

# Crystal structures of solid solution $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ system

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**Abstract.** The solid solutions of  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  are synthesized in a wide composition range with a solubility limit of  $x = 0.8$ . In the present study, the crystal structures are determined by a synchrotron X-ray diffraction and an electron diffraction method. The crystal structure of  $\text{Ba}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  ( $x = 0$ ) has a cubic symmetry ( $Fm\bar{3}m$ ) with atomic parameters of about 0.8 nm ( $2 \times 2 \times 2$  cells) judging by the appearance of very weak 111 reflections. The reflection intensity depends on the ordering in the B-cation. Furthermore, structural changes occur in the crystal symmetry, where the symmetries tend to decrease with increasing Ca content. This is controlled by the  $\text{BO}_6$  tilting system, since the cell sizes become smaller with increasing Ca content. Consequently, in the B-site,  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$  ions come to have an orderly arrangement with increasing Ca content.

## 1. Introduction

The development of high-performance dielectric material is needed for microwave communication circuits. In general, the paraelectric properties of the perovskite oxides change as a matter of course by partial substitutions of their A-site ion or B-site ion. Various double perovskites have been studied with systems of  $(\text{A}_{1-x}\text{A}'_x)(\text{Mg}^{2+}_{1/3}\text{Ta}^{5+}_{2/3})\text{O}_3$  ( $\text{A}, \text{A}' = \text{Ba}, \text{Sr}, \text{Ca}$ ;  $\text{B} = \text{Mg}, \text{Zn}$ ) and  $\text{A}_2\text{B}^{3+}\text{M}^{5+}\text{O}_6$  ( $\text{A} = \text{Ba}, \text{Sr}$ ;  $\text{B} = \text{rare earth}$ ,  $\text{M} = \text{Sb}, \text{Nb}, \text{Ta}$ ) [1-3]. To design such new material, crystal structural analysis is important for clarifying the mechanisms of the electrical properties.

Recently, Ikawa et al. have succeeded in synthesizing a new solid solution of  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  ( $0 \leq x \leq 0.8$ ) in a wide composition range [4]. Substitution of the Sc ion in the B-site might be successful for synthesis in the wide composition range of in the solid solution. The detailed structures of  $\text{A}_2\text{B}^{3+}\text{TaO}_6$  and  $\text{A}_2\text{B}^{3+}\text{NbO}_6$  have been reported;  $\text{Ba}_2\text{ScNbO}_6$  is a cubic structure with a space group of  $Fm\bar{3}m$ , and  $\text{Ca}_2\text{ScNbO}_6$  is a monoclinic structure with  $P2_1/n$  [5]. The crystal structure of the perovskite has been investigated systematically by tilting systems describing  $\text{BO}_6$  octahedral tilting. The magnitude of distortion in the tilt systems is estimated by substitutions in the A-site or B-site of double perovskite [6]. In this solid solution system, structural change can be expected from a cubic symmetry to a monoclinic symmetry. The detailed structure was determined with a synchrotron X-ray diffraction and an electron diffraction method. We discuss the changes in the structure related to the tilt system of the perovskite structure.

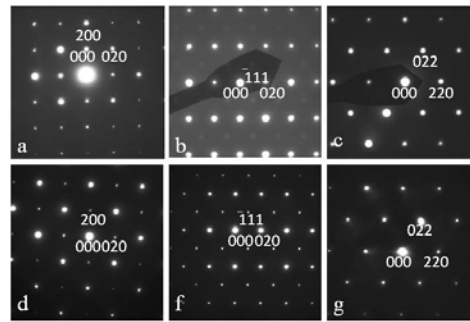
## 2. Experimental procedure

Starting materials used were BaCO<sub>3</sub>, CaCO<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> (> 99.9% grade) to prepare the solid solution of (Ba<sub>1-x</sub>Ca<sub>x</sub>)(Sc<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>. After the first and second calcinations at 1473 K for 12 h and 9 h, respectively, the mixtures were sintered at 1923 K for 12 h in air. The detailed procedure was previously described [4].

The structures of the obtained specimens were analyzed by electron diffraction (JEM-2100F, JEOL, Tokyo, Japan) and by synchrotron X-ray diffraction at the KEK-PFBL-4B2 experimental station in Tsukuba, Japan.

The high-resolution images and chemical compositions were taken by a transmission electron microscope (TEM) equipped with energy-dispersive spectroscopy (EDS).

## 3. Results and discussions



**Figure 1.** SAED patterns of oxides in (a)-(c)  $x = 0$ , (d)-(g)  $x = 0.3$ . Zone axes are [001] in (a) and (d), [101] in (b) and (f), and [111] in (c) and (g).

