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Synthesis of 12-Layer Modification of Hexagonal $BaFeO_3$ Under High Oxygen Pressure

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The modification of hexagonal $BaFeO_{2.85}$ with $a = 5.700$ Å and $C = 28.03$ Å has been synthesized at high oxygen pressure. The c/a ratio of 4.917 indicates that it has 12-layer sequence according to the general equation $c/a = 0.4107n$. From Mossbauer spectra at 300 K, it is revealed that there are two different valance states of iron, the isomer shifts are 0.03 mm/sec for Fe^{4+} and 0.37 mm/sec for Fe^{4+}, respectively.

Introduction

During the past ten years a considerable number of investigation of the structural chemistry of perovskite-like compounds with the chemical formula ABO_3 have been performed. Examples are the studies of $Ba_{1-x}Sr_xRuO_3$ (*1*), $BaCrO_3$ (*2*), $BaMnO_3$ and $SrMnO_3$ (*3*) as the application of high pressure, but among these compounds barium chromium oxides with 12-layer structure is reexamined by Evans and Katz (*4*) and the chemical formula of this phase is determined to be $Ba_2Cr_{7-x}O_{14}(x \simeq 0.5)$. On the other hand, since some authors (*5*, *6*) noted that the ferrates involving alkaline-earth ions of the perovskite type contained highly oxidized iron ions, probably Fe^{4+}, synthesis of $SrFeO_3$ (*7*, *8*), $BaFeO_3$ (*9*, *10*) and $CaFeO_3$ (*11*) were carried out to examine the effect of the Fe^{4+} ions on physical properties of the products.

Among these compounds, barium ferrates, $BaFeO_{3-x}$, are one of the most excellent examples to examine the existence of iron in disproportioned oxidation states within a single phase (*10*). In view of these facts, the ferrates were prepared under the oxygen pressure of 0.21–1.0 atm by the use of quenching and slow-cooling methods. As seen in the results already reported, there are some inconsistencies among the nature of the phases within this compositional range. MacChesney et al. (*9*) prepared a hexagonal form with 6-layer. Mori (*12*) reported the existence of a number of $BaFeO_{3-x}$ phases with x values ranging from 0.50 to 0.10. They are: hexagonal form of 6-layer and the forms belonging to cubic, tetragonal and monoclinic system. Recently, Negas and Roth (*10*) studied the phase relations in the system of $BaO–Fe_2O_3–FeO_2$ in detail to determine the stability of hexagonal and cubic phases of $BaFeO_{3-x}$. In very recent years, Zanne and Gleitzer (*13*) reported the presence of polytype of $BaFeO_{3-x}$ belonging to 12-layer hexagonal perovskite.

In the course of crystallochemical studies on perovskite-type compounds containing Fe^{4+} ions, we obtained a single crystal of the phase with the structure similar to that of the above polytype. The present paper deals with the results of single crystal X-ray study and the Mossbauer effect measurement for the material.

Experimental Results

The starting material was $Ba_2Fe_2O_5$ powder prepared by calcining an intimate mixture of Fe_2O_3 and $BaCO_3$ at 1200°C for 24 hr in air. From the X-ray powder diffraction pattern, the material was identified as orthorhombic brownmillerite.

$Ba_2Fe_2O_5$ prepared in this way was subjected to certain temperature and oxygen pressure as mentioned below. First, the sample was heated at 1000°C in streams of oxygen for 24 hr and quenched to room temperature. The X-ray powder diffraction patterns of the product was completely indexed as the 6-layer hexagonal phase. The calculated hexagonal cell dimensions of $a = 5.675$ and $c = 13.74$ Å are in good agreement with the reported values (*9*, *10*, *12*).

Secondly, $Ba_2Fe_2O_5$ was charged in a gold tube capsule with an open end and it was placed in a test-tube-type reactor. And then, the specimen was compressed by oxygen gas using the apparatus for generating high oxygen pressure (*14*) and heated by an electric furnace. After being maintained at 1500 bars and 600°C for 48 hr, the oxidized sample was cooled with the reactor to room temperature. The X-ray powder diffraction pattern of the product is in good agreement with that of 12-layer hexagonal perovskite presented by Zanne and Gleitzer (*13*). Assuming that the crystal structure of this phase hexagonal, its lattice constants were calculated to be $a = 5.700 \pm 0.002$ Å and $c = 28.03 \pm 0.01$ Å.

