

Incommensurate phase of the stuffed tridymite derivative BaSrFe<sub>4</sub>O<sub>8</sub>Y. Ishii<sup>a,\*</sup>, S. Kawaguchi<sup>b</sup>, K. Asai<sup>a</sup>, S. Mori<sup>a</sup><sup>a</sup> Department of Materials Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan<sup>b</sup> Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Sayo, Hyogo 679-5198, Japan

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## ABSTRACT

We demonstrate a new modulation for a high-temperature polymorph of BaSrFe<sub>4</sub>O<sub>8</sub> via synchrotron powder X-ray diffraction and transmission electron microscopy (TEM) experiments. Although the powder X-ray diffraction pattern was successfully analyzed using a structure model of space group *Pnma*, an unusually large isotropic atomic displacement parameter ( $U_{\text{iso}}$ ) was observed for the O1 atom. A split atom model that was applied to the O1 site and the adjacent Ba/Sr site, both of which are on the two-fold axis along the *c*-axis, indicated that positional disorder occurred in these atoms along the *c*-axis. The electron diffraction pattern and high-resolution TEM observations combined with the structure refinements revealed an incommensurate structure with a modulation vector  $q = 0.4270(1)a^*$  and a displacement vector perpendicular to the *a*-axis, which gave rise to the large  $U_{\text{iso}}$  value of the O1 atom. The modulation observed in this study may be a signature of structural instability, which has commonly been discussed in the stuffed tridymite-type oxides.

## 1. Introduction

AB<sub>2</sub>O<sub>4</sub> compounds with a silica-like framework can contain a wide variety of elements; alkali and alkaline earth elements can occupy the *A* site, and Mg, divalent to tetravalent transition metals and trivalent to tetravalent *p*-block elements can occupy the *B* site. These compounds also exhibit rich structural chemistry that depends on the way the BO<sub>4</sub> tetrahedra are linked together through common vertices to form upward (U) and downward (D) connections in the anionic network. An alternating arrangement of UDUDUD results in the so-called stuffed tridymite-type structure of space group *P6<sub>3</sub>22*. Examples of compounds with this structure are the high-temperature (HT) phases of BaAl<sub>2</sub>O<sub>4</sub> [1,2], SrAl<sub>2</sub>O<sub>4</sub> [3], BaGa<sub>2</sub>O<sub>4</sub> [4], and BaFe<sub>2</sub>O<sub>4</sub> [5]. BaCoSiO<sub>4</sub> [6] and BaZnGeO<sub>4</sub> [7] also crystallize in this structure.

The manner by which the U and D linkage types combine allows several UD sequences to be produced, which provides various stuffed tridymite derivatives. CaAl<sub>2</sub>O<sub>4</sub> [8] and the low-temperature (LT) phase of SrAl<sub>2</sub>O<sub>4</sub> [3] are examples of compounds having a UUDUDD sequence. SrFe<sub>2</sub>O<sub>4</sub> [9], the LT phase of BaGa<sub>2</sub>O<sub>4</sub> [10], and CsAlTiO<sub>4</sub> [11] are known to crystallize with a UUUDDD sequence. The LT phase of BaFe<sub>2</sub>O<sub>4</sub> [12] is known to have a UUUUUD pattern. These derivatives often show distorted crystal structures due to cationic displacement at the *A* site or significant tilting of the BO<sub>4</sub> tetrahedra.

BaSrFe<sub>4</sub>O<sub>8</sub> is a compound having a regular UUUUUU sequence [13,14]. This sequence causes the Fe<sub>2</sub>O<sub>7</sub> pillars along the *c*-axis to form six-membered rings, the centers of which are occupied by Ba ions.

