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Direct Observations of β'''-Structures in a K_2O–Fe_2O_3–CdO System by High-Resolution Electron Microscopy

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The direct confirmation of the existence of Cd-stabilized β'''-ferrite prepared as a stable phase in a K_2O–Fe_2O_3–CdO system was done by high-resolution electron microscopy. It was confirmed that the Cd-stabilized β'''-ferrite had a rhombohedral symmetry with lattice constants $a = 0.600$ and $c = 5.026$ nm. The structure is composed of an alternate stacking of ion-conductive layers and spinel-like blocks which have six cubic close-packed oxygen layers expressed as $\cdots A_1(BCABCA)B_1(CABCAB)C_1(ABCABC)A_1 \cdots$. In addition, twins which had reversed stacking sequences were observed in the spinel-like blocks. © 1994 Academic Press, Inc.

1. INTRODUCTION

β-Ferrites and β''-ferrites are compounds well-known for high K^+ ion conductors which have crystal structures analogous with those of β- and β''-aluminas (1–5). These ion-conductive ferrites have an alternate stacking structure of ion-conductive layers and spinel-like blocks which have four cubic close-packed oxygen layers (stacking sequence expressed as [ABCA]). The chemical composition of β- and β''-ferrites is approximately expressed as $K_{1+x}Fe_{11}O_{17}$ ($0 \leq x \leq 1$). However, the crystal structures of β- and β''-ferrites show obvious differences in their symmetries. Namely, the β-structure is hexagonal ($P6_3/mmc$) (6, 7), while the β''-structure is rhombohedral ($R\bar{3}m$) (4, 8–13).

It is well known that β'''- and β''''-structures exist in a Na_2O–Al_2O_3–MgO system in addition to the β- and β''-structures mentioned above (14–18). The relations between β'''- and β''''-structures are similar to those of the β- and β''-structures except that the spinel-like blocks contain six cubic close-packed oxygen layers (stacking sequence expressed as [ABCABC]). While β'''-ferrite was prepared as a stable phase above 1400°C in a K_2O–Fe_2O_3 system (3), the existence of β''''-ferrite has not been reported before. Recently, we have succeeded in preparing β''''-ferrite as a stable phase in a K_2O–Fe_2O_3–CdO system. However, there is no conclusive proof that the β''''-ferrite prepared in a K_2O–Fe_2O_3–CdO system has a rhombohedral symmetry.

The purpose of the present paper is to report the existence of β''''-ferrite. Lattice images of Cd-stabilized β''''-ferrite are observed directly by high-resolution electron microscopy. The crystal symmetry, in other words, the stacking sequence of oxygen layers of Cd-stabilized β''''-ferrite, has been resolved.

2. EXPERIMENTAL PROCEDURES

The samples were prepared by conventional ceramic techniques. The sample had a composition of $K_2O \cdot 10Fe_2O_3 \cdot 2.6CdO$. Mixtures of the weighted raw materials in the forms of K_2CO_3, Fe_2O_3, and CdO were pressed into a pellet, and the pellet was introduced into a platinum crucible and calcined at 1173 K for 1 hr in air. After the pellet was crushed and pressed again, it was fired at 1673 K for 2 hr. The samples were cooled to room temperature in the furnace.

The samples were crushed into fragments for electron microscopy observation in an agate mortar; a drop of suspension of the fragments was then transferred to a holey carbon-film-coated copper grid. Observations were made with a 300-kV high-resolution electron microscope (JEM-3010). The instrument, equipped with a side-entry specimen double-tilting stage (±30° tilt), has a resolving power of 0.21 nm.

