TEM Study of Over-Stoichiometric BaRCo₄O₇₋₈ (R: Y, Dy-Lu)

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Over-stoichiometric BaRCo₄O₇₋₈ phases have been investigated by powder XRD, TG-DTA, and high resolution TEM. Three ordered structures of excess oxygen atoms were confirmed. In the case of Lu compound with the oxygen composition of δ = 0.80, an orthorhombic superlattice with the triple periods, 3a₀, based on the fundamental orthorhombic structure of stoichiometric phase. In the case of Y compound with the oxygen composition of δ = 0.96 equilibrated in the 1 atm O₂ at 364°C, we observed the 2a₀ superlattice, which agrees with the results of recent neutron diffraction study. For the Y compound slowly cooled down to room temperature, a superlattice with a = 5a₀ was observed although the superlattice period is heavily disordered.

Key words: oxygen uptake, superlattice, thermo-gravimetry (TG), electron diffraction, lattice image

1. INTRODUCTION

Mixed valence and non-stoichiometric ternary or quaternary cobaltates are known to show interesting properties; such as thermo-electricity of Na₃CoO₂ [1] or oxide ion conduction of (La,Sr)CoO₃ [2]. In these cobaltates, Co atoms are octahedrally coordinated by oxygen atoms. BaRCo₄O₇₋₈ (R: Y, Dy-Lu, In) are novel cobaltates in which all the Co atoms are tetrahedrally coordinated to form a corner-shared tetrahedral network.[3, 4] They show interesting structural and magnetic phase transitions.[5-8] Another outstanding property of BaRCo₄O₇₋₈ is the wide range over-stoichiometry of oxygen composition, which may be utilized for oxygen storage or oxide ion conduction. Although several studies have been reported on the oxygen uptake properties [9-11], the crystal structures of over-stoichiometric phase are not so well studied. Very recently, a neutron diffraction study on the superlattice ordering in BaYCo₄O₇₋₈ has been reported [12]. Figure 1 shows the crystal structures of the stoichiometric and over-stoichiometric BaYCo₄O₇₋₈. The unit cell is hexagonal (P6₃mc) and it is distorted to be orthorhombic (Pbn2₁) at lower temperatures. Ba and O atoms form ABAC-type close-packed stacking. The cobalt atoms occupy the tetrahedral sites to form corner shared 3-dimensional network. In another viewpoint, two kinds of tetrahedral cobalt layers are stacked along c-axis. One of them contains only cobalt atoms to form Kagomé lattice. Another layer contains tetrahedral cobalt and octahedrally coordinated rare-earth metals to form a 2×2 ordered triangular lattice. The average valence of cobalt is 2.25; Co(III) : Co(II) = 1 to 3. If all the cobalt atoms are in trivalent state, the oxygen composition is δ = 1.5 in BaCo₄O₇₋₈ and about 4 wt.% uptake of oxygen is expected. In the over-stoichiometric BaYCo₄O₇₋₈, the excess oxygen atoms coordinate to Co atoms to form the ordered arrangement of tetrahedral and octahedral Co as shown in Fig. 1(b). All the Y atoms are coordinated by seven O atoms. The superlattice period is twice the a-dimension (2a₀) of the orthorhombic fundamental lattice.

TEM studies on the superstructures of over-stoichiometric BaRCo₄O₇₋₈ are very interesting to clarify (a) the dependence on the oxygen composition, (b) the dependence on the R ion size, and (c) the regularity of the ordering. In this paper, the results on Lu and Y compounds are mainly described. Trivalent Lu has the smallest ionic radius (0.861 Å for 6-coordination) among the rare earth elements to form BaRCo₄O₇₋₈, whereas Y³⁺ shows the larger ionic radius (0.900 Å) close to that of Ho³⁺ (0.901 Å).

2. EXPERIMENTAL

Samples were prepared by normal ceramic method in air at 1050°C. The starting materials are BaCO₃, Co₂O₃ and R₂O₃. The phase identification was performed by powder XRD, using Cu-Kα radiation. The over-stoichiometric phases were obtained by annealing in O₂ gas stream, using several temperature programs. The oxygen content was determined from TG measurements in H₂/10%He or O₂ gas stream. Electron diffraction (ED) patterns and high-resolution lattice images were observed in a JEM-2100F 200kV TEM.

