Perovskite-Type Oxyfluoride Phases in the $\text{ABO}_3\text{--BaLiF}_3$ Systems ($\text{A} = \text{Ba}, \text{Ca}$ and $\text{B} = \text{Ti}, \text{Zr}$)

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$\text{ABO}_3\text{--BaLiF}_3$ におけるペロブスカイト型酸フッ化物相 ($\text{A} = \text{Ba}, \text{Ca}$, $\text{B} = \text{Ti}, \text{Zr}$)

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Perovskite-type oxyfluoride systems, $\text{ABO}_3\text{--BaLiF}_3$ ($\text{A} = \text{Ba}, \text{Ca}$ and $\text{B} = \text{Ti}, \text{Zr}$) were investigated. In the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system, cubic phases appeared in the range, $0.2 \leq x \leq 0.4$. In the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system, orthorhombic phases different from CaZrO_3 appeared in the range, $0.4 \leq x \leq 0.5$. The lattice volumes of the new phases were larger than those of the respective end-members. On the other hand, the $\text{Ca}_{1-x}\text{Ba}_x\text{Ti}_{1-x}\text{Li}_x\text{O}_{3(1-x)}\text{F}_{3x}$ samples showed two phases of CaTiO_3 and BaLiF_3 , of which lattice constants were almost independent of the composition. [Received April 19, 2006; Accepted October 19, 2006]

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1. Introduction

Though many perovskite-type oxides have been synthesized, there are only few reports concerning perovskite-type oxyfluorides. Benziada and Claverie¹⁾ tried to add $\text{CaF}_2\text{--}4\text{LiF}$ to BaTiO_3 in order to revise the sintering behavior and the dielectric properties. Benziada and Kermoun²⁾ have reported that an orthorhombic phase having a NaNbO_3 -type structure was obtained by firing $(1-x)\text{SrTiO}_3 + x\text{SrF}_2 + x\text{LiF}$ ($0.03 \leq x \leq 0.05$) mixtures at 1223 K in air. Recently, Benziada³⁾ has found that an orthorhombic phase of CaTiO_3 remained up to $x = 0.25$ in the $(\text{Ca}_{1-x}\text{Sr}_x)(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ system.

On the other hand, many oxyfluorides having a fluorite-related structure have been reported in relation with ionic conduction. Esaka et al.⁴⁾ reported LaOF-type phase in a $\text{La}_2\text{O}_3\text{--MgF}_2$ system. Takashima et al.^{5)–7)} have studied the crystal structure and ionic conductivity of binary rare-earth metal oxyfluorides.

In the present study, existing phases were investigated in the perovskite-type oxyfluoride systems, $\text{ABO}_3\text{--BaLiF}_3$ ($\text{A} = \text{Ba}, \text{Ca}$ and $\text{B} = \text{Ti}, \text{Zr}$).

2. Experimental procedures

All the samples for the $(1-x)\text{ABO}_3\text{--}x\text{BaLiF}_3$ system were prepared by a solid-state reaction ($\text{A} = \text{Ba}, \text{Ca}$ and $\text{B} = \text{Ti}, \text{Zr}$). BaCO_3 (99.9%, Wako Chem. Co.), CaCO_3 (99.9%, Wako Chem. Co.), TiO_2 (anatase type) (99.9%, Wako Chem. Co.) and ZrO_2 (99.9%, Tosoh Co.) were used as starting materials for the corresponding perovskite-type oxides. BaLiF_3 was prepared by firing the mixed powders of BaF_2 (99.9%, Wako Chem. Co.) and LiF (98%, Wako Chem. Co.) at 973 K for 10 h under the Ar gas flow ($200 \text{ dm}^3 \text{ min}^{-1}$), before the preparation of the solid solution samples. The powder compacts of the starting materials for the perovskite oxide and BaLiF_3 were placed into a powder-bed which has the same composition as the compact sample, and then calcined at 873 K. After regrinding the calcined samples, the powder compacts were fired at 1073–1273 K for 10 h in the same powder bed under the Ar gas flow. In order to prevent from vaporization of Li and F, the firing procedures were

Table 1. Firing Conditions of the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ System

Composition (x)	Calcination	Sintering
0.0	1273 K-10 h	1573 K-10 h
0.2	873 K-10 h	1173 K-10h
0.4	873 K-10 h	1073 K-10 h
0.5	973 K-10 h	1073 K-10h
0.6	873 K-10 h	1073 K-10 h
0.8	873 K-10 h	973 K-10 h
1.0	823 K-10 h	973 K-10 h

Remarks: The samples containing Li and F were fired under Ar gas flow.

carried out at lower temperatures than their vaporization temperature determined from thermogravimetry (TG) and mass spectrometry (MS) for the calcined powders. The typical firing conditions are summarized in **Table 1** for the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ samples. The samples of the other systems were also fired under the similar firing conditions.

