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Flux Single Crystal Growth of $BaFe_{12-x}Ti_xO_{19}$ with Titanium Gradient

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Abstract: Titanium substituted barium hexaferrite $BaFe_{12-x}Ti_xO_{19}$ single crystal was grown by the top seeded solution growth method from flux on the seed with controlled cooling below 1175 °C. Titanium substitution level gradient in the single crystal in the vertical and horizontal directions was studied. Two planes were cut and polished. A justification for the linear gradient of Ti substitution in a $BaFe_{12-x}Ti_xO_{19}$ single crystal is proposed; substitution levels in the center and periphery were determined. It was shown that upon growth by the top seeded solution growth method, crystals with a linear Ti substitution level gradient from x = 0.73 to x = 0.77 for a distance of 11 mm along pulling direction were obtained. The study led to the conclusion about the relationship of the gradient and changes in the composition of the nutrient solution.

Keywords: hexaferrite; single crystal growth; doping; substitution level gradient

1. Introduction

M-type hexaferrites with space group P6₃/mmc have found applications in various fields of technology as hard magnetic materials for permanent magnets and magnetic composites, information storage devices, and magneto-optical devices [1,2]. The growth of doped hexaferrite single crystals and study of their properties was the subject of many works in our laboratory [3–8].

In recent years, hexaferrites are increasingly being used in millimeter and sub-terahertz frequency ranges. Such devices are, for example, tunable resonators [9], insulators [10], and radar absorbing coatings in which hexaferrites are used both in the form of films and bulk materials [7].

Doping of parent crystals opens up wide opportunities for fine-tuning of the electrical and magnetic properties of functional materials thus obtained to the levels of these properties that are required by manufacturers of microwave devices, as well as other electronic devices that use the hexaferrites [11–19].

Single crystals of a wide range compounds can be grown from fluxes. This might be of particular importance for materials with an incongruent melting pattern, or in cases where melt methods cannot provide the necessary low density of defects. The flux methods allow the growth process to be carried out at relatively low temperatures.

A thorough experimental study of the structure and properties of crystals obtained in this way, in some cases, demonstrates the formation of not just substituted structures, but crystals, in which the substitution level changes smoothly. In fact, the crystal formation with a substitution gradient is observed. This might happen due to a changes of the flux composition, which influences the process conditions.

In this article, we present the results of the controlled formation of a gradient of the level of substitution in the crystal. Crystalline hexaferrite phases with gradient substitution can be the next step in developing the ability to control the properties of materials, since gradient substitution will provide wide opportunities for smoothly adjusting the properties of hexaferrite matrices over a wide range due to the smooth quantitative changes in their composition. Gradient substitution can expand the range of radiation frequencies that can be obtained in microwave devices made on the basis of such crystals.

However, on the way to creating such devices, it is necessary to investigate what factors affect the gradient formation. An experimental and theoretical study of the effect of the formation of hexaferrites crystals with a gradient substitution of iron atoms will provide information that will allow one to control the magnitude of the gradient, obtaining structures with the desired parameters.

The aim of this study is to determine the uniformity of iron substitution in a $BaFe_{12-x}Ti_xO_{19}$ single crystal grown by the top seeded solution growth (TSSG) method and revealing the factors affecting the titanium substitution level gradient.

2. Materials and Methods

The single crystal was grown using the TSSG flux method. The solvent type and content were chosen according to what was previously published for pure barium hexaferrite matrix data [20]. The batch components for the crystal growth were iron and titanium oxides, and barium and sodium carbonates with purity 99.9% (Ural Plant of Chemicals, Russia) were used as starting materials. Calculation of the batch was performed for the formula $BaFe_9Ti_3O_{19}$ with the sodium carbonate as the solvent (Table 1).

Mass Fraction of Components				
BaCO ₃	Fe ₂ O ₃	TiO ₂	Na ₂ CO ₃	
0.1335	0.4864	0.1623	0.2176	

Table 1. Mass fraction of the components in the batch.

A mixture of the starting components was placed in a platinum crucible in a vertical tube furnace. The furnace was heated for 5 h to a temperature of 1175 °C, which corresponds to the temperature of complete melting of the batch. To homogenize the solution, the crucible with the melt was isothermally held at this temperature for 3 h. As it was established with previous experimental results that this duration was enough for the CO₂ equilibration. Since the flux viscosity is rather low, the CO₂ from carbonates does not produce foam (as usual for silicate melts), and liquid comes to equilibrium much faster, than silicate/borate glasses. A BaFe₁₂O₁₉ single crystal previously obtained by spontaneous crystallization was used as a seed crystal.