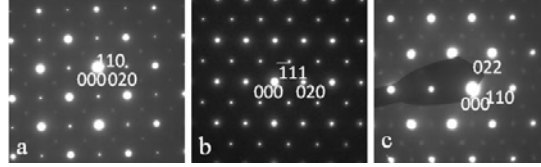
The selected area diffraction (SAED) patterns of oxides ( $x = 0, 0.3, 0.5, 0.8$ ) were taken from several zone axes, and the chemical composition of each grain was determined by EDS. These chemical compositions were calculated from the EDS results as 1.0 of the total metal cations: Ba(Sc<sub>0.43</sub>Nb<sub>0.57</sub>)O<sub>3</sub>, Ba<sub>0.72</sub>Ca<sub>0.28</sub>(Sc<sub>0.45</sub>Nb<sub>0.55</sub>)O<sub>3</sub>, Ba<sub>0.54</sub>Ca<sub>0.46</sub>(Sc<sub>0.43</sub>Nb<sub>0.57</sub>)O<sub>3</sub>, and Ba<sub>0.21</sub>Ca<sub>0.79</sub>(Sc<sub>0.44</sub>Nb<sub>0.56</sub>)O<sub>3</sub>. In the B-site, the ratio of Sc ion was lower because a small amount of a second phase of Sc<sub>2</sub>O<sub>3</sub> was detected in the matrix. The charge valence of the oxide might be maintained by a defect of the A-cation.

**Table 1.** Atomic parameters of oxides refinement by Rietveld analysis

	site	Atom	Occupancy	$x$	$y$	$z$
Ba <sub>0.98</sub> (Sc <sub>0.48</sub> Nb <sub>0.52</sub> )O <sub>3</sub> $a = 0.823810(1)$ nm $R_{wp} = 8.57$ %	8c	Ba <sup>2+</sup>	0.980(10)	1/4	1/4	1/4
	4a	Nb <sup>5+</sup> /Sc <sup>3+</sup>	0.52/0.58	0	0	0
	4b	Sc <sup>3+</sup> /Nb <sup>5+</sup>	0.48/0.52	1/2	1/2	1/2
	24e	O <sup>2-</sup>	1	0.25(8)	0	0
(Ba <sub>0.7</sub> Ca <sub>0.3</sub> ) <sub>0.98</sub> (Sc <sub>0.48</sub> Nb <sub>0.52</sub> )O <sub>0.3</sub> $a = 0.815908(0)$ nm $R_{wp} = 5.60$ %	8c	Ba <sup>2+</sup> /Ca <sup>2+</sup>	0.686/0.294	1/4	1/4	1/4
	4a	Nb <sup>5+</sup> /Sc <sup>3+</sup>	0.787/0.213	0	0	0
	4b	Sc <sup>3+</sup> /Nb <sup>5+</sup>	0.748/0.252	1/2	1/2	1/2
	24e	O <sup>2-</sup>	1	0.2483(7)	0	0

Figure 1 shows typical SAED patterns of oxides ( $x = 0$  and  $0.3$ ). The reflections were indexed as cubic structures of about 0.8 nm ( $2 \times 2 \times 2$  cells) in the oxides. These SAED patterns were clearly different with increasing Ca content. In Fig. 1(b), very weak 111 reflection and equivalent reflections were detected. The reflections were caused by the ordering of the Sc and Nb ions in the B-site [5]. The unit cell size should be  $2 \times 2 \times 2$  cells by the appearance of the 111 reflection. The crystal symmetry of the oxide was expected to be cubic with a space group of  $Fm\bar{3}m$ . In the oxide ( $x = 0.3$ ), the 111

reflection intensity became stronger with increasing Ca content in the same crystal symmetry. This means that the Sc and Nb ions were arranged in a more orderly manner in the B-site due to the reduction in cell size with increasing Ca content. The synchrotron X-ray diffraction analysis was carried out based on the results. Atomic parameters refined by Rietveld analysis are shown in Table 1. The  $R_{wp}$  value of the oxide ( $x = 0$ ) was higher, since very weak 111 reflections could not be detected by the synchrotron X-ray diffraction method.



**Figure 2.** SAED patterns of oxide ( $x = 0.5$ ) taken from the [001] axis in (a), [101] axis in (b), [111] axis in (g).

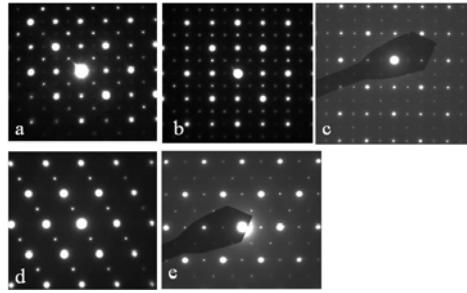
In the oxide ( $x = 0.5$ ), weak 110 reflection appeared as shown in Fig. 2. Therefore, the crystal symmetry was not in agreement with  $Fm\bar{3}m$ . The crystal structure with  $Fm\bar{3}m$  belongs to a non-tilting system described as  $a^0 a^0 a^0$  in the perovskite structure [5]. By reduction of the cell size, the structure should change from a non-tilting to a tilting system. The pattern of the synchrotron X-ray diffraction showed broad peaks in the high-angle range. This means that the crystal structure is not a cubic symmetry. We considered some possible crystal symmetries based on the extinction rule from the SAED patterns. Finally, the space group of  $C2/c$  (No. 15) was adopted as the most possible symmetry. The symmetry belongs to a two-tilt system as  $a^0 b^+ c^-$ . Atomic parameters refined by Rietveld analysis are shown in Table 2.