3. RESULTS AND DISCUSSION

An X-ray diffraction pattern of the Cd-stabilized β''''-ferrite (Fig. 1) shows that all reflections could be consistently indexed by rhombohedral symmetry. The diffraction pattern of β''''-ferrite is similar to that of β'''-ferrite (5) except for the reflection from the (1 0 16) plane (indicated by an arrow in Fig. 1), which is unique to β''''-ferrite. The diffraction pattern was indexed as a single β''''-ferrite phase with lattice constants (hexagonal setting) $a = 0.600$

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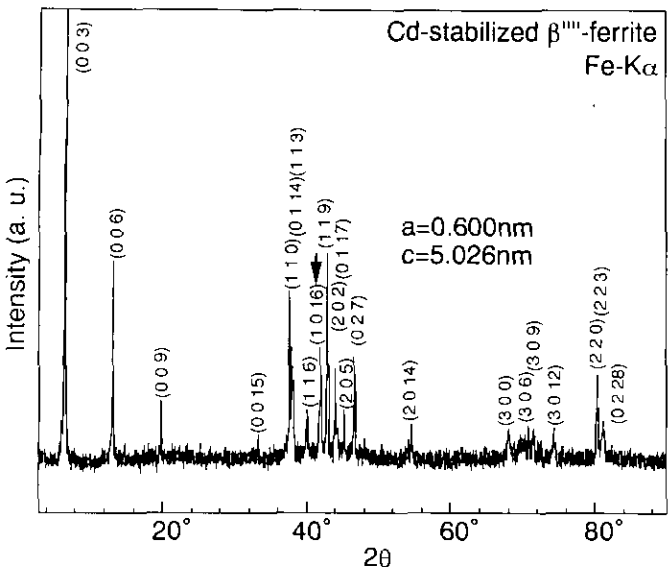

FIG. 1. X-ray powder diffraction pattern of Cd-stabilized β''''-ferrite indexed with rhombohedral symmetry; a = 0.600 and c = 5.026 nm. The arrow indicates the reflection (1 0 16), which is unique to the β''''-structure.

and c = 5.026 nm, because the observed 2θ and d value of Cd-stabilized β''''-ferrite agree well with the calculated ones using lattice constants a = 0.600 and c = 5.026 nm as shown in Table 1. These lattice constants were larger than those of β''''-alumina: a = 0.56 and c = 4.8 nm (17).

TABLE 1
X-Ray Powder Diffraction Data for Cd-Stabilized β''''-Ferrite

h	k	l	2θ (Obs.)	d (nm) (Obs.)	I/I_{max} (Obs.)	2θ (Calc.)	d (nm) (Calc.)
0	0	3	6.64	1.6714	100	6.62	1.6753
0	0	6	13.22	0.8409	41	13.27	0.8377
0	0	9	19.82	0.5624	13	19.96	0.5584
0	0	15	33.32	0.3376	4	33.58	0.3351
1	1	0	37.70	0.2996	30	37.65	0.3000
0	1	14	38.04	0.2970	23	38.26	0.2953
1	1	3				38.27	0.2953
1	1	6	39.96	0.2832	6	40.09	0.2824
1	0	16	41.94	0.2704	21	42.21	0.2688
1	1	9	42.92	0.2645	40	42.97	0.2643
2	0	2	44.02	0.2582	16	44.00	0.2584
0	1	17	44.36	0.2564	6	44.26	0.2569
2	0	5	45.26	0.2515	9	45.27	0.2515
0	2	7	46.66	0.2444	21	46.69	0.2443
2	0	14	54.72	0.2106	4	54.76	0.2106
3	0	0	67.94	0.1732	4	67.96	0.1732
3	0	6	70.90	0.1668	7	69.60	0.1696
3	0	9	71.50	0.1656	6	71.63	0.1654
3	0	12	74.50	0.1599	6	74.43	0.1601
2	2	0	80.36	0.1500	15	80.38	0.1500
2	2	3	80.52	0.1497	11	80.77	0.1494
0	2	28	81.24	0.1486	7	81.91	0.1477

Note. a = 0.600, c = 5.026 nm.