This crystal was attached to a platinum crystal holder using a platinum wire. The seed crystal was oriented in such a way that the c axis was perpendicular to the melt plane. In the next 48 h the furnace was slow cooled at a rate of 1 °C/h, while the crystal was pulled at a speed of 0.5 mm per day. The crystal rotation speed was maintained at 15 rpm. At the end of growth period the crystal was lifted up, cooled and boiled in a concentrated nitric acid to remove flux.

Powder X-ray diffraction patterns of BaFe₁₂O₁₉ and BaFe_{11.25}Ti_{0.75}O₁₉ single crystals were obtained after grinding a part of the single crystal (Figure 1). A diffraction experiment was done using a Rigaku Ultima IV diffractometer (Rigaku, Tokyo, Japan) at Cu_{Kα} radiation with a DeTex energy dispersive detector at 40 kV and a 30 mA power supply, and a 1°2θ/min scan rate. Analysis of the patterns with Rietveld method using Rigaku PXDL software (Rigaku, Tokyo, Japan) package confirms that both samples are single phase materials and have similar cell parameters which are in good agreement with published data [21] (Table 2). In accordance with previously obtained data on Ti-doped hexaferrites [22] the Fe³⁺ substitution with Ti⁴⁺ cation leads to growth of unit cell volume. The reason for this influence might be in ionic radii deference. For coordination number 6 (octahedra) the ion radius of Ti⁴⁺ is 0.605 A

and those of Fe³⁺ are 0.55 (low spin) and 0.645 A (high spin) [23]. For coordination number 4 (tetrahedra) the ion radii of Ti⁴⁺ and Fe³⁺ are 0.42 and 0.49 A (high spin). The unit cell parameters increase to BaFe_{12-x}Ti_xO₁₉ with $x \approx 0.8$, despite the smaller ionic radius of the Ti⁴⁺ ions compared to the Fe³⁺ ions, as was discussed before [22]. Supposedly this is due to a dominating charge balance mechanism of Fe-reduction to Fe²⁺ since the increase in ionic radii from Fe³⁺ to Fe²⁺ would overcompensate the volume reduction effect by the smaller Ti⁴⁺ ions (CN = 6: r(Fe²⁺) = 0.78 Å).



Figure 1. Powder X-ray diffraction patterns of single crystals grown from a Na₂O flux: (**a**) $BaFe_{11.25}Ti_{0.75}O_{19}$ with Rietveld refinement, (**b**) $BaFe_{12}O_{19}$.

Formula	a, Å	<i>c,</i> Å	Volume, Å ³
BaFe _{11.25} Ti _{0.75} O ₁₉	5.9014(1)	23.224(1)	700.4(1)
BaFe ₁₂ O ₁₉	5.8935(3)	23.193(3)	697.6(3)
BaFe ₁₂ O ₁₉ [21]	5.8920(1)	23.183(1)	696.9(1)

Table 2. Unit cell parameters of the obtained single crystals.

The concentration gradient of Ti was studied on polished sections obtained after sawing a crystal. The crystal was cut in two directions: parallel and perpendicular to the c axis of the crystal. Figure 2a shows the lines along which the crystal was cut. The upper part of the crystal in Figure 2a,b corresponds to the seed.



Figure 2. Photographs of a single crystal of titanium doped barium hexaferrite grown by the TSSG method: (**a**,**b**) side view, (**c**) bottom view, (**d**) top view. On panel (**a**), the lines show the crystal cutting directions along which the elemental analysis was carried out.

The distribution of titanium over polished sections was studied using a Jeol JSM-7001F electron microscope (Jeol, Tokyo, Japan) equipped with an Oxford INCA X-max 80 X-ray energy dispersive spectrometer (Oxford, High Wycomb, USA). Accelerating voltage of electron gun was set to 20 kV required for quantitative EDX analysis.

Figure 2 clearly shows that the crystal has two crystallization zones. The upper zone is associated with the growth of the crystal due to its continuous pulling from the flux, and has a length of 12 mm from the seed crystal. This zone has many growth steps. The second zone, located below meniscus of melt, has a habit with pronounced smooth faces and is due to crystallization in the free volume of the flux.

