

Space group determination of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phase using a convergent-beam electron-diffraction technique

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Abstract

The space group of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ ($\delta = 0.03\text{--}0.17$) phase was studied by selected-area electron diffraction and convergent-beam electron diffraction (CBED). The CBED patterns for $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ grains taken from the zone axes of [111], [001] and [010] had the symmetries of m , $4mm$ and $2mm$, respectively. Forbidden reflections were observed neither in selected-area electron diffraction nor in the CBED patterns. From these results, the space group of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ was determined to be $P4/mmm$. Since the presence of a mirror plane parallel to the $(\text{Cu},\text{Fe})\text{O}_2$ planes was confirmed, Cu and Fe were found to be randomly distributed in the $(\text{Cu},\text{Fe})\text{O}_2$ planes. The same analyses were performed for $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ grains and the space group was also found to be $P4/mmm$. The change in the magnetic properties of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ samples due to the high-pressure heat-treatment was concluded to be caused by excess of oxygen.

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1. Introduction

The oxygen-deficient double perovskite $\text{BaRE}(\text{Cu}_{1-x}\text{Fe}_x)_2\text{O}_{5+\delta}$ (RE is a rare earth element) may be considered as the $n = 1$ member of the $01(n-1)n$ homologous series of multi-layered copper oxides [1]. Among known high T_c superconducting cuprates, the thinnest “blocking” block (charge reservoir block and two rock-salt layers) is found for members of the homologous series, $02(n-1)n$. From purely crystallographic point of view, the members of the $01(n-1)n$ series should have an even thinner “blocking block” than those of the $02(n-1)n$ series, with the thickness consisting of a single rock-salt layer [2]. Improvements in the H_{irr} characteristics have been achieved by hole doping in the charge reservoir block [3] and by short-

ening the thickness of the non-superconducting block [4]. It would thus be useful to synthesize superconducting $01(n-1)n$ compounds. As the $\text{BaRE}(\text{Cu}_{1-x}\text{Fe}_x)_2\text{O}_{5+\delta}$ compound is not superconducting [5], reduction of x is the primary task in order to achieve this goal. For the first time, Nagase et al. reported the synthesis of 0112 compounds with Cu-rich $(\text{Cu},\text{Fe})\text{O}_2$ planes, i.e. with $0.3 \leq x \leq 0.5$ [6]. The synthesis and properties of non-superconducting 0112 compounds lacking Fe but containing Co [6–8] and with both Fe and Co [9] have also been reported.

Within the 0112 phase, samples with $x = 0.5$ and $RE = Y$ ($\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$) were synthesized with a range of oxygen content ($\delta = 0.03\text{--}0.17$) using high-pressure heat-treatment [10]. Magnetic properties of the phases were changed due to the high-pressure heat-treatment. The Néel temperature decreased by 100 K and the second magnetic transition at 190 K disappeared [5]. For 0112 phases with $RE = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Yb}$ and Lu , oxygen content can be further increased as high as 0.40 [11]. Due to the high-pressure heat-treatment, not only the oxygen content but also the occupancy of

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cation sites in the $(\text{Cu,Fe})\text{O}_2$ planes could be changed. In the unit cell of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phase having the double perovskite structure, two $(\text{Cu,Fe})\text{O}_2$ planes are present and two possible ways of distributing the Cu and Fe atoms are present: (a) all Cu atoms occupy a single site in one of the two layers while the Fe atoms occupy the other or (b) the Cu and Fe atoms are randomly distributed in the two planes. The distribution of Cu and Fe influences the crystal structure. The space groups of (a) $P4mm$ [5] and (b) $P4/mmm$ [12] were accordingly proposed for each crystal structure using powder neutron diffraction. In order to investigate the cation sites in the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phase, determination of the space group is required. However, X-ray and neutron diffraction are limited in the space group determination because of the consequences of Friedel's law.