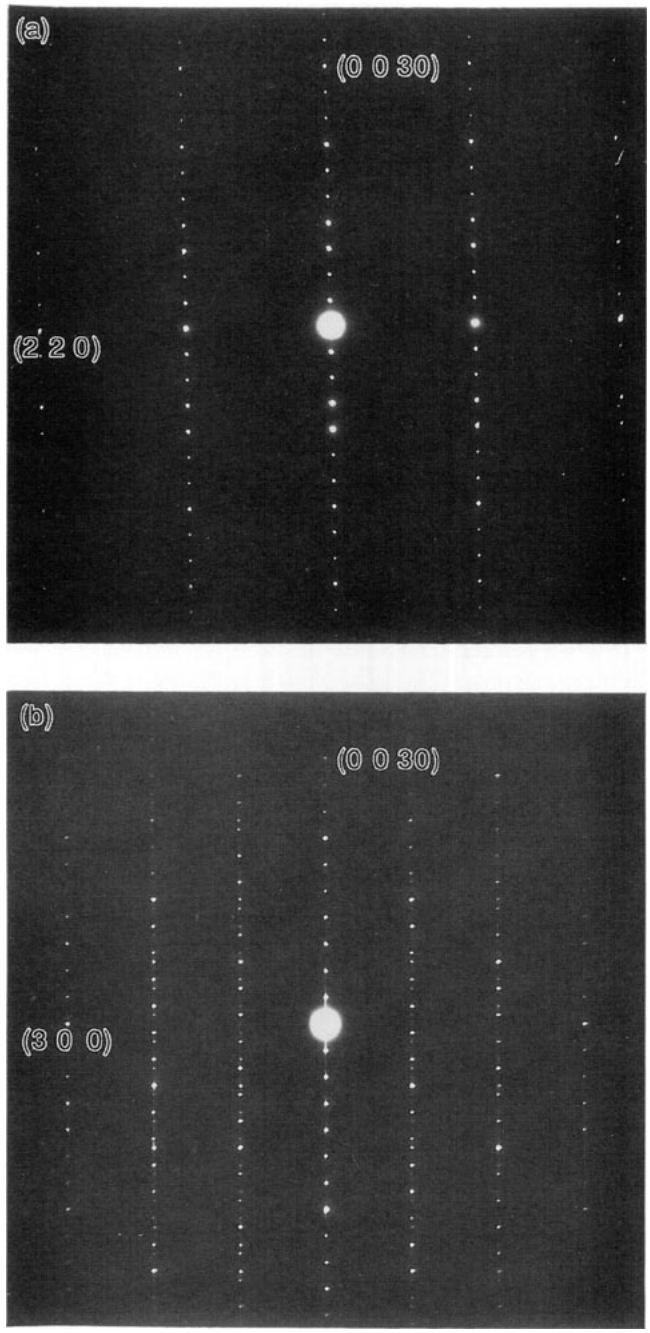

FIG. 2. Electron diffraction patterns of Cd-stabilized β''''-ferrite taken with the incident beam parallel with the zone axis (a) [1 $\bar{1}$ 0] and (b) [0 1 0], respectively.

These differences in lattice constants are interpreted as arising from different cation sizes [each ionic radius is 0.060 (Fe^{3+}) and 0.050 (Al^{3+}) nm]. It is also found that the a-axis length (0.600 nm) of Cd-stabilized β''''-ferrite is equal to that (0.600 nm) of Cd-stabilized β''-ferrite (8). This agreement suggests that the stabilizing Cd^{2+} ion can