3. Results

The polished cross sections of a crystal were examined with EDX along the lines indicated in Figure 2 on the rectangular areas $1 \times 0.1 \text{ mm}^2$. The composition averaged over all areas of the crystal corresponds to the mean formula BaFe_{11.25}Ti_{0.75}O₁₉. Figures 3–5 show the dependencies of the substitution level x(Ti) along the lines indicated in Figure 2. The same figures show the results of a linear approximation of the dependence of the titanium content on the distance. The error of measurement on each graph is about ±0.02 x(Ti).



Figure 3. Dependence of the substitution level x(Ti) along the vertical axis of the crystal (the distance origin is the seed).



Figure 4. Distribution of the substitution level x(Ti) in the x direction, perpendicular to the axis of the pulling of the crystal (the origin is the edge of the crystal).



Figure 5. Distribution of the substitution level x(Ti) in the y direction, perpendicular to the axis of pulling of the crystal (the origin is the center of the crystal).

Figure 3 shows that the concentration of titanium along the vertical axis of the crystal monotonically increases from top to bottom. This can be explained by the fact that, as the crystal grows, the TiO_2 content in the flux feed increases due to the fact that titanium is incorporated into the crystal in smaller quantities than it is contained in the flux, and as a result it accumulates in flux.

Indeed, at the beginning of growth, the Ti:Fe ratio in the melt was 3:9 = 0.333 in accordance with the formula BaFe₉Ti₃O₁₉. After crystallization of a crystal with mass 10 g and average composition of BaFe_{11.25}Ti_{0.75}O₁₉ from 100 g of such melt, the Ti:Fe ratio in the remaining melt will be 0.387. An increase in the titanium content in the flux leads to an increase in its thermodynamic activity in the melt. That in turn, in accordance with chemical thermodynamics, leads to an increase in the activity of titanium in the solid phase, which results in a gradual increase in the substitution level with titanium in the crystal. Note that the distribution coefficient of titanium between the melt and the crystal is equal to 5; that is in good agreement with previously published data on spontaneously grown crystals [22].

The substitution mechanism investigation which significantly depends on material producing method is not presented in the current study. But one can assume, by indirect signs (which could be the cell parameters' changes for example), the possible Fe^{3+} aliovalent substitution with Ti^{4+} and Fe^{2+} formation.

The fact that titanium is incorporated into the grown crystal in smaller quantities than it is contained in the flux is obviously due to the fact that Fe^{3+} substitution with Ti^{4+} might initiate formation of equal number of Fe^{2+} (to keep charge balance having all cation and anion sites completely occupied), as was shown recently by Mössbauer spectroscopy for solid state calcinated ceramics [24]. It is formally includes a redox reaction ($Fe_2O_3 = 2 FeO + \frac{1}{2}O_2$) that needs energy. The formation of Fe^{2+} (as well as Ti^{4+} introduction), which changes the cation radius at certain sites, magnetic coupling between ions, etc., also affects the energy of crystal formation. Of course, all that will accomplishes with some vacancy formation at cationic sites. All processes affect greatly the enthalpy, entropy, and Gibbs energy of crystal. Obviously, these effects makes iron substitution with titanium in a crystal less preferable than a similar substitution in liquid flux.

It should be noted that the crystallization of a real oxide melt is a nonequilibrium process. However, the results obtained during this work could be useful in the course of subsequent creation of a complete thermodynamic model of phase equilibria realized in the BaO–Fe₂O₃–TiO₂ and BaO–Fe₂O₃–TiO₂–Na₂O systems, since the changes in the distribution coefficient of titanium between the melt and the solid phase are related with activities of titanium ions in these two coexisting phases.

Figures 4 and 5 show the dependencies of the titanium content in directions perpendicular to the axis of crystal pulling. From the data presented in these figures, it is seen that the concentration of the substituting element is almost constant over whole the crystal.

4. Conclusions

Upon growth of a single crystal of substituted hexaferrite by the TSSG method, the resultant crystals are characterized by titanium concentration gradient selectively along the *c* axis of a crystal that coincides with the pulling direction. The main factor affecting the concentration gradient of the substitute element is the change in the composition of the flux during crystal growth.

The results obtained open up opportunities for the growth of crystals of based on hexaferrites' solid state solutions with a substitution level gradient.

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