In order to determine the space group, diffraction patterns under dynamical-diffraction conditions, which utilize a breakdown of Friedel's law, have to be recorded and analyzed. Although dynamical-diffraction conditions are frequently satisfied in most electron diffractions, conventional selected-area electron diffraction lacks accuracy in measuring lattice parameters and crystal systems. On the other hand, a convergent-beam electron-diffraction (CBED) method [13] is capable of determining the space groups of crystals. By using the CBED method, the space groups of many cuprates including the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [14] and $(\text{Nd,Sr,Ce})_2\text{CuO}_{4-\delta}$ [15] phases have been successfully determined although it is difficult to obtain the space groups of crystals with large unit cells [16]. This method has not been applied to the crystal structure analysis of 0 1 1 2 phases. In this work, CBED patterns are obtained using a transmission electron microscope (TEM) with the purpose of determining the space group and the occupancies of cation sites for the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ ($\delta = 0.03\text{--}0.17$) phase. The reason behind the variations in the magnetic properties of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample after high-pressure heat-treatment is also discussed.

2. Experimental

Samples of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ were synthesized from high-purity raw materials at 1000°C for 24 h in air. Then, the samples were heat treated at 5 GPa and 1200°C for 0.5 h in a cubic-anvil-type high-pressure apparatus. Details of the synthesis and analyses are described elsewhere [10]. The oxygen contents of the samples were determined by coulometric titration to be $5 + \delta = 5.03 \pm 0.01$ for the as-synthesized sample and 5.17 ± 0.01 for the high-pressure heat-treated sample. The samples were then pulverized in an agate mortar. The crushed powders were dispersed in ethanol using an

ultrasonic homogenizer and scooped on microgrids supported by molybdenum meshes. The powders were observed in a TEM (Hitachi, H-9000NAR). In order to decrease the diffraction angles in the high-order Laue-zone (HOLZ), the TEM was operated at an accelerating voltage of 100 kV to reduce the radius of the Ewald sphere [13]. An electron beam with convergent angles of 2–6 mrad and a diameter of 30 nm was selected to minimize possible damages in samples by electron irradiation. The electron beam was focused on the surface of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ grains. The CBED patterns were recorded on emulsion films. The CBED patterns were obtained from at least two grains for each zone axis. Furthermore, in each grain, electrons were incident for at least 10 min. During this period, we observed no change in the CBED patterns due to the electron irradiation. Prior to taking the CBED patterns, the chemical composition of the grains was analyzed with an energy-dispersive X-ray analyzer (EDX) mounted on the TEM to distinguish the 0 1 1 2 grains from those of impurity phases. The compositions of samples were measured by average of ten EDX results obtained from different grains.

3. Results

The chemical compositions of the samples from which CBED patterns were obtained were analyzed with EDX. The cationic ratio of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ sample was determined to be $\text{Ba}:\text{Y}:\text{Cu}:\text{Fe} = 22(1):23(1):29(2):26(1)$ (at%). Thus essentially cation-stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ samples were successfully obtained. A CBED whole pattern taken from the [111] zone axis is shown in Fig. 1(a). It is obvious that the pattern has m symmetry.

The CBED whole patterns taken from the [010] and [001] zone axes are shown in Figs. 2 and 3(a), respectively. In Fig. 2, mirror planes parallel not only to (100) but also to (001) are observed and the whole patterns have $2mm$ symmetry. In Fig. 3(a), mirror planes parallel to the $\{100\}$ and $\{110\}$ planes are observed and a 4-fold symmetry axis lies parallel to the zone axis. The whole pattern has $4mm$ symmetry. The results of the symmetry considerations of the whole patterns are given in Table 1. Possible point groups which satisfy the symmetry of the [111], [001] and [010] zone axes CBED patterns were $m3m$ and $4/mmm$. Electron diffraction patterns and X-ray diffraction patterns indicated that the sample had a tetragonal unit cell. Thus, the point group of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ was determined to be $4/mmm$.

