Effect of Ba Substitution on the Microstructure and Electrical Conductivity of $\text{Ba}_x\text{Ca}_{1-x}\text{RuO}_3$ Thin Films Prepared by Laser Ablation

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$\text{Ba}_x\text{Ca}_{1-x}\text{RuO}_3$ (BCRO) thin films were prepared by laser ablation on quartz substrates at a substrate temperature (T_{sub}) of 973 K and an oxygen pressure (P_{O_2}) of 13 Pa. The effect of Ba substitution on the microstructure and electrical conductivity (σ) was investigated. Rectangular-shaped CaRuO_3 (CRO) island grains grew in BCRO thin films at a Ba fraction (x) below 0.1. BCRO thin films prepared at $x > 0.2$ consisted of fine grains. BCRO thin films at $x > 0.2$ showed metallic conduction, whereas those with an island structure at $x < 0.1$ showed semi-conducting behavior. The σ increased from $2.5 \times 10^3 \text{ S}\cdot\text{m}^{-1}$ to $3.8 \times 10^4 \text{ S}\cdot\text{m}^{-1}$ with increasing x from 0.1 to 1.0.

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1. Introduction

ARuO_3 ($A = \text{Ca}, \text{Sr}$ and Ba) is a conductive perovskite oxide with excellent electrical conductivity. Although the space group of CaRuO_3 (CRO) and SrRuO_3 (SRO) has a GdFeO_3 -type orthorhombic structure ($Pnma$), it can be simplified as a pseudo-cubic structure because it has almost the same a , b and c axis.¹⁾ BaRuO_3 (BRO) commonly has a 9R-type hexagonal structure ($R\bar{3}m$) with three face-sharing RuO_6 octahedra combined with corner-sharing RuO_6 octahedra.²⁾ 6H BRO ($P6_3/mmc$)³⁾ and 4H BRO ($P6_3/mmc$)⁴⁾ are known as other polytypes.

CRO and SRO could be promising electrode materials for micro devices because their lattice parameters are close to those of dielectric perovskites such as $(\text{Ba}, \text{Sr})\text{TiO}_3$ and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT).^{1,5)} However, SRO exhibits a magnetic phase transition at $T_C = 160 \text{ K}$, and therefore the paramagnetic CRO is more suitable than SRO for magnetic devices, such as Josephson devices, operating at low temperatures.^{6,7)} The magnetic behavior of CRO is different from that of SRO despite their similar crystal structure, and thus $\text{Ca}_x\text{Sr}_{1-x}\text{RuO}_3$ (CSRO) system has attracted attention in the field of magnetism due to the tunability of its lattice parameter and magnetic properties.^{8,9)}

The pseudo-cubic lattice parameter of $\text{Ba}_x\text{Sr}_{1-x}\text{RuO}_3$ (BSRO) body increases from 0.393 to 0.407 nm in the pseudo cubic system by substituting Sr with Ba.^{3,10)} A BSRO thin film electrode thus exhibits excellent compatibility with dielectric perovskite films when the Ba substitution ratio is controlled. We have previously reported the effect of Ba substitution on the microstructure and characteristics of polycrystalline BSRO thin films prepared by laser ablation.¹¹⁾

In the $\text{Ba}_x\text{Ca}_{1-x}\text{RuO}_3$ (BCRO) system, on the other hand, the crystal structure of the $\text{Ba}_3\text{CaRu}_2\text{O}_9$ single crystal¹²⁾ and the magnetic and electrical properties of the polycrystalline $\text{Ba}_3\text{CaRu}_2\text{O}_9$ body have been reported.¹³⁾ However, no report on the preparation of BCRO thin film and the effect of Ba addition to CRO has so far been published.

In the present study, BCRO thin films were prepared by laser ablation using BCRO targets, and the Ba substitution

effect on the microstructure and electrical conductivity was investigated.

2. Experimental Procedure

RuO_2 , CaCO_3 and BaCO_3 powders were used as starting materials for preparing BCRO targets with Ba fractions (x) ranging from 0 to 1.0. These powders were weighed, mixed, pressed into pellets and reacted at 1273 K for 259.2 ks to prepare BCRO pellets. These pellets were then crushed and sintered again at 1573 K for 43.2 ks to obtain the BCRO targets.

