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Crystal structure of a new compound $Er_2MnW_{0.8}O_{6.4}$ phase

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Abstract

A new compound of $Er_2MnW_{0.8}O_{6.4}$ system was synthesized by solid-state reaction method under low oxygen partial pressure. A single phase with a composition $Er_2MnW_{0.8}O_{6.4}$ was obtained after trying various composition ratios and its crystal structure was refined by powder X-ray diffraction data using the Rietveld analysis. The space group was $P3_121$ belonging to trigonal system with the lattice parameters of $a = 0.725$ and $c = 0.936$ nm. The electron diffraction data also showed this size of the unit cell. The derived structure was not a pyrochlore-related structure because no systematic stacking layers by hexagonal tungsten bronze type appeared.

Keywords: Structural analysis; Compounds; X-ray diffraction; Pyrochlore-related structure; Rare earth

1. Introduction

Complex oxides $Ln_2B_{2-x}B'_xO_7$ phases with a pyrochlore and its related structure have been studied from interesting physical and chemical properties by various combinations of rare earth (Ln) and transition metal (B, B′) ions. Among them Mn-containing compounds $Ln_2Mn_2O_7$ can be prepared only under high pressure [1–3], but some compounds such as $Ln_2Mn_{1-x}M_xO_7$ (M = W, Mo, etc.) were synthesized under normal conditions [4–11]. In these Mn-containing oxides, the oxidation states of Mn ions are known to change under their varying synthesizing atmospheres. Bazuev et al. [4–6] and Chen et al. [7–9] have shown the possibility of synthesizing mixed-pyrochlores, $Ln_2Mn_xM_{2-x}O_7$ (Ln = Er or Ho, M = Ta, Nb or Mo), under an ordinary pressure and in various atmospheres. X-ray diffraction (XRD) data have shown that the compounds possess rhombohedral or hexagonal (trigonal) structures.

In recent years, some of these oxides have been investigated with XRD-Rietveld analysis and high-resolution transmission electron microscopy (HRTEM) [12–14]. From the results of structural analysis $Ho_2Mn_{2-x}Ta_xO_7$ [13] and $Er_2Mn_{2/3}Mo_{4/3}O_7$ [14] have a trigonal symmetry (zirkelite-type) and a monoclinic symmetry (zirconolite-type), respectively. This difference in the structures was caused by the stacking sequence along the *c*-direction of a pair of A cation and B cation layers; the B cations formed a hexagonal tungsten bronze (HTB)-type layer that is a characteristic frame-layer in the pyrochlore-related structure [15,16].

In the present study, a new oxide $Er_2MnW_{0.8}O_{6.4}$ was synthesized in a reducing atmosphere at 1623 K. Its crystal structure was characterized by X-ray diffraction data using the Rietveld analysis [17,18] and HRTEM.

2. Experimental

The starting materials were Er_2O_3, Mn_2O_3 and WO_3 with a purity of 99.99% (Rare Metallic Co. Ltd.). In order to adjust the stoichiometry of the starting materials Er_2O_3 was prepared at 1273 K for 24 h in an Ar atmosphere, WO_3 was heated at 673 K for 12 h in air and Mn_2O_3 at 1073 K for 72 h in air and then quenched to room temperature.

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These starting materials were thoroughly mixed in various molar ratios to obtain a single phase of Er–Mn–W–O system. The mixtures were pressed into pellets and heated at 1623 K for 48 h in Ar containing 1% H_2. The products were identified with a powder X-ray diffractometer using Cu Kα radiation, and the experimental data were further analyzed by the Rietveld method. The specimen of TEM was crushed in a mortar and scooped with carbon-coated microgrids on a copper mesh. Then the crushed specimen was investigated with a JEM-2000EX TEM operating at 200 kV. High-resolution structure imaging was performed by JEM-3000F TEM operating at 300 kV with spherical aberration of $C_S = 1.0$ nm.

3. Results and discussion

When the syntheses were done with the molar ratio Mn:W = 1:1, Er_2MnWO_7 with a pyrochlore-related structure was not obtained as a single phase because $ErMnO_3$ was also found as the second phase. However, it is shown that $Er_2MnW_{0.8}O_{6.4}$ synthesized by the molar ratio Mn:W = 1:0.8 was most similar to a single phase since only small quantity of MnO was found as the second phase. For Mn:W > 1:0.8, more much quantity of MnO was found, while Mn:W < 1:0.8 $ErMnO_3$ phase was found.