The presence of forbidden reflections was studied both by selected area electron-diffraction and CBED. An example of this is shown in Fig. 3(b) which is a zeroth-order Laue-zone (ZOLZ) pattern. In the 100 and

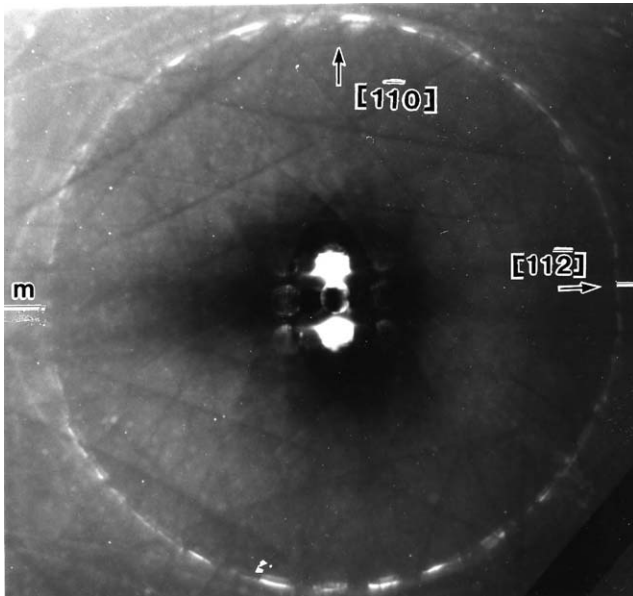


Fig. 1. A $[111]$ zone-axis CBED whole pattern of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ showing symmetry of m .

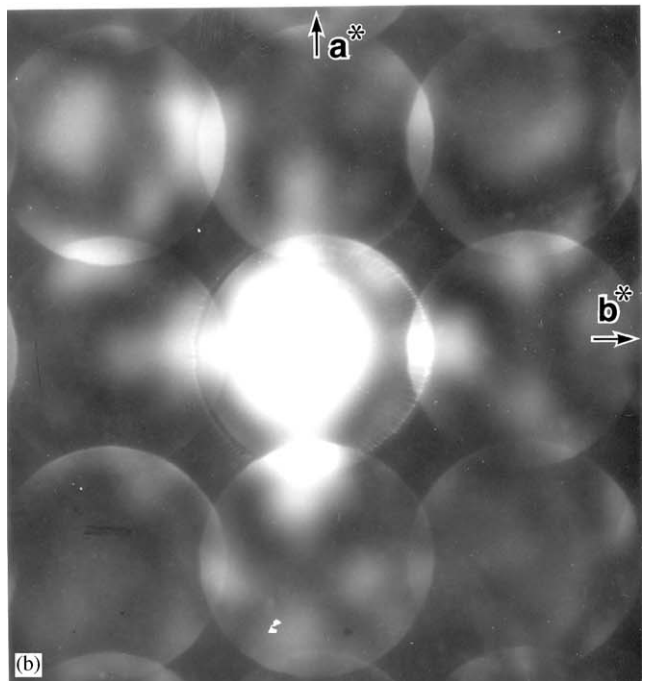
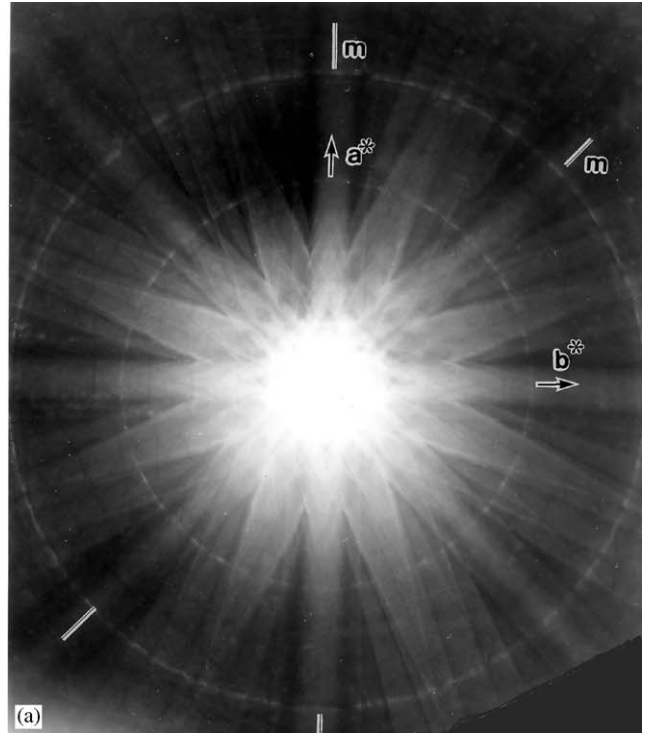


Fig. 3. $[001]$ zone-axis CBED patterns of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$: (a) a whole pattern which shows symmetry of $4mm$ and (b) ZOLZ disks.

