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Short communication

A crystal structure consideration of an orthorhombic $BaEu_2Mn_2O_7$ phase

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Abstract

The electron microscopic study was performed on an orthorhombic $BaEu_2Mn_2O_7$ phase. The electron diffraction patterns of this phase showed some series of superlattice spots such as $h\,0\,0$ (h = odd), $h\,k\,0$ (h,k = odd) and $h0l$ (h,l = odd) that were forbidden for face centered cell. A possible space group $P112_1/m$ (11) was derived from the reflection conditions. And then, a superstructure of this phase was discussed in this paper.

Keywords: B. Defects; D. Perovskite; Ceramics; Crystal structure; Microstructure

1. Introduction

$BaEu_2Mn_2O_7$ phase possesses $Sr_3Ti_2O_7$ type structure which belongs to Ruddlesden–Popper homologous series [1,2]. It is known that this phase shows two different types of orthorhombic structures. One type of the orthorhombic structure has the lattice parameters a and $b \approx a_t$ and $c \approx c_t$ where a_t and c_t denote the lattice parameters of fundamental tetragonal cell. And another type has the lattice parameters a and $b \approx \sqrt{2}a_t$ and $c \approx c_t$. The latter orthorhombic phase can be easily obtained by the sintering in argon atmosphere [2].

In the stoichiometric composition of $BaEu_2Mn_2O_7$, manganese ion has trivalent state. Because trivalent manganese ion is a Jahn–Teller ion, the oxygen octahedra in the stoichiometric $BaEu_2Mn_2O_7$ phase elongated along c axis as our previous report [2]. Where, it was considered that a high spin state electron occupied d_z2 orbital. The powder X-ray diffraction pattern of this phase satisfied *Fmmm* (69) symmetry without superlattice reflections.

In this study, the crystal structure of an orthorhombic $BaEu_2Mn_2O_7$ phase was studied by electron diffraction method and a new superstructure model was proposed.

2. Experimental procedures

Crystalline $BaEu_2Mn_2O_7$ was prepared by solid-state reaction. High purity $BaCO_3$, Eu_2O_3 and Mn_2O_3 powders (all 99.99% purity) were used as the starting materials. A stoichiometric composition of these powders ($BaCO_3$:Eu_2O_3:Mn_2O_3 = 1:1:1) were mixed in agate mortar and then, pressed into pellets. The pellets were heated at 1350 °C for 3 days in Ar atmosphere. The phase identification was performed by powder X-ray diffraction method. The orthorhombic phase was successfully prepared. For electron diffraction data collection, the sintered pellet was crushed and mounted on micro grid mesh.

3. Results and discussion

This phase possessed $Sr_3Ti_2O_7$ type structure [1] and the powder X-ray diffraction pattern of this phase shows *Fmmm* (69) symmetry as our previous report [2]. No forbidden

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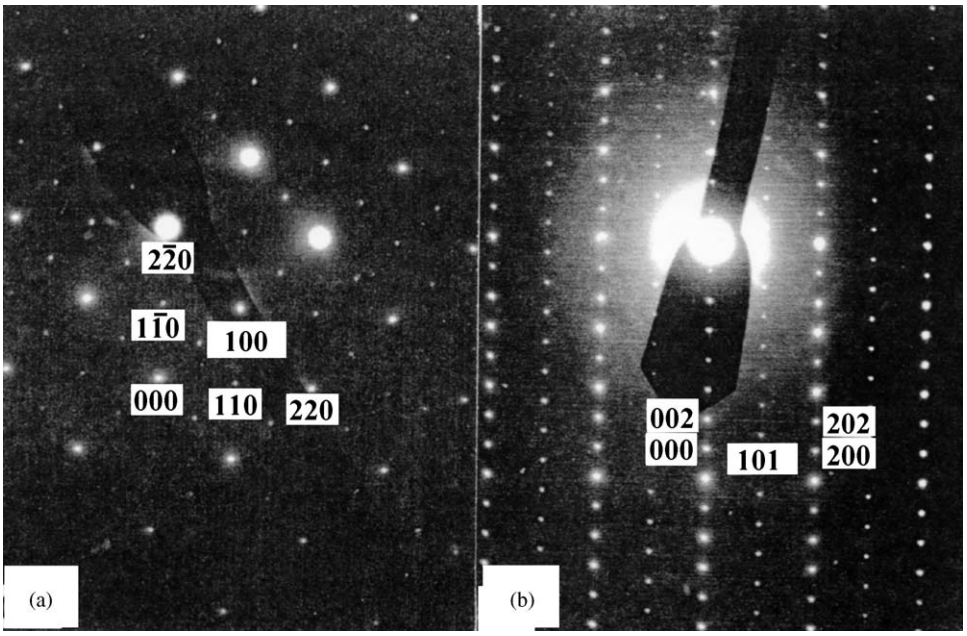

Fig. 1. The electron diffraction patterns of $BaEu_2Mn_2O_7$ phase from $[0\ 0\ 1]_o$ and $[1\ 0\ 0]_o$ zones.

peaks of *Fmmm* symmetry can be observed in the powder X-ray diffraction pattern. The lattice parameters of this orthorhombic phase were $a_o \approx \sqrt{2}a_t$, $b_o \approx \sqrt{2}a_t$ and $c_o \approx c_t$, where a_o, b_o and c_o denote orthorhombic cell and a_t and c_t denote fundamental tetragonal cell.