The X-ray diffraction patterns of $Er_2MnW_{0.8}O_{6.4}$ are similar to those of Ho_2MnTaO_7 [13] having a pyrochlore-related structure as is shown in Fig. 1. The diffraction peaks are indexed based on a hexagonal cell, but the cell lattice parameters were $a = 0.7252$, $c = 0.9369$ nm, which was half the size of the c-dimension in Ho_2MnTaO_7.

In order to investigate the structure of $Er_2MnW_{0.8}O_{6.4}$, a Rietveld analysis was carried out by the XRD data based on two structure models, the type 1 and the type 2, with the space group $P3_121$. Tables 1 and 2 list the refined atomic coordinates. From these data it was shown that the type 2 (the value of the lattice parameter c was one half the type 1) gives better results than those of the type 1. The reliability factor R_{wp} of structural refinement had 14.33% for the type 1, while R_{wp} had the smaller 13.12% if the type 2 was used. The XRD patterns calculated with the structural model of the type 2 were in agreement with the observed ones.

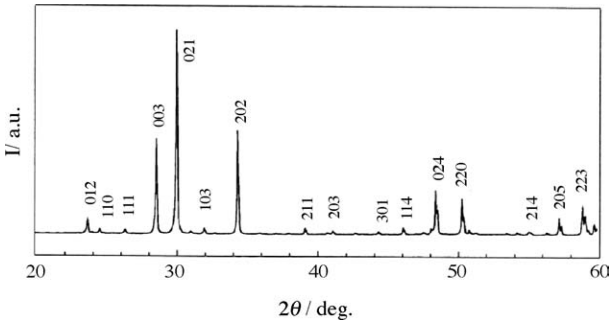

Fig. 1. Powder XRD pattern of $Er_2MnW_{0.8}O_{6.4}$. The peaks are indexed as a hexagonal cell with lattice parameters of $a = 0.7242$ and $c = 0.9365$ nm.

Table 1
Atomic coordinates of $Er_2MnW_{0.8}O_{6.4}$ (type 1)

Atom	Site	Atomic coordinates		
		x^a	y^a	z^a
Er(1)	3(a)	0.8779(9)	0	1/3
Er(2)	3(a)	0.3341(4)	0	1/3
Er(3)	6(c)	0.6621(9)	0.1586(1)	−0.0102(5)
Mn, W(1)	3(b)	0.8685(3)	0	5/6
Mn, W(2)	3(b)	0.3254(2)	0	5/6
Mn, W(3)	6(c)	0.5166(3)	0.3424(2)	0.1577(1)
O(1)	6(c)	0.2035(2)	0.2283(1)	0.1577(1)
O(2)	6(c)	0.5633(1)	0.6084(1)	0.1955(2)
O(3)	6(c)	0.1955(1)	0.6400(3)	0.1464(1)
O(4)	6(c)	−0.0493(1)	0.3164(1)	0.0547(1)
O(5)	6(c)	0.0363(2)	0.8235(2)	0.0547(1)
O(6)	6(c)	0.560(3)	0.4000(1)	0.0565(5)
O(7)	6(c)	0.555(5)	0.8235(1)	0.0591(1)

Space group: $P3_121$; $a = 0.7252(2)$ nm, $c = 1.8739(9)$ nm. $R_{wp} = 14.33\%$, $R_P = 10.23\%$. $R_E = 5.17\%$. $R_I = 6.62\%$. $R_F = 6.44\%$. Site occupancies of (Mn,W(1)), (Mn,W(2)) and (Mn,W(3)) are 0.9, 0.9 and 1.0, respectively.

[a] The standard deviation of the last digit is given in parenthesis.

The crystal structure of $Er_2MnW_{0.8}O_{6.4}$ based on the structural model of the type 1 and 2 is shown in Fig. 2. In the case of type 1, the crystal structure is similar to Ho_2MnTaO_7 [13] in which A and B cation layers arranged alternately form a pair of layers along the c-direction. On the other hand, in the case of type 2, no pair was observed in the structure, and accordingly, the c-dimension was up to half the size of that in pyrochlore-related compounds. The results indicated that this structure in $Er_2MnW_{0.8}O_{6.4}$ is not a pyrochlore-related structure. In addition, the B cations did not come to form a characteristic layer of an HTB-type layer [15,16].