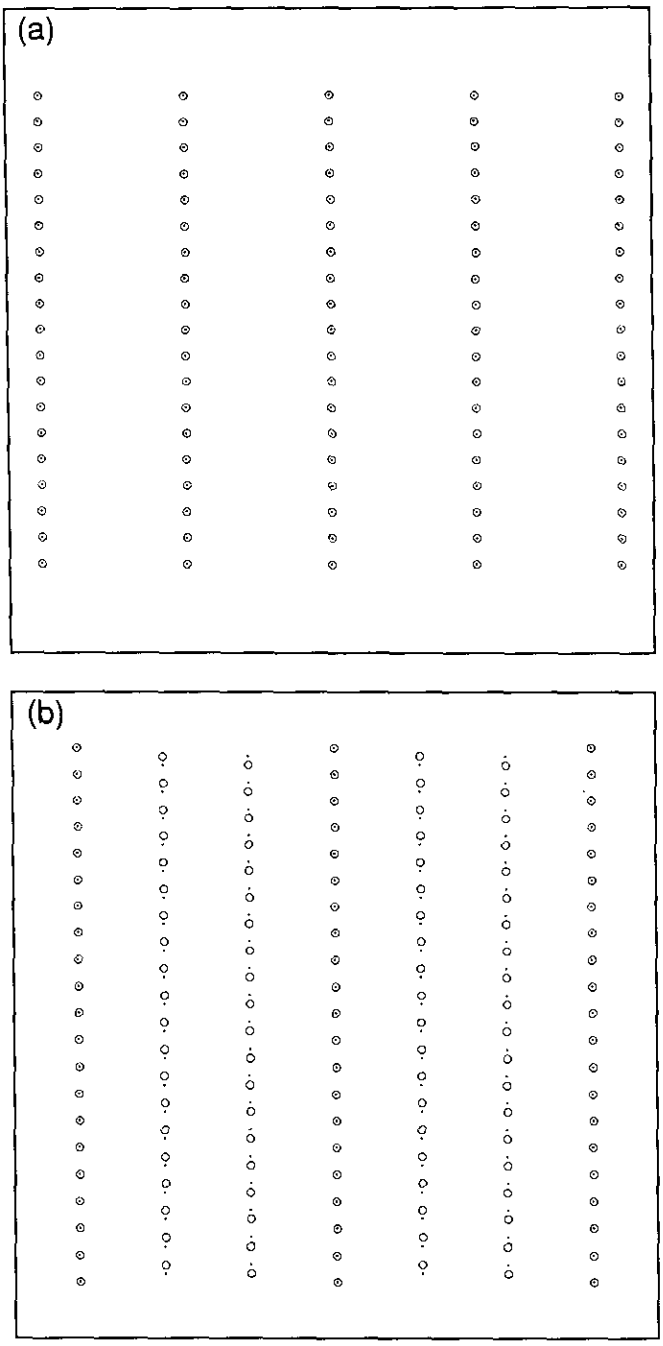

FIG. 3. Calculated diffraction patterns of Cd-stabilized β''''-ferrite provided the incident beam parallel with the zone axis (a) [1 $\bar{1}$ 0] and (b) [0 1 0], respectively. The circle spots are due to the matrix, while dot spots are due to twins.

exist on the tetrahedral sites in the spinel-like blocks of β''''-ferrite.

The electron diffraction patterns taken with the incident electron beam parallel with the zone axis [1 $\bar{1}$ 0] and [0 1 0], respectively, show systematic absences of the reflections with $-h + k + l \neq 3n$ in Figs. 2a and 2b. These

