Correlation between Iron Substitution Degree in the M-Type Hexaferrites Based Crystal Structures and Dopant Content in the Crystal Growth Feeding Melt

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Abstract. In this paper the results of the investigation of the properties of the obtained crystals of hexaferrites grown from the sodium carbonate flux doped with 1–12 mass % of metal oxide (aluminum, titanium, manganese, cobalt, and copper) are presented. The ratio of concentration of doping elements in the crystal and in the feeding melt has strong dependence on nature of dopant. Doping metals can be ordered in a line Ti > Al > Mn > Co > Cu where Ti has maximal ratio of 0.5 and Cu of 0.005. Hexagonal M type ferrites attract the researchers interest due to great capacity for the accommodation of different metals at high doping levels that provides a possibility for wide tuning of physical properties by cation substitution.

1. Introduction

M-type hexaferrites with a magnetoplumbite structure have found application in various branches of science and technology as single magnetic materials and magnetic composites fillers for information storage devices, magneto-optical devices [1, 2]. In recent years, hexaferrites are increasingly used in devices in the millimeter and subterahertz frequency ranges. Such devices are, for example, tunable resonators [3], insulators [4] and radio-absorbing coatings, in which hexaferrites (primarily barium) are used both in the form of films and in the form of bulk materials [1].

A promising area of research is the creation of materials with a minimum reflectivity of electromagnetic radiation to protect large objects [5, 6]. The main requirement for materials is absorption in a wide frequency range [7]. In the microwave (GHz) region, hexaferrites are of greatest interest. Substitution (i.e. substitution iron atoms with other elements atoms) can tune the of ferromagnetic resonance frequency. At the same time, hexaferrites can be used as emitters in information and telecommunication systems, where, on the one hand, a low level of losses is important, and on the other hand, an increase in the resonance frequency (which can be achieved by partial substitution of iron atoms in the hexaferrite matrix with dopant element) expands the capabilities of devices and devices based on such material. In particular, the transition to frequencies up to 100 GHz and higher will provide an increase in data transmission between satellites. This will lead to the development of new generation telecommunication services based on space systems [8, 9].

By virtue of all the above, the study of the structure and properties of these materials is of both scientific [10, 11] and practical interest. In the last 15 years, the direction in which the researchers interest is focused on the preparation and study of M-type hexaferrites doped with different elements
(Al/Ti/Mn/Co/Ni/Cu/W/Zn/Cr) has acquired great relevance [12]. Atomic substitutions in ferrites are commonly studied to manipulate the magnetic and electrical properties of the resulting materials.

It has been found that the functional properties of ferrites can be significantly changed by partial or complete substitution of iron cations with dopants. Such changes in the structure allows one to significantly vary the ferrites properties, in particular, to change the uniaxial magnetic anisotropy level, the magnitude of the coercivity, and the Curie temperature [13, 14].

In the literature, there are quite a few data on the substitution nature of atoms in the lattice of ferrites by dopants. There is a series of works related to the hexaferrites production in the form of a fine-crystalline material doped with La, La-Co, La-Nd, Er-Zn-Co. But the authors of the works disagree about the nature of the replacement of REE cations and cations of codopants. Some authors argue that REE\(^{3+}\) are embedded in the Fe\(^{2+}\) position [15], others claim that bivalent codopants replace the iron cation, and REE\(^{3+}\) – barium atoms [16] (when it comes to barium hexaferrite). Still others argue that both REE and bivalent codopant substitution barium positions [11, 17–21].

At the same time, no serious X-ray diffraction studies were performed in any of the above works. The study of the mechanism of substitution of REE and codopant cations is an important task for understanding the effect of impurities on the magnetic properties of hexaferrites.

Obviously, the powder or nano-scaled materials do not allow one to study their crystal structure with the required degree of accuracy. This requires large enough single crystals.

Summarizing the brief analysis of publications, the following should be said:

Work on the creation of crystalline substituted hexaferrites (in particular, in the form of single crystals) is relevant, and their results will be in demand by modern high-tech industries. Of particular relevance are works aimed at the development and improvement of methods for alloying hexaferrites in order to purposefully modify their properties, as well as to obtain and study new types of ferrite structures, stabilized due to the partial replacement of iron atoms with atoms of other elements. The development of this direction is hindered by the lack of sufficient information on the mechanisms of substitution of iron atoms, on the effect of the composition and number of substituents on the crystal structure of substituted ferrites, as well as on the structure and properties of doped ferrites.