Fig. 1(a) and (b) show the electron diffraction patterns of this phase. The zone axis of Fig. 1 (a) is $[0\ 0\ 1]_o$. Where two different types of superlattice spots series can be clearly observed. The super lattice spots of $h\ k\ l$ ($h + k$ = odd and l = even) such as 1 0 0 can be observed between fundamental spots of $h\ k\ l$ (all even). In addition to this type superlattice spots, $h\ k\ l$ (h and k = odd and l = even) type superlattice spots such as 1 1 0 can be also observed in Fig. 1(a). On the other hand, $[1\ 0\ 0]_o$ zone pattern also shows a series of superlattice spots, where the super lattice of *hkl* ($h + k$ = odd and l = even) type can be observed. These superlattice spots are weak, however, that can be clearly seen in the electron diffraction patterns. These reflections are

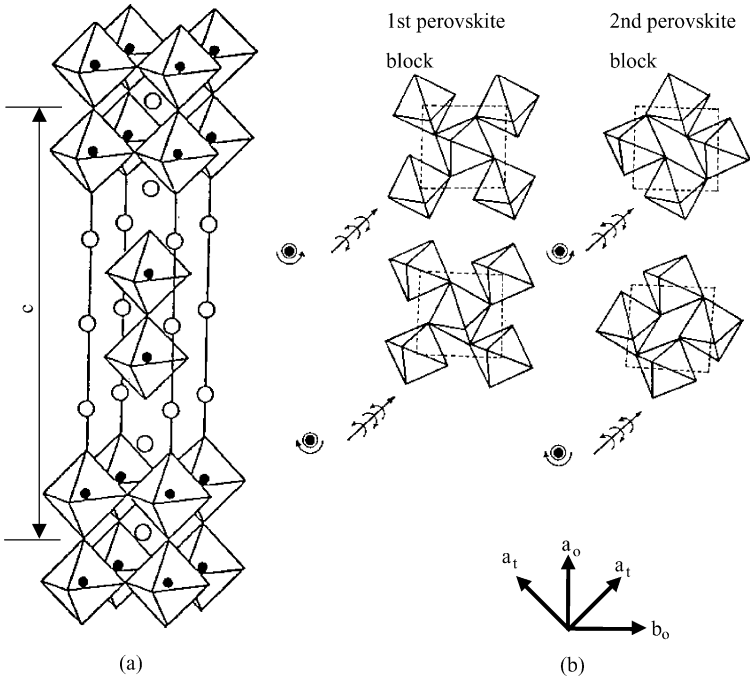

Fig. 2. The fundamental crystal structure of $Sr_3Ti_2O_7$ and a possible superstructural model for an orthorhombic $BaEu_2Mn_2O_7$ phase.

forbidden for *Fmmm* symmetry. Hence, a possible space group is needed for the consideration of the new superstructure.

From these diffraction patterns, the general rule of reflection conditions for this orthorhombic $BaEu_2Mn_2O_7$ phase can be derived as 0 0 *l*; *l* = even. From this extinction rule, a monoclinic symmetry space group $P112_1/m$ (11) can be derived as one possible space group.

Aleksandrov and Bartolome summarized the possible superstructures for $Sr_3Ti_2O_7$ type structure derived using tilted oxygen octahedron model [3]. According to their superstructural model, a tilted oxygen octahedron model can be assumed as a superstructure for orthorhombic $BaEu_2Mn_2O_7$ phase. The fundamental structure of $Sr_3Ti_2O_7$ and the superstructural model of this case are drawn in Fig. 2(a) and (b). In the superstructural model, a_t and c_t axis are the axes of rotations of oxygen octahedron. Each oxygen octahedron in this model tilted around a_t axis alternatively. $Sr_3Ti_2O_7$ type structure possess perovskite block where two block of oxygen octahedron linked along *c* axis. The oxygen octahedron tilted around a_t axis alternatively along c axis as shown in Fig. 2(b). On the other hand, c_t axis is also the axis of rotation. The tilting manner is also alternatively along a_t and c_t axes as shown in the figure.

The ionic state of manganese in $BaEu_2Mn_2O_7$ phase is +3 valence in the stoichiometric composition. Mn^{3+} ion possess a high spin state electron at e_g term, thus, this phase may be distorted by Jahn–Teller effect as reported previously [2,4], even if this phase does not possess the tilted oxygen octahedron mode. Thus it is considered that the orthorhombic $BaEu_2Mn_2O_7$ phase possess a distortion by Jahn–Teller effect due to trivalent manganese ion and oxygen octahedron tilting along a_t and c_t axis.

4. Conclusion

The orthorhombic $BaEu_2Mn_2O_7$ phase possesses a superstructure corresponding to the superlattice reflections. A possible space group of this phase and a possible superstructure model for this phase were proposed. The oxygen octahedron in this phase tilted around a_t and c_t axis.

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