Single Crystal Growth of Strontium Ferrite with Magnetoplumbite Structure Using the Traveling Solvent Floating Zone Method

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Abstract
We report single crystal growth of the strontium hexaferrite SrFe$_{12}$O$_{19}$ by the traveling solvent floating zone (TSFZ) method using self flux. After improving various conditions, such as preparation of feed rods, atmosphere and pressure during crystal growth, growing speed, and the flux, we successfully obtained large single crystals. The crystals have cylindrical shapes with 4-5 mm in diameter and 40-60 mm in length. They grew along a direction nearly perpendicular to the c axis. It was demonstrated that the TSFZ technique provides large single crystals of SrFe$_{12}$O$_{19}$ of good quality.

Key Words: Magnetoplumbite, Traveling solvent floating zone method, Floating zone method, Single crystals, SrFe$_{12}$O$_{19}$

I. INTRODUCTION
The strontium hexaferrite SrFe$_{12}$O$_{19}$ has the magnetoplumbite structure with a space group of $P6_3/mmc$, which is called M-type ferrite. It has been experimentally proved that atomic replacement with various ions affect magnetic properties, such as the Curie temperature and magnetocrystalline anisotropy. As a matter of fact, these modifications are relevant to the technological applications of hexagonal ferrites, such as production of permanent magnets. Measurements of magnetic properties of single crystals give us further information on magnetic anisotropy. Therefore, it is necessary to obtain good quality and sizable single crystals of SrFe$_{12}$O$_{19}$.

In air, SrFe$_{12}$O$_{19}$ melts incongruently at 1410°C and decomposes to X-type ferrite and liquid [1]. This phenomenon disturbs operations for crystal growing of SrFe$_{12}$O$_{19}$. Single crystals of SrFe$_{12}$O$_{19}$ have been grown by flux method using Na$_2$O[2,3], B$_2$O$_3$[4] or NaFeO$_2$[5] as fluxes. Floating zone methods are one of the most useful growth techniques for large single crystals with minimum contamination. For SrFe$_{12}$O$_{19}$, a directional solidification from stoichiometry composition using a floating zone method was reported. This method requires high O$_2$ pressure of 50 atm [6].

Pseudo-binary equilibrium phase diagram of the SrO - Fe$_2$O$_3$ system, representing an isobaric section in air, was reported by Langhof et al. [1]. It is noteworthy that SrFe$_{12}$O$_{19}$ coexists with a liquid phase corresponding to a portion of the liquidus curve. Such a liquid phase is useful as a solvent for single crystal growth of SrFe$_{12}$O$_{19}$ by application of the zone leveling technique in which the material is crystallized from one side of the solvent zone onto a seed crystal while source material is fed into the other side. The absence of introduction of a third component would be an interesting feature of this technique. The floating zone crystal growth apparatus is suitable for establishing zone leveling action. The established zone leveling scheme is called the traveling solvent float zone (TSFZ) system.

In this study, single crystals of SrFe$_{12}$O$_{19}$ were successfully grown by the traveling solvent floating zone (TSFZ) method.

II. EXPERIMENTS
Single-crystal growth of SrFe$_{12}$O$_{19}$ was carried out by the TSFZ method in an infrared radiation furnace equipped with two ellipsoidal mirrors. Two 1000-W halogen lamps were used. Feed rods of SrFe$_{12}$O$_{19}$ were prepared through solid state reactions of appropriate amounts of SrCO$_3$ (99.9% purity) and Fe$_2$O$_3$ (99.99% purity). After grinding the mixture thoroughly, cylindrical rods (5 mm in diameter and 100 mm in length) were made by hydrostatically pressing under 90 MPa and the rods were sintered at 1000°C in air for 12 hours. A pellet of SrCO$_3$ weighing 100 mg was attached to the end of the lower rod to form solvent. The feed rod and the growing crystal were rotated at 1 rpm each in opposite directions. Crystals were grown under 3 atm oxygen pressure at a rate of 1 mm/h. At the end of the run, the feed rod and the grown crystal boule were separated and the power supply was reduced rapidly.

Magnetization was measured using a hand-made magnetic balance. Measured sample was cut as a cube of 2 mm in each edge.
III. DISCUSSION

During initial stages of the crystal growth of SrFe$_{12}$O$_{19}$, we encountered following difficulties; (i) ununiformity of feeding rod melting, (ii) poor stability of the melting zone caused by generation of bubbles, and (iii) intergrowth of secondary phase(s). These difficulties were overcome to a large extent (i) by using pre-melt rods instead of as-sintered rods, (ii) by carrying out the growth under 3 atm oxygen pressure, and (iii) by using enough solvent SrCO$_3$ to lower the temperature.

When we grew a single crystal using as-sintered rod, the liquid was absorbed by the rod. The reduction of the liquid phase and subsequent inhomogeneous melting of the rod prevented the stable crystal growth. This instability was mainly caused by porousness of the rod. To make the rod imporous, we have conducted pre-melting of the rod using almost the same condition as the crystal growth except for the growing speed of 20 mm/h instead of 1 mm/h. By using this pre-melted rod for crystal growth, the liquid absorption was hardly observed, and stable melting of the rod was achieved.

The generation of bubbles in melting zone also made crystal growth unstable. When a bubble broke, melting zone vibrated and rapidly changed the shape and at worst the liquid resulted in dropping. We speculate these bubbles are O$_2$ gas generated by reduction of samples. From the viewpoint of equilibrium, O$_2$ generation is suppressed under high O$_2$ pressure. We found that 3 atm O$_2$ pressurization completely suppresses the generation of the bubble using above mentioned pre-melted rods.

According to the phase diagram, a sample in low SrO region melts incongruently to generate secondary phases. To suppress secondary phase generation, high SrO contents are preferred. However, excess SrO enlarge the melting zone and the zone becomes unstable. Finally, we found 100 mg SrCO$_3$ is suitable for our purpose.

We finally obtained single crystals consist of M-type ferrite by using TSFZ. Fig. 1 shows one of the single crystals. Typical size of the single crystals is 4-5 mm in diameter and 40-60 mm in length. Lattice parameters determined by single crystal X-ray diffraction measurement is consistent with those of M-type ferrite. Each obtained sample has a definite cleavage plane as shown in Fig. 2. In general, the cleavage planes tend to be parallel to growth direction although that of the crystal in figure 2 has an angle of approximately 30° to the growth direction. Magnetic anisotropy measurement indicates this cleavage plane is the ab plane. It is well-known that the easy axis of SrFe$_{12}$O$_{19}$ is the c axis. Our experiments suggest that a single crystal made by this method has the tendency that c axis is perpendicular to the growth direction.

We measured Curie temperature of this single crystal. The result is shown in Fig. 3. The sample exhibits ferromagnetic-paramagnetic transition at about 730 K, which is consistent with that of M-type ferrite. At the Curie point, the magnetization decreases more steeply than conventional ferromagnets. This is likely due to strong uniaxial anisotropy of the sample.

![Fig. 1 Obtained single crystal of SrFe$_{12}$O$_{19}$](image1.jpg)

![Fig. 2 A cleavage plane of a single crystal of SrFe$_{12}$O$_{19}$](image2.jpg)
IV. CONCLUSION
We have successfully grown large single crystals of the ferrimagnetic compound SrFe$_{12}$O$_{19}$ by the TSFZ method using self flux. Typical size of obtained single crystals is 4-5 mm in diameter and 40-60 mm in length. They have a good quality in the sense of largeness and purity. We expect further measurements of single crystals synthesized by this method will reveal magnetism of SrFe$_{12}$O$_{19}$ system.

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