Powdered samples were characterized by X-ray diffractometry (XRD) (model: RAD-A, Rigaku Co.) with monochromated $\text{Cu K}\alpha$ radiation. The lattice constants were determined by a least square method, using Si powder as an external standard. The Rietveld refinement for the powder XRD patterns of BaLiF_3 was carried out using the RIETAN-2000 program⁸⁾ at room temperature. X-ray photoelectron spectrometry (XPS) was applied in order to confirm the existence of F and Li. F content for the typical samples was estimated from the XPS data. As chemical analysis has not been carried out, the nominal composition (x) was presented in this paper.

Fig. 1. XRD patterns for the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system in the 2θ ranges, a) $44\text{--}46^\circ$ and b) $55\text{--}57^\circ$.

3. Results and discussion

(a) $\text{BaTiO}_3\text{--BaLiF}_3$ system

BaTiO_3 was a tetragonal perovskite-type phase ($a=0.3995$, $c=0.4031$ nm, $V=0.06433$ nm³) and that BaLiF_3 was a cubic perovskite-type one ($a=0.3995$ nm, $V=0.06377$ nm³). These observed lattice parameters agreed well with the reported values.^{9),10)} The lattice volume of BaTiO_3 was close to that of BaLiF_3 . Furthermore, the Rietveld refinement confirmed that BaLiF_3 has Ba^{2+} at A site and Li^+ at B site in ABF_3 perovskite structure with the space group of $Pm\bar{3}m$. Traces of oxygen were detected for BaLiF_3 by XPS.

BaTiO_3 changed to a cubic phase at $x=0.2$ and then a set of new broad diffraction peaks appeared at $x=0.4$, as shown in Fig. 1. The new peaks were indexed on the basis of the cubic perovskite lattice. The estimated lattice parameter of $x=0.4$ was $a=0.4017$ nm. The observed and calculated d -values of the cubic phase are given in Table 2. Though the lattice volume of BaTiO_3 was close to that of BaLiF_3 , the lattice volume of $x=0.4$ (0.06482 nm³) was larger than their values. Two phases composing of the new cubic phase and BaLiF_3 appeared in the composition range, $0.5 \leq x \leq 0.8$. The lattice volume of BaLiF_3 decreased by increasing the composition (x) (Fig. 2). The broad diffraction peaks of the new cubic phase may originate from a crystal imperfection and/or a compositional fluctuation.

The F contents for the typical samples are summarized in Table 3, where the area intensity of the F peak in XPS was normalized using that of BaLiF_3 ($x=1.0$). Though the F content did not agree completely with the nominal composition, the vaporization of F could be suppressed to a minimum.

(b) $\text{CaZrO}_3\text{--BaLiF}_3$ system

Figure 3 shows XRD patterns of the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ samples. A set of new diffraction peaks appeared at $x=0.4$, suggesting the formation of a new oxyfluoride phase. In the composition range, $0.6 \leq x \leq 0.8$, two phases of the oxyfluoride and BaLiF_3 appeared. The diffraction peaks of the new phase were tentatively indexed on the basis of the orthorhombic lattice of CaZrO_3 . Most of the peaks were indexed by the orthorhombic lattice different from CaZrO_3 , while the peaks having $d=0.3153$ and 0.2012 nm were not

Table 2. Observed and Calculated d -values for the Sample with $x=0.4$ in the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ System

hkl	Intensity	$d_{\text{obs.}}$ (nm)	$d_{\text{calc.}}$ (nm)*
100	17	0.4016	0.4017
110	100	0.2839	0.2841
111	38	0.2320	0.2319
200	46	0.2009	0.2009
210	17	0.1797	0.1797
211	54	0.1640	0.1640
220	28	0.1421	0.1420
300	8	0.1339	0.1339
310	19	0.1271	0.1270

Note 1) $d_{\text{calc.}}$ was calculated by use of lattice constant,

$$a = 0.4017 \text{ nm.}$$

2) Standard deviation between $d_{\text{obs.}}$ and $d_{\text{calc.}}$ was 0.0001 nm.

