p}} = 6.28\%$, $R_{\mathrm{I}} = 4.81\%$, $R_{\mathrm{F}} = 8.31\%$, $S = 2.45$.
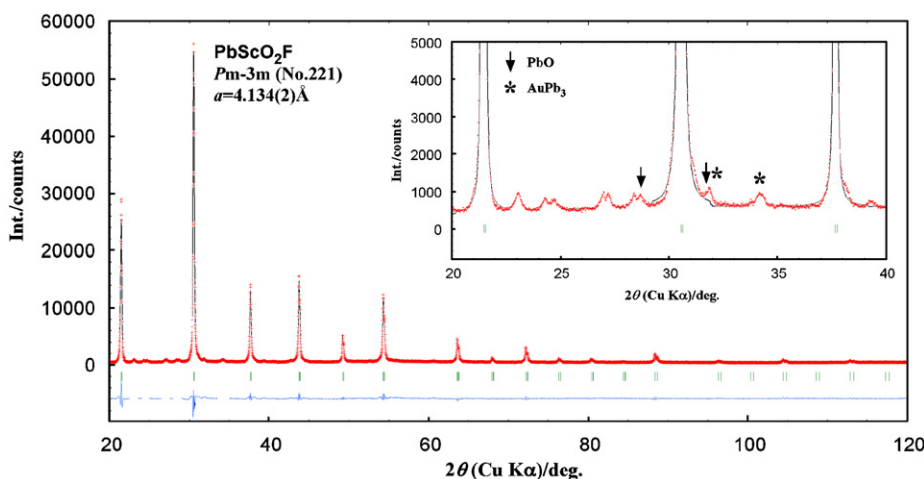

Fig. 1. Experimental (red cross), calculated (black line) and difference (blue line) X-ray patterns for PbScO$_2$F. The green bars indicate the calculated peak positions. The inset shows the weak peaks due to the impurities in the low angle region.
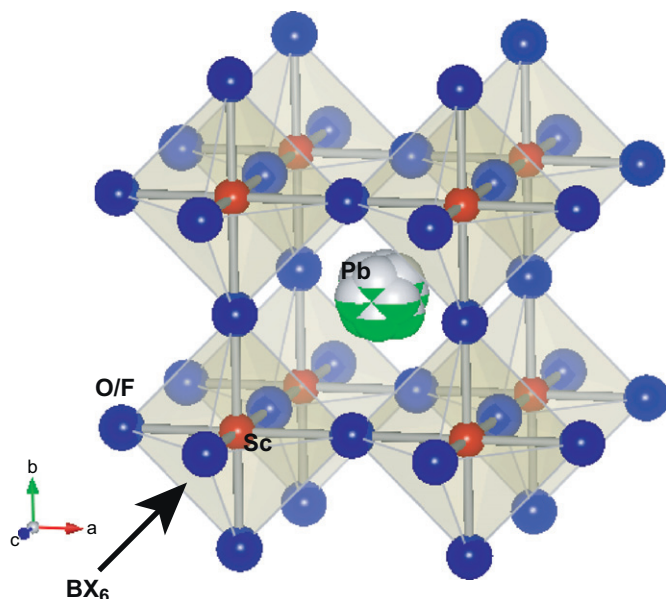
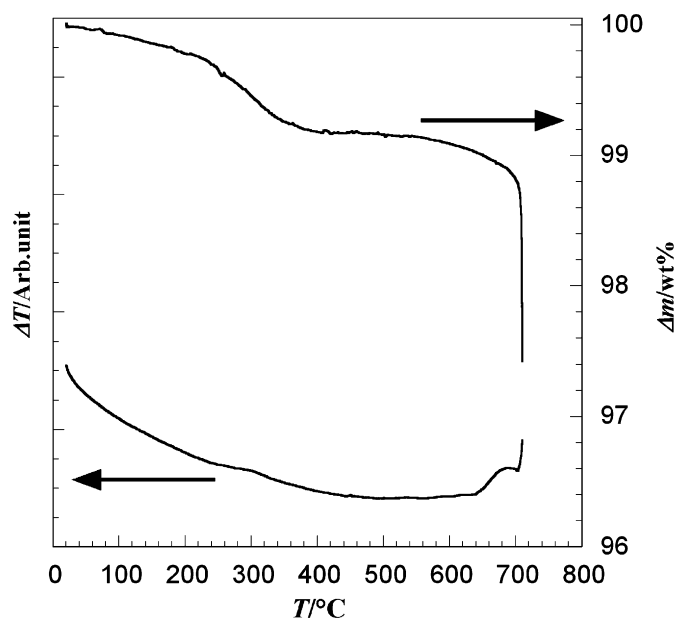**Fig. 2.** Crystal structure of $PbScO_2F$ produced by the program VESTA [14].

Fig. 4. Temperature dependence of the dielectric permittivity and the dielectric loss for $PbScO_2F$.

Fig. 3. TG/DTA curve of $PbScO_2F$.

Fig. 5. Temperature dependence of the dielectric permittivity of perovskite-type oxyfluorides, $PbScO_2F$, $PbFeO_2F$, and $KTiO_2F$.

other hand, it was confirmed by powder X-ray diffraction that the $PbScO_2F$ decomposed to PbO, PbF_2, Sc_2O_3, and an unknown phase after the TG/DTA measurement. Therefore, the $PbScO_2F$ decomposed at 690 °C and the decrease in the mass in the vicinity of 700 °C is likely due to the volatilization of PbF_2 and/or PbO.