In a few runs where either the mixture of BaO_2 and 1/2 Fe_2O_3 or $Ba_2Fe_2O_5$ was treated under high oxygen pressure in the case when a large thermal gradient was given along the long axis of reaction bomb, several large single crystal of about 2 mm in diameter and 0.1 mm long were formed at the cooler end of the gold tube. The crystals are seen in Fig. 1. It would be considered that the crystal would be grown by action of BaO_2 as a flux under high oxygen pressure. Single crystal precession photograph showed that the possible space group for this phase was $R\bar{3}m$ and cell dimensions were $a = 5.70$, $c = 28.0$ Å. These results confirm those of reported by Zanne and Gleitzer (*13*).

Thermogravimetric analysis was applied for quantitative determination of the oxygen contents. From the results of TGA, the chemical formula of this phase was determined to be $BaFeO_{2.85}$.

On different $BaMO_3$ variants (M: transition metal ions) there is a linear relationship between the c/a ratio of a hexagonal $BaMO_3$ cell and the number "*n*" of repeat sequences, being $c/a = 0.4107n$ (*15*). From the hexagonal cell dimensions of the polytype of $BaFeO_3$ under investigation, the c/a ratio of 4.917 indicates that it is a 12-layer sequence according to the general equation $c/a = 0.4107n$.

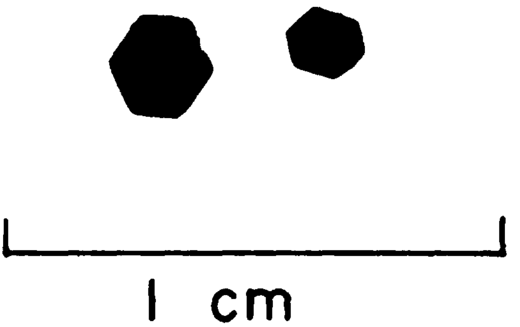

FIG. 1. Crystals of $BaFeO_{2.85}$ grown at 450°C and 1500 bars of oxygen pressure.

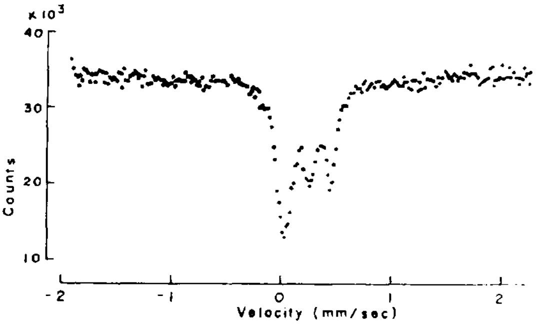

FIG. 2. Mossbauer absorption spectra of 12-layer hexagonal perovskite $BaFeO_{2.85}$. Velocity scale is relative to an iron metal at room temperature.

Analysis of the Mossbauer spectra of 12-layer hexagonal $BaFeO_{2.85}$ were recorded at room temperature using the radiation from ^{57}Co in Cu with a 400 channel multichannel analyzer. The velocity was calibrated with $Na_2Fe(CN)_5NO \cdot 2H_2O$ standard. The spectra were shown in Fig. 2. Each absorption spectrum has been fitted three Lorentzian curves with line widths between 0.3 and 0.35 mm/sec. The spectra consist of a single absorption line and a single quadrupole doublet, which have a isomer shift of 0.03 mm/sec for the former and that of 0.37 mm/sec and quadrupole splitting of 0.20 mm/sec for the latter peaks. The value of isomer shift of 0.03 mm/sec was considered to be due to Fe^{4+} ions in the octahedral sites and is in good agreement with those of other perovskite compounds containing Fe^{4+} ion such as $SrFeO_3$ (*8*), $BaFeO_3$ (*9*) and $CaFeO_3$ (*11*).

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