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Research articles

Growth and properties of yttrium-iron garnet films with a higher iron content

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ABSTRACT

Preparation of a novel yttrium-iron garnet of the chemical formula $Y_{3\text{-}x}Fe_{5+x}O_{12}$, where $0.1 \leq x \leq 1.5$, is reported. Epitaxial films of this garnet were grown by the liquid phase epitaxy technique from the $PbO–B_2O_3$ solution containing weakly dissociated both yttrium-iron garnet $Y_3Fe_5O_{12}$ and yttrium orthoferrite $YFeO_3$ as the charge materials. It has been shown that crystallization from such a solution-melt results in the clusters which contain some structural fragments of $Y_3Fe_5O_{12}$ and $YFeO_3$ inside the liquid phase of the growing films and crystals forming in such a way a structure of the novel ferrite. Structural and magnetic properties of the obtained garnet films are also discussed.

1. Introduction

The yttrium iron garnet (YIG) films have been researched for decades because of their wide range of applications in the microwave, communication and magnetic detection areas such as delay lines, oscillators, filters, resonators, pulse separators, multichannel and compressive receivers, core devices in many microwave generators and analyzers, phase shifters and tuners in phased array radar systems and magnetic field sensors [1–3]. The principle of operation of these devices is based both on the uniform precession of magnetic moments and on the propagation of magnetostatic spin waves in films, the latter is the subject of intense research today [4].

YIG films is one of the most common ferrite materials used in modern electronics. It has a number of remarkable properties, one of which is an extremely small ferromagnetic resonance (FMR) linewidth of 0.2 Oe, which corresponds to the very low microwave loss. However, both of the saturation magnetization and the magnetic anisotropy of YIG are sufficiently low ($4\pi M_s = 1750$ Gs and the anisotropy field $H_A = 40$ Oe, respectively) as compared with another ferrite materials. It causes the limitations of increase in the operating frequency of YIG-based devices [5].

Epitaxial YIG films with the thickness of 0.1–100 μm are produced by liquid phase epitaxy (LPE) on a substrate of gadolinium gallium garnet (GGG) [6]. The quality of the films obtained by this method is quite high; it approaches the quality of bulk crystals.

Recently, in view of progress in spintronics, very thin YIG films with thicknesses less than 100 nm became necessary [7]. Obtaining high-quality films with such thicknesses by the LPE method is quite problematic. This is due to the fact that the epitaxial growth is limited by the transition diffusion layer, which is formed at the substrate-liquid phase interface and reaches a thickness of up to 100 nm [6]. As a result of dissolution of the substrate in this layer, the chemical composition of films with a thickness of less than 100 nm is inhomogeneous and deviates from stoichiometry. To produce very thin films, different deposition techniques are used. The first YIG films obtained by sputtering methods had an imperfect structure and a rough surface and, as a consequence, possessed large damping parameters [8–10]. Recently, it has been reported to obtain very thin films having a perfect crystal structure, a smooth surface, and a damping parameter close to that of thick YIG films obtained by the LPE method [11–14].

In this paper, we will focus on films used in microwave devices. As noted above, such films are produced predominantly by the LPE method, i.e., by crystallization from the liquid phase.

When considering the mechanism of crystallization from the liquid phase, atomic nature of the transition from the liquid substance to the solid phase is usually postulated. On the other hand, a lot of experimental data has been accumulated in the physics of crystallization that demonstrate a phenomenon of the structural and chemical micro ordering in liquids. This micro ordering results in the formation of quasi-crystal clusters in liquids, which are formed from the solute particles. These clusters significantly affect

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the elementary crystallization acts providing cooperative diffusion in the liquid phase and cluster mechanism of crystallization [15–17]. The formation of such clusters has random and uncontrolled nature; therefore, prediction of their structure is not possible. This circumstance increases probability of both spontaneous crystallization and deterioration of obtained crystals or films.

Besides to the discussed above, there is another mechanism of cluster formation in the liquid phase. It relates to the fact that clusters are formed in the solution or melt as a result of the partial or weak dissociation of a substance, from which the crystals or films are planned to grow [18,19]. The important feature of such clusters is that their structure may be predicted. Additionally, they may carry hereditary information from parent substance to the growing single crystal or film, in particular, information about the ratio between the chemical elements or a structure of the original material. Such clusters are logically named as hereditary clusters. Phenomenon of the structural heredity is successfully used in modern metallurgy [20] where such a transfer of the specific structure through intermediate liquid state to the solid one improves quality of the castings.

In the technologies of crystalline materials, crystallization by hereditary clusters can provide both advantages: an improvement in properties of the known crystals and obtaining of the new ones. Such a possibility of the crystallization by hereditary clusters has been firstly implemented on the example of epitaxial growth of $(Y,Eu)_3(Fe,Ga)_5O_{12}$ garnet films from the $PbO–B_2O_3$ solution containing previously synthesized polycrystalline garnet with a specific chemical composition as a trial charge material [21]. It was shown that the chemical composition of the films grown by hereditary clusters does not depend on both the growth temperature and the growth rate and corresponds to the composition of the parent garnet, unlike traditional growth by individual atoms where the composition of the films depends on the growth conditions.