Fig. 2. Lattice volume as a function of composition (x) in the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system; BaTiO_3 (●), new cubic phase (■) and BaLiF_3 (▲) phases.

indexed. The lattice parameters estimated for $x=0.5$ were $a=0.5964$, $b=0.8369$ and $c=0.5941$ nm ($V=0.2965$ nm³ for $Z=4$). The observed and calculated d -values of $x=0.5$ are given in Table 4, where the d -values agreed with each other. The lattice volume of the new phase was also larger than those of CaZrO_3 ($V=0.258$ nm³ for $Z=4$) and BaLiF_3 ($V=0.2554$ nm³ for $Z=4$), as seen in the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system. On the other hand, the lattice volume of $x=0.5$ was close to that of BaZrO_3 ($V=0.2948$ nm³ for $Z=4$). Since the new phase might have been corresponded to BaZrO_3 , $\text{Ba}(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ samples were synthesized. The XRD of $x=0.5$ showed the mixed phases composing of BaZrO_3 and BaLiF_3 . The new orthorhombic phase of $x=0.5$ in the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system could be the oxyfluoride. The F contents in the $\text{CaZrO}_3\text{--BaLiF}_3$ system are also given in Table 3.

Table 3. F Content Estimated from XPS Peaks in the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ and $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$

comp.(x)	calc. value (3x)	obs. value	
		$\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$	$(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$
0.2	0.6	0.57	0.90
0.5	1.5	1.3	1.7
0.8	2.4	2.5	2.7

Table 4. Observed and Calculated d -values for the Sample with $x=0.5$ in the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ System

hkl	Intensity	$d_{\text{obs.}}$ (nm)	$d_{\text{calc.}}$ (nm)*
020	1	0.4189	0.4184
121	100	0.2965	0.2968
012	1	0.2829	0.2809
220	8	0.2420	0.2421
131	< 1	0.2326	0.2325
202	62	0.2096	0.2105
310	5	0.1933	0.1927
301	< 1	0.1875	0.1880
042	49	0.1711	0.1713
150	2	0.1617	0.1611
242	22	0.1482	0.1484
060	< 1	0.1398	0.1395
421	< 1	0.1365	0.1363
161	18	0.1326	0.1324
062	1	0.1264	0.1263
260	< 1	0.1256	0.1263
351	< 1	0.1252	0.1250
440	< 1	0.1210	0.1211

Fig. 3. XRD patterns for the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system. The peaks of $x=0.5$ were indexed by the orthorhombic lattice.

(c) $\text{CaTiO}_3\text{-BaLiF}_3$ system

There existed two phases of CaTiO_3 and BaLiF_3 in the composition range, $0.2 \leq x \leq 0.8$ of in the system $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$. The lattice volumes of CaTiO_3 and BaLiF_3 were almost independent of the composition (Fig. 4).

4. Summary

- (1) The cubic perovskite phase was obtained for $x=0.4$ in the $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system, of which lattice parameter ($a=0.4017$ nm) was larger than those of the end-members.
- (2) The new orthorhombic phase having lattice parameters, $a=0.5964$, $b=0.8369$ and $c=0.5941$ nm was observed at $x=0.5$ in the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Zr}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system, of which lattice volume was also larger than those of the end-members.
- (3) There was no solid solution in the $\text{CaTiO}_3\text{-BaLiF}_3$ system.

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Note 1) d_{calc} was calculated using the lattice constant, $a = 0.5941$, $b = 0.8369$, $c = 0.5964$ nm.

2) Standard deviation between $d_{\text{obs.}}$ and $d_{\text{calc.}}$ was 0.0006 nm.

Fig. 4. Lattice volume as a function of composition (x) in the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3(1-x)}\text{F}_{3x}$ system; CaTiO_3 (●) and BaLiF_3 (■) phases.

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