A third harmonic wavelength of a Q-switch pulsed Nd:YAG laser was used for ablation. The experimental procedure and deposition conditions have been reported in detail elsewhere.¹⁴⁾ Quartz glass plates were used as substrates. The deposition was conducted at a substrate temperature (T_{sub}) of 973 K and an oxygen pressure (P_{O_2}) of 13 Pa for a deposition time of 3.6 ks. The thickness of the BCRO thin films was approximately 100 nm.

The crystal structure of the targets and that of the BCRO thin films were studied by X-ray diffraction (θ - 2θ XRD, Rigaku RAD-2C, and α - 2θ XRD; incident angle of $\alpha = 2.0^\circ$, Rigaku RU-200B). The thickness was measured by a profilometer (Taylor-Hobson Talystep). The composition was examined by an electron probe microanalyzer (EPMA, JEOL JXA-8621MX) and an energy dispersive X-ray microanalyzer (EDX) attached to a field-emission scanning electron microscope (FESEM, JEOL JSM-6500FT). The surface morphology was observed by FESEM. The electrical conductivity was measured from 80 to 673 K using the van der Pauw method, the specimens being cut in a square shape, and the Au wires being attached to the four corners of the specimen with Ag paste.

3. Results and Discussion

Figure 1 shows the relationship between the Ba fraction in the targets (x) and that in the BCRO thin films ($C_f = C_{\text{Ba}}/(C_{\text{Ba}} + C_{\text{Ca}})$). The C_f was almost in agreement with x except for $x = 0.1$; hence, the Ba fraction in the BCRO thin

Fig. 1 Ba fraction analysis of BCRO thin films by EPMA (squares) and EDX (triangles).

film was represented by x in the present study. The Ba deficiency at $x = 0.1$ might be caused by such as a re-evaporation from the surface of BCRO thin film, because the authors have previously reported that the Ba tended to be slightly absent in the BaRuO_3 thin films.¹⁵⁾

Figure 2 shows the XRD patterns of BCRO thin films prepared at various x . The XRD patterns of the CRO ($x = 0$)¹⁶⁾ and BRO thin films ($x = 1.0$)¹⁵⁾ have been reported elsewhere by the present authors. The XRD peaks were assigned to the CRO phase at $x < 0.1$ (Fig. 2(a)). At $x = 0.2$, (110) BRO and (200) (121) (002) CRO peaks were identified (Fig. 2(b)), suggesting that the BCRO thin films consisted of CRO and BRO phases. With increasing x from 0.2 to 0.8, the peak intensity of the CRO phase decreased, whereas that of the BRO phase increased (Figs. 2(b)–2(d)). A 9R BRO phase was observed at $x > 0.8$ (Fig. 2(e)).

Figure 3 shows the surface morphology of BCRO thin films prepared at various x . Rectangular-shaped island grains ranging from 100 to 200 nm in width grew on the BCRO thin films at $x < 0.1$ (Fig. 3(a)). The dense films consisted of fine grains at $x > 0.2$ (Figs. 3(b)–3(f)). Figure 4 illustrates results of the EDX spot analysis of the rectangular-shaped island structure and the matrix of BCRO thin films prepared at $x = 0.1$ as shown in Fig. 3(a). The rectangular-shaped island grains contained no Ba, and the composition was almost stoichiometric CRO (Figs. 4(a)–4(e)). On the other hand, the matrix had a Ba fraction 5 or 6 times greater than that of the target (Figs. 4(f), 4(g)). Figure 5 depicts the EDX line section analysis for the area of L in Fig. 4. Only the matrix contained a high amount of Ba. The Ru content in the BCRO thin films was around 0.5 at each point. The results of EDX (Figs. 4 and 5) implied that rectangular-shaped, (100)_C-faceted CRO grains grew dominantly in the BCRO thin films at $x = 0.1$.