The complex of work has the task to start the next step in the preparation of substituted crystalline materials with magnetoplumbite structure – to prepare the samples and to study the structure and properties of this type crystalline phases with a gradually varying degree of substitution. The results that are planned to be obtained in the future will be aimed at managing the crystallization process - i.e. the possibility of targeted production of single crystals of hexaferrites with gradient substitution or targeted prevention of the formation of crystals with inhomogeneous substitution. In the published literature, there is no information on works aimed at obtaining such a result.

One of the obvious ways of producing structures with a gradient substitution is the growing of relatively large crystals in a relatively small amount of melt thereby, that the proportion of dopant in the process of growing the crystal is gradually regularly varied, which will lead to a natural change in the degree of iron substitution in the growing crystal ... To understand the possibilities and limitations of this approach, as well as to carry out preliminary calculations of the charge and determine other conditions for growing crystals with, it is useful to know how the degree of iron substitution is related to the concentration of the dopant in the melt feeding the crystal growth. Analysis of experimental data of this kind is a main part of the study.

2. Experimental technique

Single crystals of barium hexaferrite partially substituted with aluminum, titanium, manganese, cobalt, and copper, up to 12 mm in size, were grown from a flux based on sodium carbonate by spontaneous crystallization. The growth of single crystals was carried out in platinum crucibles with a volume of 60–300 ml. Exposure at a maximum temperature of 1300–1350 °C was carried out for 24 hours, after which it was slowly (at a rate of 4 °C/h) cooled to the lower limit of the temperature range (900 °C). In this case, iron oxide (Fe\(_2\)O\(_3\)), barium carbonate, dopant oxide and sodium carbonate were
used as starting components. The use of a flux allows the crystallization process to be carried out at temperatures below 1300 °C, while other methods require heating to significantly higher temperatures. After crystallization, the content of the crucibles was washed in boiling nitric acid in order to extract crystals from flux residues.

Since in the implementation of the method of spontaneous crystallization, the growth rate of crystals located in different parts of the crucible can differ significantly, which leads to a different concentration of the dopant, then for averaging the composition, 3–4 of large well-faceted crystals were selected from each experiment. After that, the composition, structure and properties of the samples were studied. The composition of the samples was investigated using a scanning electron microscope with an energy dispersive spectrometer.

3. Results and discussion

On the whole, it is obvious that an dopant content increasing in the melt should lead to an increase in the substitution degree. But whether this process occurs gradually or abruptly, is there a threshold after which an increase in the dopant content in the melt ceases to affect the substitution degree in the crystal and the threshold value up to which the dopant present in the melt does not integrate into the lattice of the growing crystal – the answers to such questions are extremely important for realizing the process of growing a crystal with gradient substitution.

The obtained dependences of the degree of substitution $x$ in structures of the $\text{BaFe}_{12-x}\text{M}_x\text{O}_{19}$ type on the mass fraction of $\text{M}$ in the melt are shown in Figure 1–2.

![Figure 1](image.png)

**Figure 1.** Dependence of $x$ in the $\text{BaFe}_{12-x}\text{M}_x\text{O}_{19}$ on the mass fraction of $\text{M}$ (Ti, Al, Mn, Co) in the melt when growing crystals by the method of spontaneous crystallization.

The results allow us to conclude that the proportion of the dopant gradually increases depending on its presence in the melt. In addition, they make it possible to select from the total number of studied systems those that are most promising from the point of view of growing larger crystals with a noticeable gradient in the dopant distribution. A first systems in which the crystals are formed were $\text{BaFe}_{12-x}\text{Ti}_x\text{O}_{19}$, $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ and $\text{BaFe}_{12-x}\text{Mn}_x\text{O}_{19}$. It is in them the relatively small changes in the dopant concentration in the melt lead to the maximum change in the dopant content in the crystal.
Figure 2. Dependence of $x$ in the BaFe$_{12-x}$M$_x$O$_{19}$ on the mass fraction of M (for cobalt and copper) in the melt when growing crystals by the method of spontaneous crystallization.

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4. Conclusions

The results of experiments accompanied by the formation of substituted crystal structures based on hexaferrites are analyzed. Crystals of substituted hexaferrites investigated (primarily by EPMA method) in order to study the relationship between degree of iron substitution in forming crystalline structures based on M-type hexaferrite with a dopant concentration in the feed growth melt. From the total number of studied systems, we selected those that are most promising from the point of view of growing large crystals with a noticeable gradient in the dopant distribution. Such systems are primarily the system in which BaFe$_{12-x}$Ti$_x$O$_{19}$ crystals are formed, as well as the BaFe$_{12-x}$Al$_x$O$_{19}$ and BaFe$_{12-x}$Mn$_x$O$_{19}$ systems. It is in them the relatively small changes in the dopant content in the melt lead to the maximum change in the crystal dopant content. Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.

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Acknowledgments
The work was supported by Russian science foundation, project No. 19-73-00144.