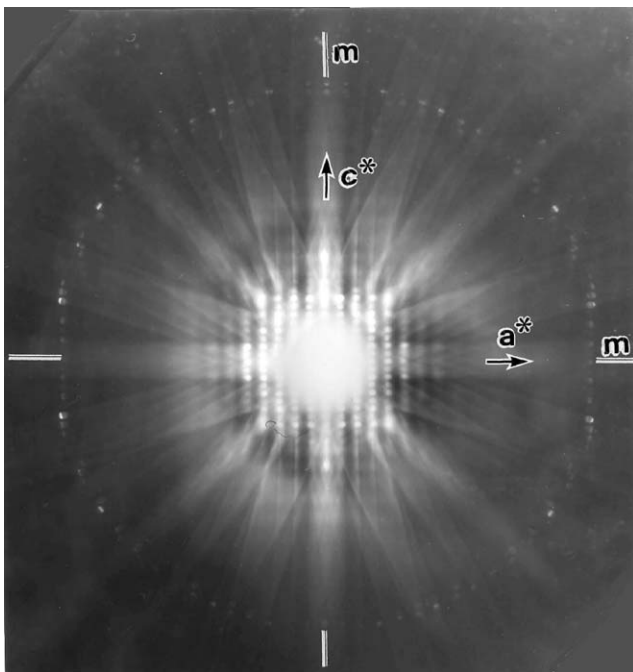


Fig. 2. A $[010]$ zone-axis CBED pattern of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ showing symmetry of $2mm$.

010 disks, no Gjønnes–Moodie (G–M) lines [17,18] which would appear as black lines parallel to the $[010]$ and $[100]$ directions, respectively, are visible. This implies that no dynamical absences occur. All results are given in Table 2. Forbidden reflections were observed neither in the electron diffraction patterns nor in the CBED patterns. From the tables of the relationship between space groups and forbidden

reflections in selected-area electron diffraction [19] and CBED [20], possible space groups are given in Table 3. Using the result of Table 2 and the point group of $4/mmm$, the space group of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ was uniquely determined to be $P4/mmm$.

After the high-pressure heat-treatment, the sample was investigated by TEM. The cationic ratio of the

Table 1
Symmetries of CBED whole patterns, possible diffraction groups and point groups [13] for the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ ($0.03 \leq \delta \leq 0.17$) phase

Zone	Whole pattern	Possible diffraction groups	Possible point group
[111]	m	m $m1_R$ 2_Rmm_R	$m, mm2, 4mm, 42m, 3m, 6, 6mm, 6m2, 43m$ $mm2, 4mm, 42m, 6mm, 6m2, 43m$ $2/m, mmm, 4/m, 4/mmm, 3m, 6/m, 6/mmm, m3, m3m$
[010]	$2mm$	$2mm$ $2mm1_R$	$mm2, 6m2$ $mmm, 4/mmm, 6/mmm, m3, m3m$
[001]	$4mm$	$4mm$ $4mm1_R$	$4mm$ $4/mmm, m3m$

The point group was determined to be $4/mmm$.

Table 2
The presence of forbidden reflections in electron diffraction patterns and CBED patterns

Experimental methods	Forbidden reflections. h and l : odd
Electron diffraction (kinematical)	$h00$: None
CBED (dynamical, G–M line)	$00l$: None 100 : None

Table 3
Possible space groups selected by the kinematical extinction rule, dynamical forbidden reflections [13] and the determined point group in Table 1

Conditions	$P4$	$P\bar{4}$	$P4/m$	$P422$	$P4mm$	$P\bar{4}2m$	$P\bar{4}m2$	$P4/mmm$
No kinematical forbidden reflections, $k00, 00k$	$P4$	$P\bar{4}$	$P4/m$	$P422$	$P4mm$	$P\bar{4}2m$	$P\bar{4}m2$	$P4/mmm$
No G–M lines, 100	$P4$	$P\bar{4}$	$P4/m$	$P422$	$P4mm$	$P\bar{4}2m$	$P\bar{4}m2$	$P4/mmm$
Point group, $4/mmm$								$P4/mmm$