Fig. 1 Crystal structures of stoichiometric BaYCo₄O₇ (a) and over-stoichiometric BaYCo₄O₇₋₈ (b). Two kinds of layer units are stacked along c-axis. (a) a = 6.3 Å, b = 10.94 Å, c = 10.23 Å for BaYCo₄O₇ at room temperature. [5]
3. RESULTS AND DISCUSSION

3.1 BaLuCo$_3$O$_{7.8}$

Figure 2(a) shows powder XRD patterns of BaLuCo$_3$O$_{7.8}$ annealed in air and O$_2$, respectively. The sample annealed in O$_2$ at 300°C shows remarkable peak shifts with respect to the sample annealed in air; the unit cell shrinks mainly in the c-plane due to the oxygen uptake. The hexagonal lattice parameters are $a = 6.259$ Å and $c = 10.221$ Å ($V_{\text{unit}} = 346.76$ Å$^3$) when annealed in air and $a = 6.232$ Å and $c = 10.212$ Å ($V_{\text{unit}}=343.48$ Å$^3$) when annealed in O$_2$. The volume change is ~0.95%. The peak broadening suggests the cell symmetry lower than hexagonal for the over-stoichiometric phase.

The oxygen composition and the oxidation state were evaluated by TG-DTA in reducing 10%H$_2$/He gas stream as shown in Fig. 2(b). On heating, the sample annealed in O$_2$ releases the excess oxygen at around 300°C to form stoichiometric phase. At 1000°C, cobalt atoms are reduced to the metallic state. The oxygen composition estimated from this weight change of this gas stream, the definite oxygen uptake is observed in Fig. 2(c).

Figure 3 shows ED patterns of over-stoichiometric phase of Lu compound with the oxygen composition of $\delta = 0.82$. The indexes of diffraction spots are based on the fundamental orthorhombic lattice. The [001] and [010] zone ED patterns show fine extra spots, indicating the formation of a centered 6$a_0$×2$b_0$ superlattice. The [100] zone ED pattern does not show superlattice spots, although the 0$k$0 spots with $k = 2n+1$ ($n$: integer) forbidden in the fundamental lattice show fairly large intensity. The patterns (d), (e), and (f) obtained by tilting from the basal planes indicate a C-centered 6$a_0$×2$b_0$×$c_0$ superlattice. The reciprocal lattice of the superlattice reconstructed from the observed ED patterns is shown in (g). The extinction for 00$L$ reflections with odd $L$ is suggested from the [010] and [100] zone ED patterns. The pseudo-hexagonal symmetry of the superlattice agrees with the XRD pattern shown in Fig. 2(a).

Figure 4(a) shows a lattice image of the superlattice viewed along the [010]$_h$ direction. It shows the periodic contrast modulation of (200) lattice fringes with 1.88 nm spacing corresponding to 3$a_0$. The electron irradiation damage is seen in the left part of the image near the crystal edge. Figure 4(b) shows a lattice images viewed along the $c_0$-axis ([001]$_h$). The periodic contrast modulation of 3$a_0$ superlattice period along three equivalent directions. However, the contrast due to the superlattice period shows somewhat domainic characters probably because of the strong electron irradiation damage. At around the region marked by white arrows, the contrast of C-centered 6$a_0$×2$b_0$ superlattice is seen.

It is well assumed that the observed 3$a_0$ superlattice period is caused by the ordered arrangement of excess O atoms octahedrally coordinated to Co atoms, according to the 2$a_0$ superlattice of BaYCo$_3$O$_x$[12] in Fig. 1(b). An one-dimensional 3$a_0$ superlattice as shown in Fig. 5(a) can be derived by simply inserting the one unit layer of the stoichiometric tetrahedral structure. The composition...
of this structure is $\delta = 0.66$. A model structure, which agrees with the observed supercell symmetry, is shown in Fig. 5(b). The composition of this structure, $\delta = 0.83$, well agrees with the observation. A model structure of $5a_0$ superlattice with $\delta = 1.20$ is also shown in Fig. 5(c).