**Table 2.** Atomic parameters of  $(Ba_{0.5}Ca_{0.5})_{0.98}(Sc_{0.48}Nb_{0.52})O_3$  refinement by Rietveld analysis

site	Atom	Occupancy	$x$	$y$	$z$
4e	Ba <sup>2+</sup> /Ca <sup>2+</sup>	0.4925/0.4925	0	0.0053(2)	1/4
4e	Ba <sup>2+</sup> /Ca <sup>2+</sup>	0.4925/0.4925	0	0.4975(2)	1/4
4c	Nb <sup>5+</sup> /Sc <sup>3+</sup>	0.823/0.177	1/4	1/4	0
4d	Sc <sup>3+</sup> /Nb <sup>5+</sup>	0.793/0.207	1/4	1/4	1/2
8f	O <sup>2-</sup>	1	0.2352(3)	0.0100(2)	0
8f	O <sup>2-</sup>	1	0.00100	0.2648	-0.0421(2)
8f	O <sup>2-</sup>	1	0.2079(12)	0.25	0.24

$$a = 0.868(8) \text{ nm}, b = 0.80865(3) \text{ nm}, c = 0.80876(8) \text{ nm}, \beta = 90.000(10) \text{ degree}, R_{wp} = 5.11\%$$

Furthermore, the crystal symmetry became lower in the oxide ( $x = 0.8$ ). We noticed that there were many nano-twin domains in the TEM images taken from the [001] zone axis as a pseudo-cubic cell. In the cubic cell, no domains could be observed along the [001] zone axis because [100] and [010] are equivalent. Therefore, we took the SAED pattern using the smallest aperture of the selected area diffraction. The diffraction patterns in Fig. 3(a) and (b) are taken from the near area. The superposed pattern was composed by twinning in Fig. 3(c). The (100) spacing was nearly equal to the (010) spacing, and the split reflections were not observed in Fig. 3(c). Along the [111] zone axis, the superposed pattern of Fig. 3(e) is composed of three patterns in Fig. 6(d) rotated by 60°. Such a nano-twin structure has also been observed in a double perovskite  $(Sr_{0.67}Sm_{0.33})(Mn_{0.33}Ti_{0.67})O_3$  with a space group of  $Pnma$  [7]. Finally, the space group of  $P2_1/n$  (No. 14) was adopted as the most possible symmetry. The symmetry belongs to a three-tilt system as  $a^+ b^- c^-$ . Atomic parameters refined by Rietveld analysis are shown in Table 3.



**Figure 3.** SAED patterns of oxide ( $x = 0.8$ ) taken from the  $[001]$  axis in (a) -(c),  $[111]$  axis in (d)-(e) as a pseudo-cubic.

**Table 3.** Atomic parameters of  $(\text{Ba}_{0.2}\text{Ca}_{0.8})_{0.96}(\text{Sc}_{0.46}\text{Nb}_{0.54})\text{O}_3$  refinement by Rietveld analysis

Atom	Occupancy	$x$	$y$	$z$
$\text{Ba}^{2+}/\text{Ca}^{2+}$	0.1927/0.7671	0.0004(4)	-0.01573(13)	0.26389(5)
$\text{Nb}^{5+}/\text{Sc}^{3+}$	0.741/0.259	0	1/2	0
$\text{Sc}^{3+}/\text{Nb}^{5+}$	0.668/0.332	1/2	0	0
$\text{O}^{2-}$	1	0.2539(7)	0.2591	-0.0460(2)
$\text{O}^{2-}$	1	0.2591	0.2539	0.5460
$\text{O}^{2-}$	1	0.4080	0.0100(10)	0.2526

$a = 0.56312(2)$  nm,  $b = 0.563484(18)$  nm,  $c = 0.79673(3)$  nm,  $\beta = 89.951$  degree,  $R_{\text{wp}} = 6.13\%$

## 5. Conclusion

The crystal structures of oxides of  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  ( $0 \leq x \leq 0.8$ ) were determined with a synchrotron X-ray diffraction and an electron diffraction method. The chemical compositions were analyzed by energy-dispersive spectroscopy. The oxide ( $x \leq 0.3$ ) possessed a cubic cell ( $Fm\bar{3}m$ ) in a non-tilt system due to the ordering of Sc and Nb ions. With increasing Ca content, Sc and Nb became arranged in a more orderly way. Through a reduction in the cell size, the structure changed from a non-tilting to a tilting system. The oxide ( $x = 0.5$ ) possessed a monoclinic cell ( $C2/c$ ) in a two-tilt system, and the oxide ( $x = 0.8$ ) possessed a monoclinic cell ( $P2_1/n$ ) in a three-tilt system. In the A-site, however, Ba and Ca ions were arranged randomly. We clarified the relationship between Ca content and the structural symmetry in the  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  system.

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