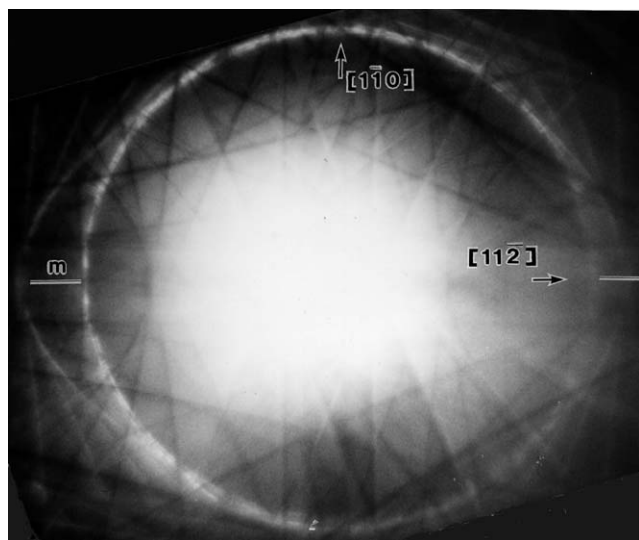


Fig. 4. A [111] zone-axis CBED whole pattern of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$.

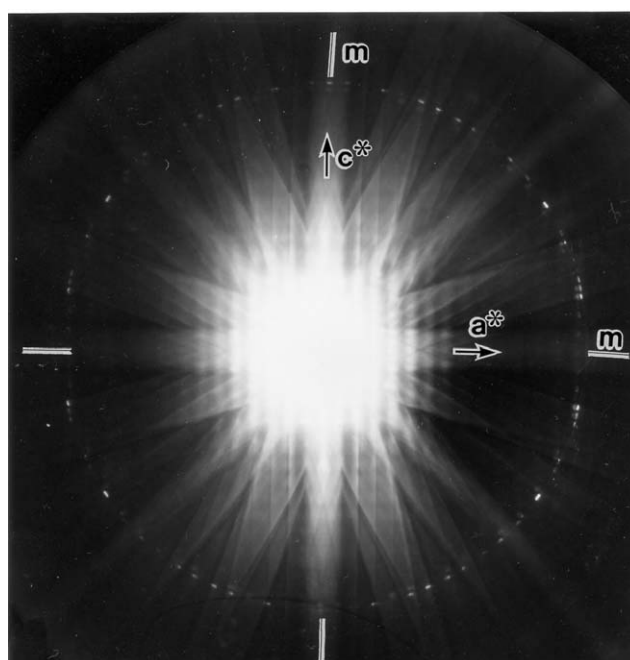


Fig. 5. A [010] zone-axis CBED pattern of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ showing symmetry of $2mm$.

$\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ sample was determined to be $\text{Ba:Y:Cu:Fe} = 22(1):24(1):27(2):27(1)$, i.e. the high-pressure high-temperature treatment did not change the cation stoichiometry. The CBED whole patterns taken from the [111], [010] and [001] directions are shown in Figs. 4, 5 and 6(a), respectively. They have m , $2mm$ and $4mm$ symmetries which are the same as those of the

$\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ sample. A [001] zone axis ZOLZ pattern is shown in Fig. 6(b). No G–M lines are visible. Since forbidden reflections were not found in selected area electron-diffraction patterns, no kinematical and

