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Abstract

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ON THE INHOMOGENEITY OF THE COMPOSITION OF CRYSTALS OF SUBSTITUTED FERRITES

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Modern radioelectronic technology requires various crystals of oxide ferromagnets (ferrites) with a prescribed set of properties. These properties can be controlled over a wide range by dosed substitution of particular components of the composition.

However, the volume distribution of components (those being substituted and those substituting) in ferrite crystals of complicated composition is, as a rule, nonuniform. The nonuniformity is caused by changes in the composition and physicochemical properties of the mother medium during real (nonequilibrium) crystallization (including in connection with the volatility of some components), and also by anisotropy in the incorporation of ions into different growth pyramids. Slow diffusion in the solid does not provide the necessary equalization of concentration. Material inhomogeneity is one of the reasons for the nonreproducibility of the properties of crystals. It has an adverse effect on useful properties, since it contributes to the stressed state (^1) and to the formation of structural defects.

We have studied volume inhomogeneity in crystals of yttrium gallium ferrite garnet $Y_3(Ga, Fe)_5O_{12}$ and Mn ferrite (including with additions of Zr, Zn, Ge). Crystals of these compositions were chosen as the most important representatives of the two principal methods of synthesizing ferrite crystals: from a solution in a melt and by the Verneuil method.

The crystals were studied with an JXA-3A X-ray microanalyzer, which makes it possible to carry out quantitative elemental analysis in an area within 1 μ (^2). Continuous profiles make it possible to record the change in intensity of the line of the element being analyzed (in quanta per min.) (^3). In this work, quantitative comparative determination of the element content from point to point was carried out, although, with the aid of a standard and calculations, absolute element contents can also be established (in wt. %). Measurement errors depend on the element being analyzed, its concentration, and other elements present. For example, in the garnet $Y_3Fe_{4.38}Ga_{0.62}O_{12}$ the error of the comparative determination of the Ga content lies within 0.8%.

Crystals of the garnet $Y_3(Ga, Fe)_5O_{12}$ were grown by the method of static spontaneous crystallization from a solution in a melt of composition $8.25Y_2O_3 \cdot (16.05 - x)Fe_2O_3 \cdot xGa_2O_3 \cdot 30.70PbO \cdot 45.0PbF_2$, where x varied from 2 to 8 mole %. The capacity of the platinum crucibles was 300 cm^3. The maximum temperature of the melt was 1280°, and the cooling rate was 1.5 deg/hour. The size of the crystals was 10–15 mm. The forms {110} and {211} take part in the faceting.

The main types of inhomogeneity in the composition of the crystals are zoning and sectoriality, with zoning playing the leading role. The gallium content decreases substantially from the center of the crystal toward the periphery. Thus, in the growth pyramid ⟨211⟩ of the garnet $Y_3Fe_{4.38}Ga_{0.62}O_{12}$, over a distance of 2.8 mm the change is 10% (Fig. 1a). During growth, the crystals, as was to be expected, are continuously enriched in the less refractory component (melting temperatures: Ga_2O_3 1740°, Fe_2O_3 1565° (ˆ4)). This —

inhomogeneity appears against the background of a fine rhythmic variation in the content of the element (Fig. 1b)—microzoning caused by thermal effects at the growth front and by other causes. Similarly, in the garnet $Y_3(Al, Fe)_5O_{12}$ the amount of refractory Al_2O_3 (melting point 2015° (4)) decreases from the core toward the periphery.

The zoning of the garnet $Y_3(Ga, Fe)_5O_{12}$ can be observed directly in petrographic thin sections, since the gallium-depleted periphery of the crystal is less transparent. The bulk compositional inhomogeneity is expressed in the difference between the magnetic properties of specimens made from the central and peripheral parts of the crystal (Table 1).

Fig. 1. Change in the gallium content in a crystal of garnet $Y_3Fe_{4.38}Ga_{0.62}O_{12}$ from the center to the periphery in the growth pyramid ⟨211⟩. *a*—graph; *b*—portion of the profilogram.

The zoning of crystals depends on their position in the crucible. It is most strongly expressed in the crystals considered above, which grew at the surface of the solution outside contact with the crucible. It is weaker in younger generations localized on the walls of the crucible and especially in those located completely inside the solution. In the same sequence, the absolute gallium content in the central parts of the crystals also decreases. The stratification of the solution may exert a definite influence on the structure of crystals situated differently in the crucible.