In the present paper, we report the production of YIG films having higher $4\pi M_s$ and H_A values by the method of crystallization by hereditary clusters. To produce such clusters, polycrystalline YIG and yttrium orthoferrite compounds are used as a charge. The paper is organized as follows. First, we study kinetics of the crystallization in the solution-melts (SMs) containing either weakly dissociated YIG only (Section 2.1) or both YIG and yttrium orthoferrite (Section 2.2). Then, the chemical composition as well as structural and magnetic properties of the films, obtained in the latter case, are discussed (Section 2.3). Finally, in Section 3, a phenomenological model of the formation of iron-enriched garnet from the clusters of garnet and orthoferrite is proposed as well as all the conclusions are summarized.

2. Experiment

All experiments on film's growing by LPE were performed using standard equipment and GGG (111) substrates. For the preparation of weakly dissociated SM, the polycrystalline yttrium-iron garnet $Y_3Fe_5O_{12}$ was dissolved in the $PbO–B_2O_3$ solution and then kept by the SM stirring at the temperature of 1050 °C for 2 h. The existence region of the garnet on the phase diagram of pseudo-ternary system $PbO–B_2O_3–\sum Ln_2O_3–Fe_2O_3$ is determined by the coefficients $R_1 = Fe_2O_3/\sum Ln_2O_3$, $R_2 = PbO/B_2O_3$ and $R_4 = 2(Fe_2O_3+\sum Ln_2O_3)/[2(Fe_2O_3+\sum Ln_2O_3) + PbO + 2B_2O_3]$ [22], in our case accepting the standard values used commonly in LPE. When calculating the R_1 and R_4 coefficients for weakly dissociated SM, the number of Y_2O_3 and Fe_2O_3 moles, contained in a certain YIG amount, was taken into account.

For comparison, the films were also grown from a traditional SM, in which oxides Y_2O_3 and Fe_2O_3 were used as a charge. This SM was homogenized at 1150 °C for 8 h. The coefficients $R_{1,2,4}$ accepted to be the same values as in the compared SMs.

2.1. Hereditary clusters in a solution-melt containing weakly dissociated garnet

To prove the existence of hereditary clusters in the weakly dissociated SM, both suppositions: film's growth under different concentrations of garnet-forming components in the compared SMs and the dependence of the film growth rate on the growth temperature have been investigated.

The diagram in Fig. 1 demonstrates the dependence of the crystal formation on both parameters: the temperature of SM and the concentration of crystal-forming components therein for the traditional SM and for the weakly dissociated ones. For each system, a region of lability is located above the dashed curve, where the crystallization occurs at any value of the concentration and temperature. Under the solid curve, there is a region where crystallization never occurs in the given system. Between these two curves, there is a metastable region in which the growth of the film on the substrate occurs. The form of these curves and the width of the metastable region provide insights into the nature of physical and chemical interactions in the SM. As seen from the figure, the metastable region for the weakly dissociated SM is almost two times narrower in comparison with the traditional SM and it is shifted to the higher temperatures.

Fig. 2 depicts the temperature dependences of the film growth rate in the compared SMs. From the figure one can see that the rate of film growth from the weakly dissociated SM is 1.5 times faster as well as the growth temperature is 25 degrees higher than they are for the traditional SM. Let us note that, according to traditional concepts of crystal growth, the growth rate should decrease with increasing SM temperature [22].

Narrowing of the metastable region and increase of the growth rate with increasing of temperature range mean that the nature of interactions between the dissolved particles and the solution in the weakly dissociated SM is changed and structural units are larger than in the case when individual atoms participate in the film growth process. The role of such units in the SM can be performed by the only clusters generated as a result of the incomplete dissociation of polycrystalline YIG.

The existence of YIG structural complexes in the weakly dissociated SM and their participation in the crystallization is indicated

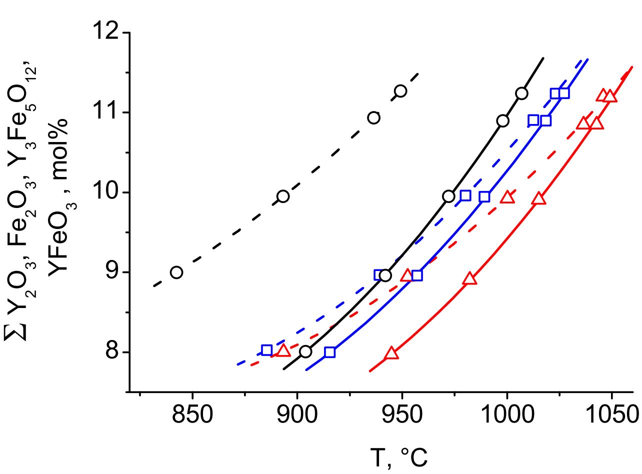

Fig. 1. Diagram of the crystallization metastable regions for the different SMs: traditional $PbO–B_2O_3–Y_2O_3–Fe_2O_3$ (circles), weakly dissociated $PbO–B_2O_3–Y_3Fe_5O_{12}$ (squares) and weakly dissociated $PbO–B_2O_3–Y_3Fe_5O_{12}–YFeO_3$ (triangles).