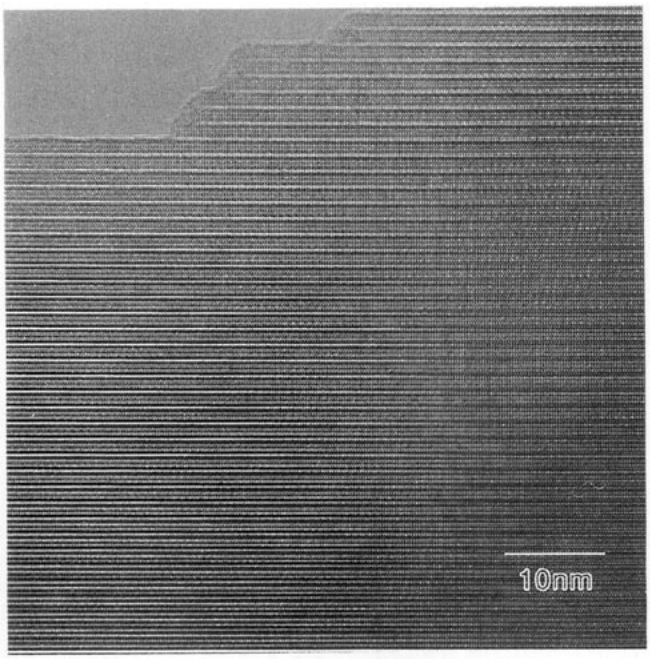

FIG. 4. Fringe image of Cd-stabilized β''''-ferrite taken with the incident beam parallel with the zone axis [1 $\bar{1}$ 0].

systematic absences of the reflections indicate that the crystal has rhombohedral symmetry. The lattice constants calculated from this diffraction were $a = 0.6$ and $c = 5.0$ nm, which agree well with the X-ray diffraction data mentioned above. A doubling of spots which would be due to twins in (1 0 x) and (2 0 x) along the c^* axis are observed in Fig. 2b. This doubling of spots is well represented in the calculated diffraction pattern shown in Fig. 3. It is clear that twins will be observed in the case of an incident electron beam parallel with the zone axis [0 1 0], because spots due to the matrix and ones due to twins are fully overlapping in Fig. 3a, which corresponds to the electron diffraction pattern taken with the incident electron beam parallel with the zone axis [1 $\bar{1}$ 0] in Fig. 2a. Images of twins will be presented later.

The 300-kV high-resolution electron microscopy image taken with the incident beam parallel with the zone axis [1 $\bar{1}$ 0] gives the fringe image in Fig. 4. Strong fringes may be interpreted as corresponding to low-electron-density regions, namely ion-conductive layers. Higher magnification images taken with the incident beam parallel with the zone axis [1 $\bar{1}$ 0] and [0 1 0], respectively, give the spot images in Figs. 5a and 5b instead of fringes as in Fig. 4. In each line of white dots, two adjoining dots are separated by 0.3 nm in Fig. 5a and by 0.5 nm in Fig. 5b. Furthermore, two neighboring lines corresponding to conduction layers separated by spinel-like blocks are mutually displaced normal to the c axis by 0.5/3 nm in Fig. 5b; the displacement will be due to the threefold screw axis in the β''''-