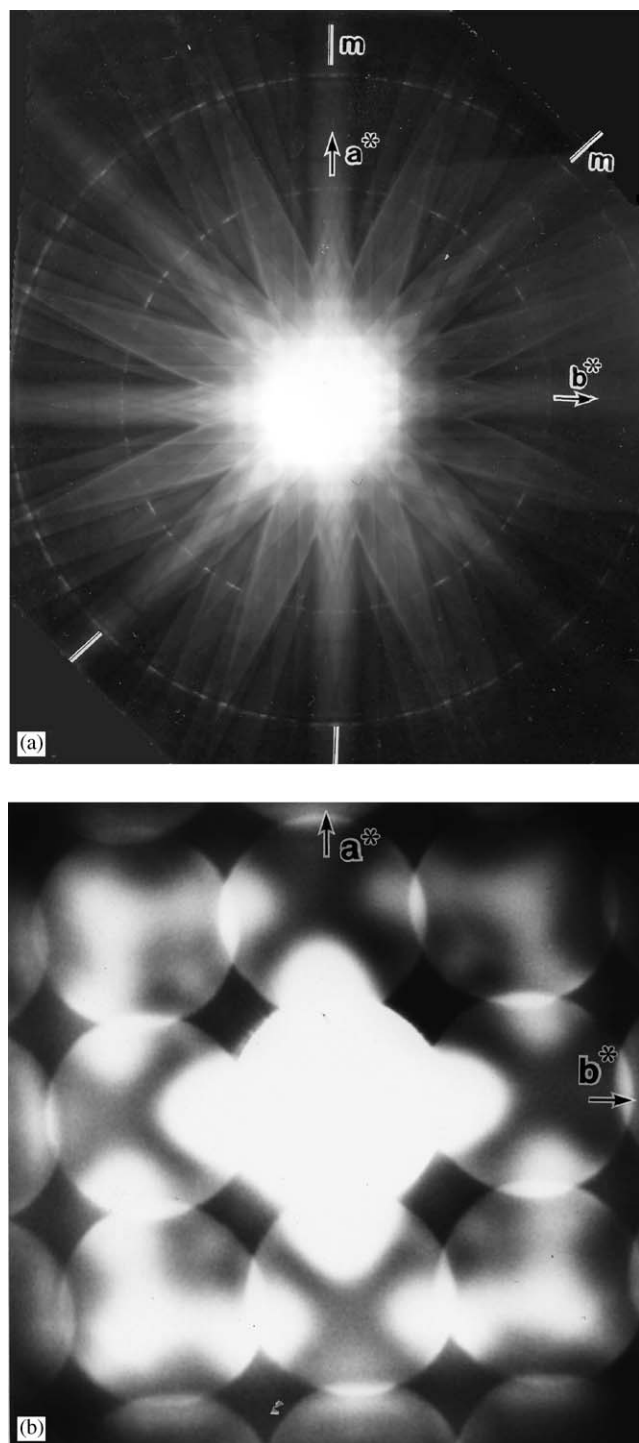


Fig. 6. [001] zone-axis CBED patterns of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$: (a) a whole pattern which shows symmetry of $4mm$ and (b) ZOLZ disks.

dynamical absences were observed for the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ sample. From the analyses given in Tables 1–3, the point group and the space group of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ sample were determined to be $4/mmm$ and $P4/mmm$, respectively. In other words, the space group and the cation sites in the $(\text{Cu},\text{Fe})\text{O}_2$

plane were not changed due to the high-pressure heat-treatment.

4. Discussion

The space group of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ sample was found to be $P4/mmm$ in the present work. Previously, two possible space groups were proposed for the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phase. Er-Rakho et al. [5] first suggested the $P4mm$ space group by using powder neutron diffraction. Analysis of low-temperature ^{57}Fe Mössbauer spectra by Meyer et al. [21] and Pissas et al. [22] supported the space group and the ordering of the Cu and Fe atoms. Later, Ruiz-Aragon et al. [12] insisted that the space group was $P4/mmm$ as judged by the result of powder neutron diffraction analyses of $\text{BaRECuFeO}_{5+\delta}$ ($RE = \text{Y}, \text{Pr}$) samples. The result was supported by Caignaert et al. [23] and Nagase et al. [10]. However, all of the experiments in the previous works were powder neutron-diffraction and Mössbauer-spectroscopy studies, such that the experimental methods were essentially the same. The occupancies of the Cu and Fe atoms were estimated by the difference in the fit of the neutron-diffraction data and then the space group was proposed from the results of the refinement. In the case of ^{57}Fe Mössbauer spectra, the evidence was likewise indirect. In the CBED patterns, the difference in the point groups graphically showed up and the analysis of the results to determine the space group has no ambiguity.