In BSRO thin films, the d -value for pseudo-cubic (110) BSRO increased linearly from 0.278 to 0.288 nm with increasing Ba-substitution ratio from 0 to 1.0, implying Sr (ionic radii, $r_i = 0.14$ nm) in the pseudo-cubic SRO cell was replaced with Ba ($r_i = 0.16$ nm).¹¹⁾ The crystal structure of

Fig. 2 XRD patterns of BCRO thin films: $x = 0.1$ (a), 0.2 (b), 0.4 (c), 0.5 (d) and 0.8 (e).

CRO and ionic radii of Ca ($r_i = 0.13$ nm) are almost same as those of SRO and Sr, respectively. However, in BCRO thin films, the d -value for pseudo-cubic (110) lattice parameter, *i.e.* the d -value for (200) (121) (002) CRO and (110) BRO peak, was almost constant with Ba fraction. FESEM-EDX results showed that the CRO grains with no Ba grew in the BCRO thin films at $x < 0.1$. Thus, although the CRO island growth was inhibited at $x > 0.2$, CRO phase might be exclusively formed, resulting in no replacement of Ca with Ba.

Figure 6 depicts the temperature dependence of the electrical conductivity (σ) of BCRO thin films prepared at various x . BCRO thin films at $x = 0.1$ exhibited a low σ at a low temperature and showed semi-conducting behavior, *i.e.*, the σ increased with increasing temperature (Fig. 6(a)). BCRO thin films at $x > 0.2$ showed metallic conduction, *i.e.*, the σ inversely increased as temperature increased (Figs. 6(b)–6(e)). It is known that the strongly hybridized orbital between Ru 4d and O 2p could be responsible to the electron conduction, resulting in the metallic conduction of CRO and BRO. However, the authors have previously

Fig. 3 Plan view FESEM images of BCRO thin films prepared at $x = 0.1$ (a), 0.2 (b), 0.4 (c), 0.5 (d), 0.6 (e) and 0.8 (f).

	Position	Ba fraction, x
Island	a	0.00
	b	0.00
	c	0.00
	d	0.00
	e	0.01
Matrix	f	0.62
	g	0.53

Fig. 4 EDX spot analysis of island structure and matrix of BCRO thin films prepared at $x = 0.1$.

reported that rectangular-shaped CRO island grains often grew in the CRO thin films and that the CRO thin films with an island structure were characterized by semi-conducting behavior due to insufficient effective thickness for electrical conduction pass of the CRO thin films.¹⁶⁾ Figure 7 summarizes the effect of x on the σ at room temperature and surface morphology of BCRO thin films. The σ increased from $2.5 \times 10^3 \text{ S}\cdot\text{m}^{-1}$ to $3.8 \times 10^4 \text{ S}\cdot\text{m}^{-1}$ with increasing x from 0.1 to 1.0 . The semi-conducting behavior of BCRO thin films at $x < 0.1$ would be associated with the island structure. The present study indicated that the addition of Ba to CRO thin film was effective in preventing the island growth of CRO grains, thus improving electrical conductivity of thin film.

4. Conclusions

BCRO thin films were prepared by laser ablation at $x = 0$ to 1.0 . $(100)_\text{C}$ -oriented BCRO thin films were obtained at $x < 0.1$. The CRO phase decreased with increasing x from 0.2 to 0.8 , whereas that of BRO increased. 9R BRO thin films were obtained at $x > 0.8$. Rectangular-shaped CRO island grains with $(100)_\text{C}$ facet grew in the BCRO thin films at $x < 0.1$. BCRO thin films prepared at $x > 0.2$ consisted of fine grains. BCRO thin films showed metallic conduction, whereas those with the island structure showed semi-conducting behavior. The σ increased from $2.5 \times 10^3 \text{ S}\cdot\text{m}^{-1}$ to $3.8 \times 10^4 \text{ S}\cdot\text{m}^{-1}$ with increasing x from 0.1 to 1.0 .

Fig. 5 EDX line section analysis of BCRO thin film prepared at $x = 0.1$.

Fig. 6 Temperature dependence of electrical conductivity for BCRO thin films prepared at $x = 0.1$ (a), 0.2 (b), 0.5 (c), 0.6 (d) and 0.8 (e).

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Fig. 7 Effects of Ba fraction and surface morphology on electrical conductivity of BCRO thin films prepared at various compositions. Open and filled circles indicate metallic conduction and semi-conducting behavior, respectively.

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