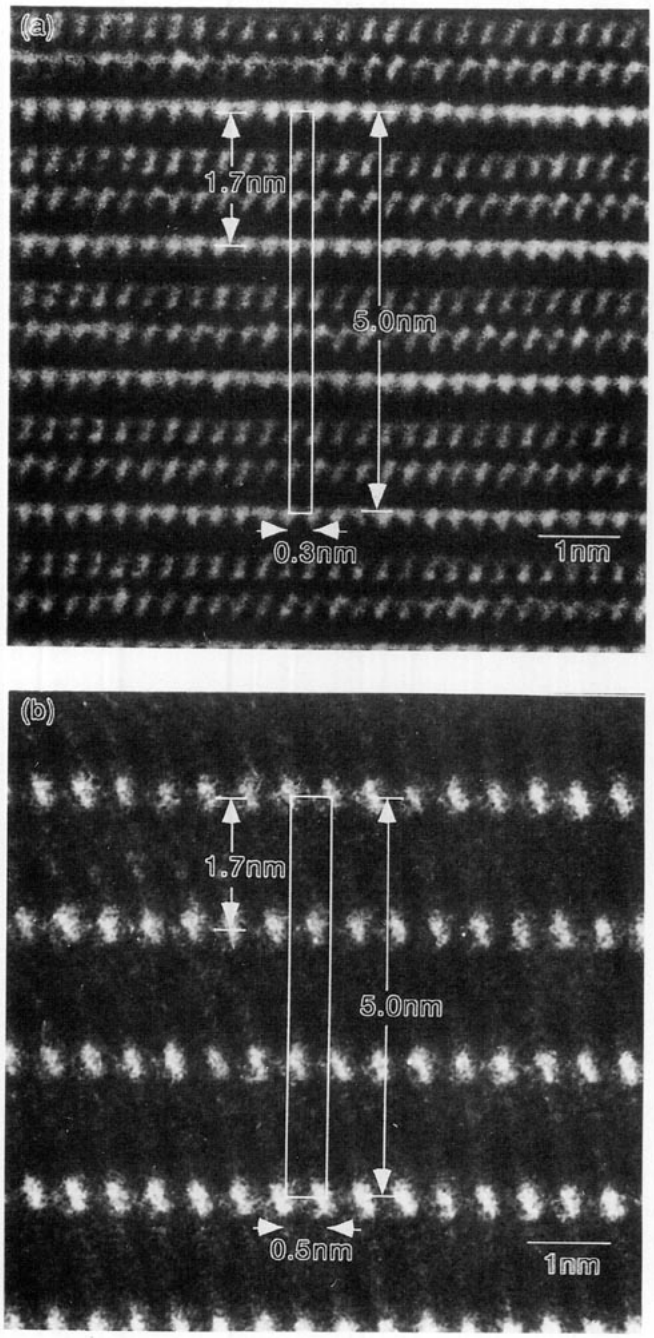

FIG. 5. Lattice images of Cd-stabilized β''''-ferrite taken with the incident beam parallel with the zone axis (a) [1 $\bar{1}$ 0] and (b) [0 1 0], respectively.

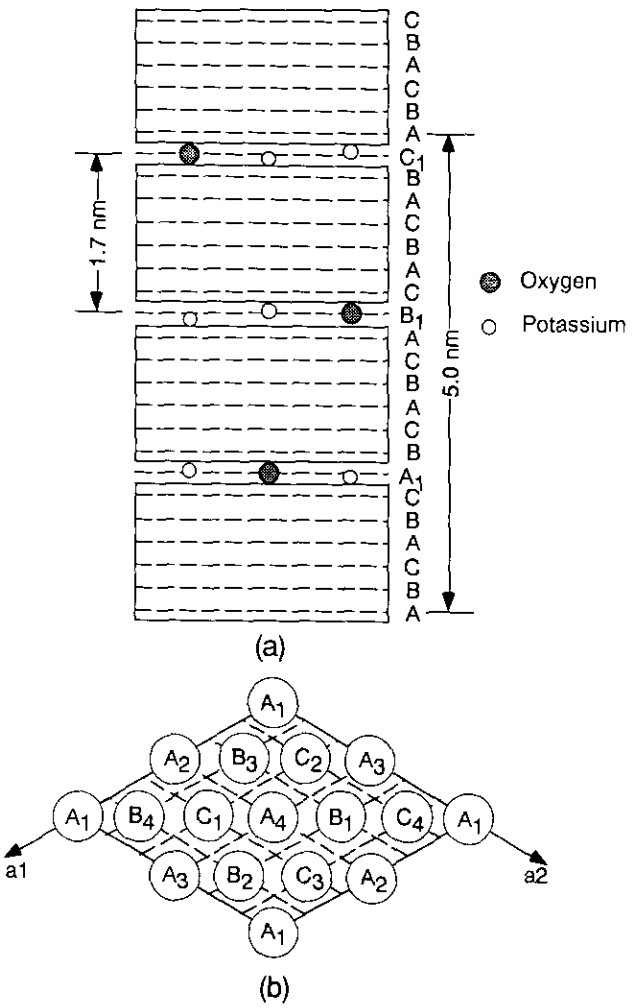

FIG. 6. (a) Schematic diagram of the crystal structure of β''''-ferrite. (b) Atomic positions in the basal plane of β''''-ferrite.