The results of the structural refinement for the type 2 shown that there are two kinds of oxygen octahedra surrounding the central (Mn, W) ions where manganese and tungsten ions are randomly distributed over the B-site. Each of these B-site ions is coordinated to six oxygen ions, but the

Table 2
Atomic coordinates of $Er_2MnW_{0.8}O_{6.4}$ (type 2)

Atom	Site	Atomic coordinates		
		x^a	y^a	z^a
Er(1)	6(c)	0.653(4)	0.147(9)	0.020(2)
Mn, W(1)	3(a)	0.848(4)	0	1/3
Mn, W(2)	3(a)	0.325(9)	0	1/3
O(1)	3(a)	0.583(1)	0	1/3
O(2)	3(b)	0.152(3)	0	1/3
O(3)	3(b)	0.538(2)	0	5/6
O(4)	6(c)	0.991(2)	0.349(5)	−0.067(5)
O(5)	6(c)	0.756(5)	0.969(5)	0.122(7)

Space group: $P3_121$; $a = 0.7252(1)$ nm, $c = 0.9369(8)$ nm. $R_{wp} = 13.12\%$, $R_P = 9.86\%$. $R_E = 5.18\%$. $R_I = 6.93\%$. $R_F = 6.65\%$. Site occupancies of (Mn,W(1)) and (Mn,W(2)) are 1.0 and 0.8, respectively.

[a] The standard deviation of the last digit is given in parenthesis.

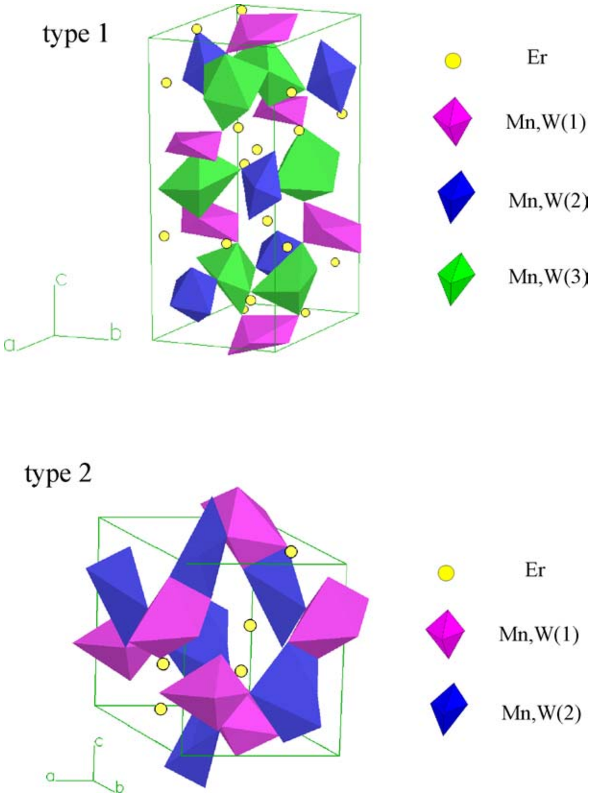

Fig. 2. The crystal structure of $Er_2MnW_{0.8}O_{6.4}$ based on the structural model of the type 1 and 2.

shape of these MO_6 field in both types are much distorted from the regular octahedron. Their stacking mode is apparently similar to those of the pyrochlore-related structures such as pyrochlore, zirkelite and zirconolite, but no regularity in the stacking of MO_6 characteristic of these structures was seen.

Fig. 3 shows the selected area diffraction (SAD) patterns obtained from the [$\bar{1}$ 0 0] in (a), [$\bar{1}$ 1 0] in (b) and [0 0 1] zone axes in (c). All of the reflections could be indexed based on the hexagonal cell determined by XRD. On the (0 0 1)* plane, the pattern was same as that of Ho_2MnTaO_7 with space group of $P3_121$ [13]. However, along the c*-axis, the cell size was calculated to be half the size of the c-dimension in Ho_2MnTaO_7. In Fig. 3(a), intensity of 0 2 1 reflection was different from that of 0 $\bar{2}$ 1 reflection, and the fact indicated that the cell was a trigonal not a hexagonal.