Nagase et al. [10] reported that Néel temperature of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample was lowered after the high-pressure heat-treatment of the sample. As mentioned before, two structural changes could occur during the high-pressure heat-treatment of it [10]; (1) a change in occupancies of Cu and Fe atoms in $(\text{Cu},\text{Fe})\text{O}_2$ planes ($P4mm$ space group) and (2) an introduction of excess oxygen. It is not likely that the space group, $P4/mmm$, of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ phase would change during a high-pressure heat-treatment to one with a lower symmetry ($P4mm$) since high-pressure phases usually have a higher symmetry than that of low-pressure phases [24]. Thus, a change in the occupancies of Fe and Cu is not likely to occur. On the other hand, the oxygen content of the sample ($5 + \delta = 5.17$) heat-treated at high pressure was higher than that of the as-synthesized sample ($5 + \delta = 5.03$) [10]. From the present CBED analyses, the structures of $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.03}$ and $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5.17}$ belonged to the same space group of $P4/mmm$, confirming the above conclusions. The difference in oxygen contents must also be the cause of the differing magnetic properties. Nagase et al. concluded that the excess oxygen must be located adjacent to Y atoms [10]. Rietveld refinement of the XRD pattern suggested that Fe atoms came closer to the excess

oxygen atoms. Since the intensity of six-coordinated Fe^{3+} in the Mössbauer spectra increased with the increase in the excess oxygen, it was thought that the excess oxygen atoms selectively occupied the site in the infinite layer block adjacent to Fe atoms to form FeO_6 octahedra. The slight difference in the positions of Cu and Fe due to the insertion of excess oxygen is the cause of the disappearance of the magnetic transition at 190 K for the as-prepared $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample [10,23].

The change in the magnetic properties with the increase in oxygen content takes place in other 0112 phases. Pissas et al. [22] reported that samples of $\text{BaRE}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ showed a similar change in magnetic properties. As the ionic radii of RE increased, the oxygen excess measured by thermogravimetry increased and Néel temperature decreased. More precise determination of oxygen content for $\text{BaRE}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ samples was performed and their results were confirmed [11]. The same authors also showed the result of Rietveld refinement for a $\text{BaNd}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample with the best fit obtained by assuming the space group of $P4mm$. No further works were reported on $\text{BaRE}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phase and intensive studies are required. However, it is also possible that the same change in the position of Cu and Fe atoms accompanying the insertion of excess oxygen takes place and is responsible for the change in the magnetic properties in $\text{BaRE}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$.

It has been shown that five coordinated Fe^{3+} ions and six-coordinated Fe^{3+} and Fe^{5+} ions exist in $\text{BaRE}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ phases by Mössbauer spectroscopy [10,25]. As the oxygen content increased, the number of five-coordinated Fe^{3+} decreased, while the portion of six-coordinated Fe^{3+} and/or Fe^{5+} ions increased. From the present results, the Fe atoms are located randomly in the two $(\text{Cu,Fe})\text{O}_2$ planes. If the distribution of the Fe atoms in the two $(\text{Cu,Fe})\text{O}_2$ planes are completely random, 50% of the Fe atoms are located above other Fe atoms along the *c*-axis. Excess oxygen may selectively be placed between two Fe atoms rather than between a Cu and an Fe atom. The Mössbauer spectra imply that the decrease in the portion of five-coordinated Fe atoms is almost twice the increase in the oxygen content for samples synthesized at ambient pressure. For high-pressure heat-treated samples, the decrease in the five coordinated Fe atoms is not as drastic. Since anti-ferromagnetic coupling between high-spin Fe^{3+} ions was weakened by the decrease in the portion of Fe^{3+} ions, the decrease in Néel temperature with increasing oxygen content is expected to be higher for as-synthesized samples than for high-pressure heat-treated samples. This was confirmed by the susceptibility measurements for $\text{BaPr}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ samples [25]. Thus, the space group determination performed by the CBED analyses contributes in explaining the Mössbauer spectra for the 0112 phases.

5. Conclusion

The space group of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ ($\delta = 0.03 - 0.17$) phase was determined to be $P4/mmm$ by selected-area electron diffraction and CBED. Excess oxygen between the $(\text{Cu,Fe})\text{O}_2$ planes in the $(\text{Cu,Fe})\text{O}_2$ – $\text{Y}(\text{Cu,Fe})\text{O}_2$ block and the decrease in the number of five coordinated high-spin Fe^{3+} ions are responsible for the observed changes in the magnetic properties of the $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ samples.

Acknowledgments

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