ferrite structure. Therefore, the structure of β''''-ferrite will be described as (17)

$$\cdots A_1(BCABCA)B_1(CABCAB)C_1(ABCABC)A_1 \cdots,$$

where letters in parentheses stand for oxygens in the spinel-like blocks. The letter A means that the A_1 to A_4 positions are all occupied as shown in Fig. 6b. Because the distance between B_1 and C_1 is 0.23×6 (thickness of spinel-like block) + 0.23 (thickness of ion-conductive layers) $\approx$ 1.61 nm, where 0.23 nm is the mean distance between two neighboring oxygen layers (for example, the A–B distance) when iron and oxygen ions are closely packed, then each spinel-like block contains six cubic close-packed oxygen layers.

A schematic diagram of β''''-ferrite resulting from this consideration is represented in Fig. 6a. This schematic diagram represents the lattice image in Fig. 5b. Large white dots represent the midpoints of two adjacent potassium positions in the ion-conductive layers in Fig. 5b.

Images of twins along the c axis in the Cd-stabilized β''''-ferrite are observed in Fig. 7. This was imaged with the incident electron beam parallel with the zone axis [0 1 0]. The arrows indicate that twins which have a reversed

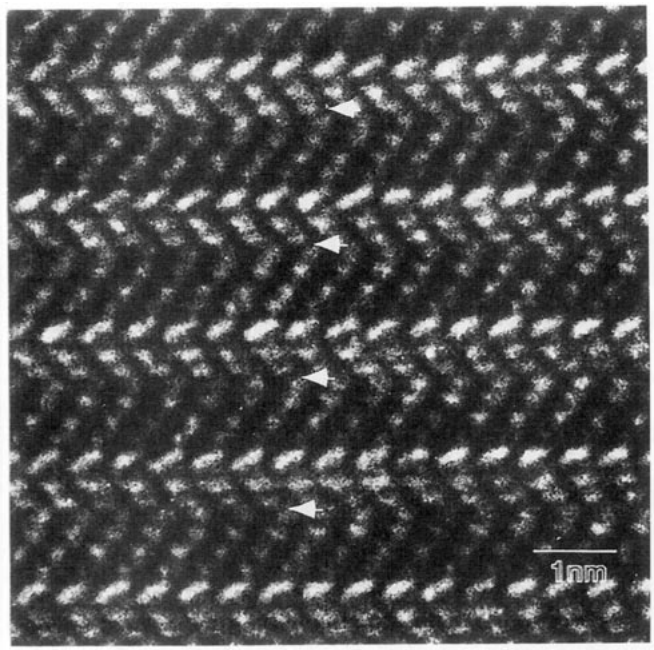

FIG. 7. Lattice image of Cd-stabilized β''''-ferrite taken with the incident beam parallel with the zone axis [0 1 0]. Twins which have a reversed stacking sequence (ABCA*CB*) are indicated by arrows.

stacking sequence exist in the spinel-like blocks. In this region, the stacking sequence can be expressed as

$$\cdots A_1(BCABAC)B_1(CABCBA)C_1(ABCACB)A_1 \cdots,$$

where the italic letters stand for the reversed sequence compared with the normal stacking sequence. Many twins along the c axis were observed in this Cd-stabilized β''''-ferrite, in accordance with the doubling of spots along the c^* axis observed in the diffraction pattern (Fig. 2b). These twins could be generated by lack of stabilizing Cd atoms, strain due to crushing, or electron beam irradiation.

4. CONCLUSION

The present paper confirms the existence of β''''-ferrite in a K_2O–Fe_2O_3–CdO system by direct lattice imaging.

The unit cell of Cd-stabilized β''''-ferrite (a = 0.600 and c = 5.026 nm) contains three spinel-like blocks which contain six cubic close-packed oxygen layers and are mutually related by the threefold screw axis parallel to the c axis. Cd-stabilized β''''-ferrite has rhombohedral symmetry. Furthermore, twins with a reversed stacking sequence were observed in the spinel-like blocks.

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