Table 1

Magnetic properties of different parts of the crystal

Figure 2

Figure 1: Figure 2

Part of crystal	Ga_2O_3 content, wt. %	Saturation magnetization, G	Curie temperature, °C
Center	7.90	890	165
Periphery	4.90	1240	215

Sectoriality is manifested much more weakly than zoning in crystals $Y_3(Ga, Fe)_5O_{12}$. The growth pyramids $\langle 211 \rangle$ contain 3-5% more gallium than the pyramids $\langle 110 \rangle$. (The compared regions are 500 μ away from the corresponding faces.) It is interesting that in the presence of Ga the morphological role of the $\{211\}$ faces increases. Some enrichment in gallium (of the order of 1.5% compared with the $\langle 211 \rangle$ pyramid) is characteristic of the boundary regions between the $\langle 110 \rangle$ and $\langle 211 \rangle$ growth pyramids. Apparently this is associated with the preferential growth of the edges of the crystal polyhedron.

Increasing the cooling rate of the solution during the growth of the garnet $Y_3(Ga, Fe)_5O_{12}$ is accompanied by an intensification of the crystal inhomogeneity. Obviously, such an effect is generally produced by a shift of crystal-growth conditions away from equilibrium. The dependence of the Ga distribution on a number of technological factors (the ratios of Ga_2O_3 and Fe_2O_3, PbF_2 and PbO in the charge) was traced in (5).

Considerable compositional inhomogeneity is characteristic of ferrite crystals grown from the melt by the Verneuil method. Below we consider the nonuniform distribution of elements that arose during the growth process. Inhomogeneities associated with valence transformations of metals in a chemically active anisotropic medium (usually during cooling of boules),

are not detected by the X-ray microanalyzer, although they are readily revealed by microchemical analysis.

The investigated Mn-ferrite boules were grown at rates of 3-6 mm per hour and at a volume ratio $H_2 : O_2 \approx 0.75 : 1$. The crystal holder was silicon carbide and rotating. The diameter of the boules was $\sim$ 6 mm. It was established that, toward the head of the boule and toward its periphery, the content increases of that component (Mn or Fe) which is present in excess over the stoichiometric ratio.

Fig. 2. Change in the metal content along the length of a boule. 1 –Mn along the growth axis of a boule of composition 60 MnO—40Fe_2O_3; 3 –Zn along the growth axis of a boule 60.6 MnO—36.4Fe_2O_3—3.0 ZnO; 5 –Ge along the growth axis of a boule 45 MnO—50.0 Fe_2O_3—5.0 GeO_2; 2, 4, and 6 – respectively Mn, Zn, and Ge parallel to the growth axis at 2 mm from it.

Figure 3

Figure 2: Figure 3

The greater the magnitude of this excess, the more strongly the inhomogeneity of the crystal is manifested. Thus, in a boule of composition 60 MnO—40Fe_2O_3, over a length of 20 mm the Mn content changes along the growth axis by 13%, and parallel to the growth axis at a distance of 2 mm from it by 18% (Fig. 2, curves 1 and 2). The error of comparative determination of Mn content is 0.6%.

During growth, the crystal evidently rejects part of the excess component, as if purifying itself of the isomorphous impurity. As a result, the residual melt is gradually enriched in this component, which explains its accumulation toward the head of the boule. The increase in concentration of the excess component at the periphery is associated with the convex shape of the growth front.

Practically homogeneous distribution of the elements increases with increasing growth rate, although it can also be achieved under equilibrium conditions, when the growth rate is infinitely small.

Similarly to the excess component, the content of the impurities Zr, Zn, and Ge in Mn-ferrite increases toward the head and toward the periphery of the boules (Fig. 2, curves 3–6). These impurities are introduced separately in amounts up to 5 mol.%. Volatile ZnO also enriches the lower near-surface parts of the boules, since it is carried downward by the flame.

Fig. 3. Influence of boule curvature on the distribution of components. *a* – schematic of a boule with positions of the growth front; *b* –change in Zn content along the bend line *AB* of a boule 60.6 MnO—36.4Fe_2O_3—3.0 ZnO.

No dependence of the inhomogeneity of the boule composition on its crystallographic orientation was found. At the same time, curvature of the boules is reflected in the distribution of components, since the growth-front profile of such boules was asymmetric (Fig. 3a). As a result, the point of inflection-

the curve of increasing content of the excess component (and impurities) in the transverse section of the boule shifts from the center to the periphery into the convex part of boule *A*. The concave part of boule *B*, in comparison with the convex part, is enriched in the excess component and impurities, when they are present, as is shown for Zn in Fig. 3b. This relationship is in fact a consequence of the dependences established above for Verneuil crystals.

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Note: Figure translations are in progress. See original paper for figures.