3.2 BaYCo$_4$O$_{7+\delta}$

Two samples of over-stoichiometric BaYCo$_4$O$_{7+\delta}$ were examined by TEM. Their oxygen compositions were measured by TG in pure O$_2$ gas stream, using stepwise temperature programs shown in Fig. 6. A sample kept at 363°C under the pure O$_2$ stream shows the oxygen composition of $\delta = 0.96$. Although the amount of oxygen uptake is larger than BaLuCo$_4$O$_{7+\delta}$, it takes much more time to get saturation at around 360°C. The sample slowly cooled down to room temperature using a stepwise temperature program shows 10% larger oxygen composition of $\delta = 1.09$.

XRD patterns of above two samples are shown in Fig. 7, compared with that of nearly-stoichiometric sample annealed in Ar at 600°C. The nearly stoichiometric sample has an orthorhombic structure with the lattice parameters of $a = 6.296$, $b = 10.939$, and $c = 10.224$ Å ($V_{\text{unit}} = 703.70$ Å$^3$). The over stoichiometric samples show fairly large peak splitting. The sample equilibrated at 364°C shows well-resolved XRD peaks. The lattice parameters are $a = 6.377$, $b = 10.847$, and $c = 10.126$ Å ($V_{\text{unit}} = 700.43$ Å$^3$). The oxygen uptake causes the lattice contraction ($-0.46\%$), similarly to the case of BaLuCo$_4$O$_{7+\delta}$. The orthorhombicity, $\sqrt{3}a/b$, increases from 0.996 to 1.018 and $c$-axis is 0.96% contracted. The amounts of the elongation along $a$-axis and the contraction along $c$-axis are prominent compared with BaLuCo$_4$O$_{7+\delta}$. In the XRD patterns, we can see some 2$a_0$ superlattice reflections as marked by filled circles. Electron diffraction patterns also show clear superlattice spots of 2$a_0$ superlattice.

The XRD pattern of the sample slowly cooled to room temperature is intermediate characters of above two diffraction patterns, although the oxygen composition is
weak against the electron beam irradiation. During lattice image observation superlattice spots began to show streaky nature and then finally disappeared. Figure 8(c) shows the lattice image viewed along [001], with the small electron dose. The damaged thin layers can be seen near the edge of the crystallites. Although the lattice fringes show almost regular spacing of about 12.5 Å, some planar defects can be seen. The enlarged images in (d) and (e) suggest that the planar defects are the lattice slabs with 3a₀ periods as shown in Fig. 5(a). Similar lattice defects are often seen in many crystallites.

Figure 9 shows ED patterns and the lattice image of the sample with δ=1.06 slowly cooled in oxygen to room temperature. ED patterns show clear extra spots indicating a superlattice period 10 times of d(200) (5a₀ superlattice). Many crystallites show heavy stacking faults. However, some crystallites showed the images with the regular 5a₀ lattice fringes as shown in Fig. 9, although a 4a₀ fringe is seen at the right side of the figure. One of the possible model structures for 5a₀ superlattice may be the one shown in Fig. 5(c).

4. SUMMARY

Three superstructures were confirmed by TEM for the over-stoichiometric BaRCo₄O₇₋δ: 6a₀ × 2b₀ × c₀ supercell for BaLuCo₄O₇₋δ, 2a₀ × b₀ × c₀ supercell for BaYCo₄O₇₋δ, and also possibly 5a₀ × b₀ × c₀ supercell for BaYCo₄O₂₋δ. The careful heat-treatments controlling oxygen partial pressure are necessary to obtain well-ordered phase particularly for the samples with the intermediate compositions. As for the R ion size dependence, our preliminary results indicated that Yb and Tm phases with 5a₀ supercell and Er and Ho phases show 6a₀ × 2b₀ × c₀ supercell and Er and Ho phases show 5a₀ × b₀ × c₀-type ones. Extended studies are now under way.

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REFERENCES


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