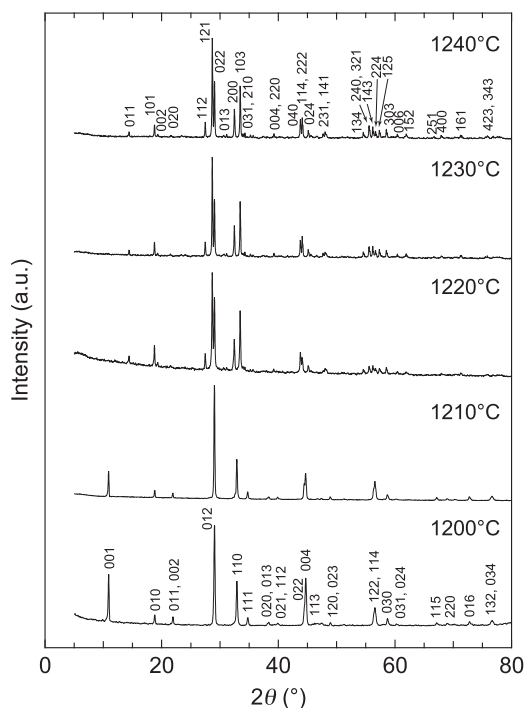
Double layers of these Fe<sub>2</sub>O<sub>7</sub> pillars are interconnected by Sr ions in an octahedral environment of oxygen, thereby forming a two-dimensional layered structure. This phase is observed below approximately 1200 °C and is reported to have the space group *P3<sub>1</sub>m*. However, another phase has been reported to exist in the narrow temperature window between ≈ 1200 °C and the melting point, 1255 °C [14]. Although the space group of this phase has been reported to be *Pnna* [15], precise structure refinement has not been performed thus far. This study examines the modulation with an incommensurate *q* vector in the HT polymorph of BaSrFe<sub>4</sub>O<sub>8</sub> via synchrotron X-ray diffraction (XRD), electron diffraction, and transmission electron microscopy (TEM) experiments.

## 2. Material and methods

BaSrFe<sub>4</sub>O<sub>8</sub> powder was prepared using a solid-state reaction in which BaCO<sub>3</sub> (99.9%, Kojundo Chemical), SrCO<sub>3</sub> (99.9%, Kojundo Chemical), and Fe<sub>2</sub>O<sub>3</sub> (99.9%, Kojundo Chemical) powder specimens were mixed in a 1:1:2 molar ratio. This powder mixture was heated at 650–700 °C for 24 h, and the obtained sample was uniaxially pressed into a pellet. After heating at 1200–1240 °C for 100 h, the samples were quenched in liquid nitrogen. Powder XRD experiments were performed using Cu-Kα and synchrotron radiation (15.5 keV, SPring-8) [16]. Structure refinements were performed via the Rietveld method using the JANA2006 software package [17]. Samples for TEM observations were prepared using a crushing method.

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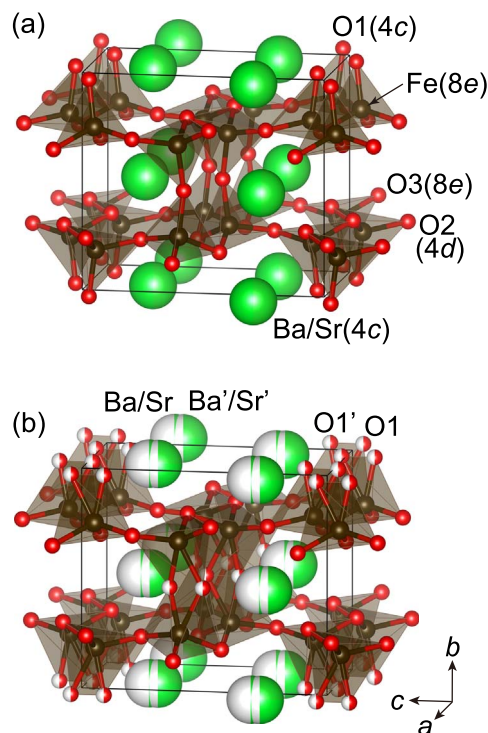
**Fig. 1.** Powder XRD patterns (Cu-K $\alpha$ ) of the samples quenched at 1200, 1210, 1220, 1230, and 1240 °C. The HT phase is obtained above 1220 °C and crystallizes in an orthorhombic structure with space group  $Pnma$ . The LT phase of  $P\bar{3}1m$  is obtained below 1210 °C.

### 3. Results and discussion

**Fig. 1** shows the powder XRD patterns (Cu-K $\alpha$ ) of samples quenched at 1200, 1210, 1220, 1230, and 1240 °C. The powder pattern of the LT phase of  $P\bar{3}1m$  is observed below 1210 °C, whereas heating above 1220 °C results in the HT phase of  $Pnma$ . The samples melted above 1250 °C, as reported previously [14]. The lattice parameters are  $a = 5.4431(1)$  and  $c = 8.1043(2)$  Å for the LT phase and  $a = 5.5136(1)$ ,  $b = 8.2644(1)$ , and  $c = 9.1832(2)$  Å for the HT phase, and these parameters are in good agreement with those in previous reports [15,18]. The obtained samples consisted almost entirely of a single phase with negligible amounts of impurities.