Fig. 4 shows the temperature dependence of the dielectric permittivity and dielectric loss. The dielectric constant was approximately 80 at room temperature and gradually decreased with decreasing the temperature. In the vicinity of 100 K, an anomaly with the frequency dispersion was observed. At this temperature, a slight peak was observed for the dielectric loss. Fig. 5 provides a comparison of the temperature dependence of the dielectric permittivity among perovskite-type oxyfluorides, $PbScO_2F$, $PbFeO_2F$, and $KTiO_2F$. The dielectric constants of $PbScO_2F$ is lower than and the same as the dielectric constant of $PbFeO_2F$ and $KTiO_2F$, respectively, at room temperature. Usually, the
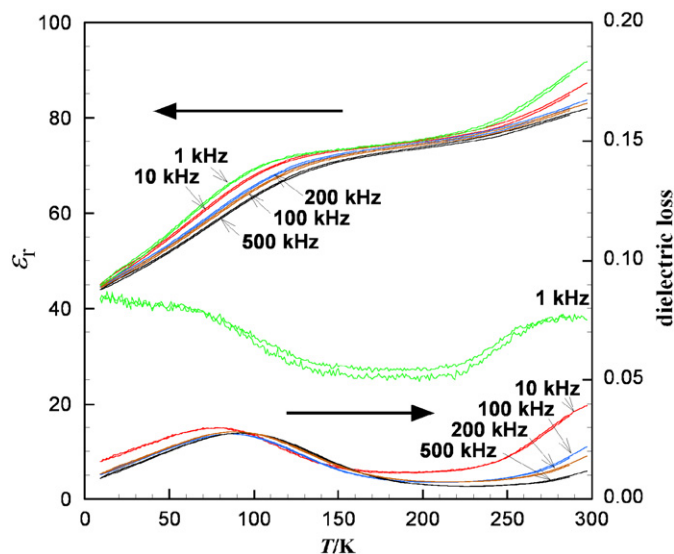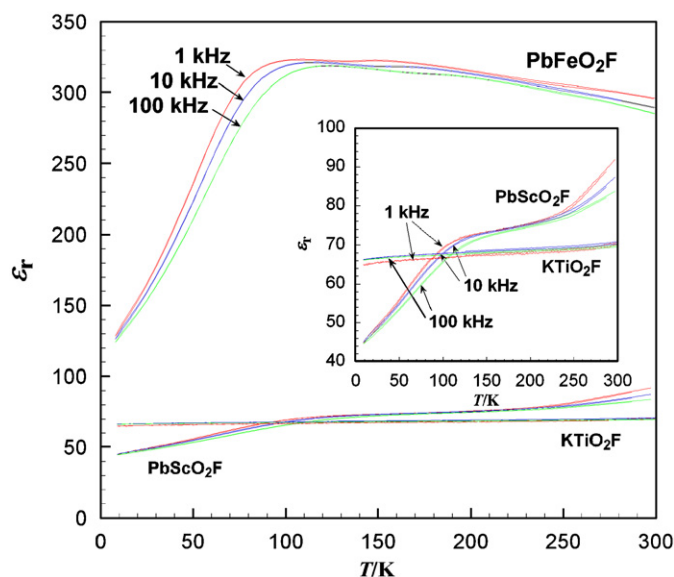
Pb-containing perovskites show a high dielectric permittivity. The dielectric permittivity of $PbScO_2F$, however, is smaller than and almost equal to that of $PbFeO_2F$ and $KTiO_2F$, respectively. The cause of the smaller dielectric permittivity of the $PbScO_2F$ has not been determined yet.

The temperature dependence of $PbScO_2F$ is similar to that of the $PbFeO_2F$, i.e. the dielectric permittivity decreases below 100 K, and a slight frequency dispersion is observed in the vicinity of 100 K. In contrast, the dielectric permittivity of $KTiO_2F$ is almost constant in this temperature range. By neutron diffraction of $PbFeO_2F$ at low temperature, it was found that the direction of the displacement of the Pb ion changes from $\langle 110 \rangle$ to $\langle 111 \rangle$ below 98 K, although obvious structural changes in accordance with a phase transition were not observed in the temperature range from room temperature to 4.8 K [15]. Therefore, we consider the anomalies in the vicinity of 100 K in the permittivity of $PbFeO_2F$

to be related to the displacement of the Pb ions and the anomalies observed for PbScO$_2$F are also probably related to the displacement of the Pb ion.

4. Conclusion

We synthesized a novel perovskite-type oxyfluoride, PbScO$_2$F, under high pressure and temperature and investigated its crystal structure, chemical stability and dielectric properties. PbScO$_2$F has a cubic perovskite-type structure where the Pb ions are displaced along the $\langle 110 \rangle$ direction. According to TG/DTA analysis, it was found that the PbScO$_2$F is stable up to 963 K (690 °C) under ambient atmosphere. The dielectric permittivity is 80 at room temperature, which is smaller than that of the analogous compound, PbFeO$_2$F. The dielectric permittivity of PbScO$_2$F decreased slightly with decreasing temperature and frequency dispersion was observed in the vicinity of 100 K, which is probably related to the displacement of the Pb ions.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.06.048.

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