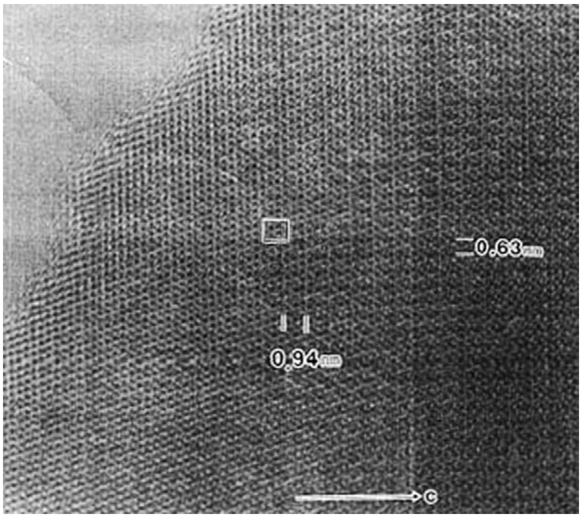

Fig. 4. HRTEM image of $Er_2MnW_{0.8}O_{6.4}$ taken from the [1 0 0] zone axis.

Fig. 4 shows a HRTEM image of $Er_2MnW_{0.8}O_{6.4}$ taken from the [1 0 0] zone axis. The lattice fringes with repeat distance of 0.94 nm was observed, where each fringe consisted of three cation layers and the repeat distance corresponded to the c-dimension. The lattice image was obviously different from that of pyrochlore-related structures, Ho_2MnTaO_7 [13] and $Er_2Mn_{2/3}Mo_{4/3}O_7$ [14], in which A and B cation layers arranged alternately form a pair of layers along the c-direction. In this case, no pair was observed in the structure and the c-dimension was up to half the size of that in pyrochlore-related compounds. These results were in agreement with those of XRD-Rietveld analysis. In Fig. 4, the weak repeat distance of 0.63 nm corresponded to (1 0 0) spacing. Black spots were believed to reflect cations in the thin crystal, and the unit cell was enclosed by the rectangle.

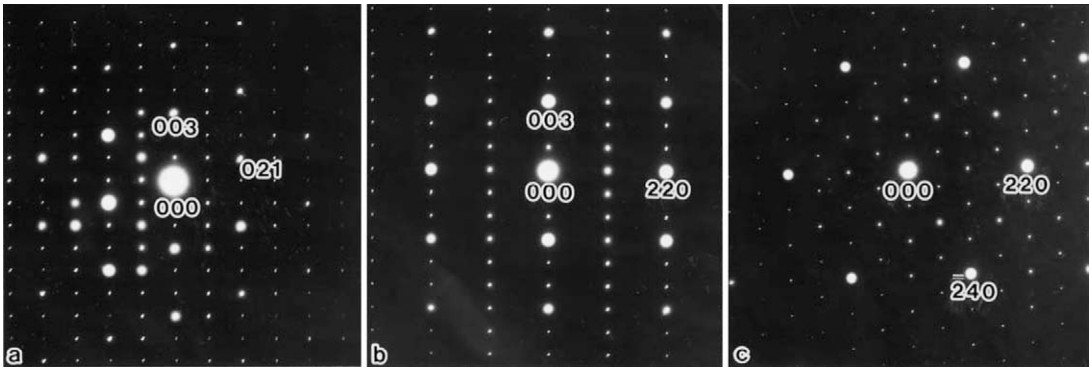

Fig. 3. Selected area diffraction patterns taken from the [$\bar{1}$ 0 0], [$\bar{1}$ 1 0] and [0 0 1] zone axes.

4. Conclusions

The new compound, $Er_2MnW_{0.8}O_{6.4}$, synthesized from a mixture of Er_2O_3, Mn_2O_3 and WO_3 was confirmed to have a trigonal cell. The cell parameters were determined to be $a = 0.725$ and $c = 0.936$ nm by Rietveld analysis and HRTEM image. The c-dimension was up to half the size of that in Ho_2MnTaO_7, which has a pyrochlore-related structure. TEM data revealed that the A-cations and B-cations did not form a pair of layers along the c-direction, and accordingly, it could be assumed that the B-cations did not form HTB-type layers as seen in pyrochlore-related structures. The same result was also proved from the Rietveld analysis of $Er_2MnW_{0.8}O_{6.4}$. Therefore, the structure in $Er_2MnW_{0.8}O_{6.4}$ is not a pyrochlore-related structure but a new type structure with $P3_121$ space group.

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