Synchrotron powder XRD and structure refinements using the Rietveld method were performed on the sample obtained at 1220 °C. High-Q diffraction data were not used for the refinement due to the substantial X-ray absorption by Ba ions. **Fig. 2(a)** depicts the initial structure model used for the refinements, in which the linking pattern of tetrahedra is UUDDDD with channels formed by six-membered rings running along the  $b$ -axis. The refinement performed using this initial structure model yielded reliability factors of  $R_{wp} = 5.09\%$  and  $R_1 = 9.36\%$ . The crystallographic parameters are shown in the upper panel of **Table 1**. The refinements were performed under the assumption of 50% occupation by each Ba and Sr at 4c. Correspondingly, the constraints  $z(\text{Ba}) = z(\text{Sr})$  and  $U_{iso}(\text{Ba}) = U_{iso}(\text{Sr})$  were used.

Among the isotropic atomic displacement parameters, a rather large value was observed for the O1 atom, which connects the tetrahedra along the  $b$ -axis that form the tetrahedral pillars. This trend is commonly observed in the parent compounds, such as the HT forms of  $\text{BaAl}_2\text{O}_4$ ,  $\text{SrAl}_2\text{O}_4$ , and  $\text{BaGa}_2\text{O}_4$  [3,10,19–21]. Significantly large atomic displacement parameters are observed in these compounds at the apical oxygens that connect the tetrahedra along the channel direction [10]. In particular, two low-energy phonons due to collective motion of the tetrahedral network exist in  $\text{BaAl}_2\text{O}_4$  [22] and give rise to the large atomic displacement parameters. In the studies of  $\text{BaAl}_2\text{O}_4$ , split atom models were applied in further refinements to address the structural fluctuation as positional disorder at these atoms.



**Fig. 2.** Crystal structures of  $\text{BaSrFe}_4\text{O}_8$  ( $Pnma$ ). (a) Structure model A (the initial structure) and (b) structure model B (the refined structure). In structure model B, the O1 and Ba/Sr sites are split into two sites along the  $c$ -axis.

We considered the large atomic displacement parameter that are observed in  $\text{BaSrFe}_4\text{O}_8$  by using a split atom model as follows. Because the 4c site of O1 is located on the two-fold axis parallel to the  $c$ -axis, the O1 site can be appropriately split into two 4c sites with different  $z$ -coordinates. Accordingly, the site occupancy  $g$  was reduced to a half that of the initial model. The refinements using this two-site split model slightly improved the reliability factors.

The positional disorder in the O1 atoms inevitably affects the adjacent Ba/Sr atoms at the 4c site, which can also split into two 4c sites, as described above. This split atom model is depicted in **Fig. 2(b)** as structure model B, where the Ba/Sr and O1 atoms are split along the  $c$ -axis according to the site symmetry. This model yielded a further improvement in the reliability factors to  $R_{wp} = 4.41\%$  and  $R_1 = 5.01\%$ . The constraint conditions were as follows:  $z(\text{Ba}) = z(\text{Sr})$ ,  $z(\text{Ba}') = z(\text{Sr}')$  and  $U_{iso}(\text{Ba}) = U_{iso}(\text{Sr}) = U_{iso}(\text{Ba}') = U_{iso}(\text{Sr}')$ .

According to this refinement, the displacements in the O1 and Ba/Sr atoms along the  $c$ -axis correspond to  $\approx 1.2$  Å and  $\approx 0.3$  Å, respectively. Significantly large displacements were found for the O1 and O1' atoms, which affected the Fe-O bond length; the Fe-O1 bond is longer than the Fe-O1' bond by  $\approx 0.2$  Å. We also analyzed the anisotropic displacement parameters of the Fe atoms. The calculation satisfactorily reproduced the observed diffraction pattern, as shown in **Fig. 3(a)**, and gave reliability factors of  $R_{wp} = 4.33\%$  and  $R_1 = 4.69\%$ . The obtained crystal parameters are listed in the lower panel of **Table 1**. **Fig. 3(b)** depicts an  $\text{FeO}_4$  tetrahedron showing the anisotropic displacement ellipsoid drawn for the Fe atom at 80% probability level. The anisotropic displacement of the ellipsoid is strongly oriented toward the O1 atom due to the long Fe-O1 distance.

TEM observations were performed on this sample. The diffraction patterns with [100] and [010] incidences are shown in **Fig. 4(a)** and **(b)**, respectively. The reflection conditions are  $k + l = 2n$  and  $h + l = 2n$ . While only the fundamental reflections are observed in **Fig. 4(a)**, satellite reflections with a wave vector of  $q = 0.43a^*$  are observed in **Fig. 4(b)** along [100] around each fundamental reflection, as indicated by closed triangles. This result indicates the formation of an incommensurate superstructure along the  $a$ -axis. The reflections

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