Synthesis of glass ceramics containing finely dispersed particles of aluminum-doped M-type strontium hexaferrite

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Glasses with nominal compositions $SrFe_{10}Al_2O_{19}+4(SrB_2O_4+Sr_2B_2O_5)$ (**1**) and $SrFe_9Al_3O_{19}+4(SrB_2O_4+Sr_2B_2O_5)$ (**2**) were prepared by rapid quenching of melts. Thermal treatment of glass samples at 600—900 °C resulted in crystallization of the magnetic phase $SrFe_{12-x}Al_xO_{19}$ ($x = 1.1\pm0.1$) and strontium borates. Platelet hexaferrite particles with average sizes from (250×60) nm^2 to (450×140) nm^2 were prepared. The coercive force of glass ceramics is 580 and 475 kA m^{-1} for glasses **1** and **2**, respectively. The coercive force of 580 kA m^{-1} is the highest known value compared to hexaferrite particles prepared earlier by glass crystallization.

Key words: M-type strontium hexaferrite, glass, glass ceramics, ferrimagnetic, coercive force, saturation magnetization.

Strontium and barium M-type hexaferrites are promising materials for the construction of high-density magnetic data storage devices and constant magnets due to their high magnetic anisotropy constants and chemical inertness.[1,2] One of procedures for the preparation of finely dispersed hexaferrites is based on crystallization of glassy oxide precursors by thermal treatment.[3—6] This procedure affords single-domain submicron magnetic particles characterized by a high coercive force. Earlier,[7—9] we have demonstrated that the chemical composition of the starting glass influences the size and shape of hexaferrite particles prepared by thermal treatment of an amorphous material. For example, crystallization of glasses in the $SrO—Fe_2O_3—B_2O_3$, $SrO—Fe_2O_3—SiO_2$, and $SrO—Fe_2O_3—B_2O_3—Bi_2O_3$ systems gave platelet strontium hexaferrite particles with an average diameter varying from 50 nm to 1 μm and the diameter to thickness ratio varying from 1.4 to 7.4. In the present study, strontium hexaferrite was synthesized for the first time by glass crystallization in the $SrO—B_2O_3—Al_2O_3—Fe_2O_3$ system. The compositions of the starting glasses were chosen based on the results of our earlier study[10] of phase equilibria in the $SrO—Fe_2O_3—B_2O_3$ system. We chose aluminum oxide as an additional component taking into account that it, serving arbitrarily as glass-forming oxide, modifies the glass properties. Besides, aluminum can replace iron in hexaferrite,[11] resulting in an increase in the coercive force of the material.[12]

Experimental

Strontium carbonate, iron(III) oxide, boric acid (all of reagent grade), and aluminum oxide, which was prepared by thermolysis of aluminum nitrate at 800 °C, were used as starting compounds. A mixture of the starting compounds was annealed at 600 °C for 10 h.

Glass samples were prepared by melting powders in a platinum crucible placed in a tube furnace at 1250 °C for 2 h. The resulting melts were quenched between two rotating steel rollers. The glasses have the following compositions: $9SrO\cdot5Fe_2O_3\cdot Al_2O_3\cdot8B_2O_3$ (**1**) and $9SrO\cdot4.5Fe_2O_3\cdot1.5Al_2O_3\cdot8B_2O_3$ (**2**), which formally correspond to the compositions $SrFe_{10}Al_2O_{19}+4(SrB_2O_4+Sr_2B_2O_5)$ (**1**) and $SrFe_9Al_3O_{19}+4(SrB_2O_4+Sr_2B_2O_5)$ (**2**), respectively. Glass-ceramic samples were synthesized by annealing the glass samples at 600—900 °C for 2 h.

X-ray diffraction patterns of the samples were obtained on a Guinier FR-552 monochromator chamber (Cu-Kα_1 radiation). The magnetic properties were studied using a Faraday balance and a Quantum Design SQUID magnetometer. Microstructural studies were carried out on a Leo Supra 50 VP scanning electron microscope equipped with an X-ray microanalysis attachment.

Results and Discussion

The glasses synthesized appeared to be completely X-ray amorphous. The powder X-ray diffraction data for annealed glass samples are given in Table 1. Crystalline phases appeared at ≥650 °C; $Sr_2B_2O_5$ was the first to crystallize from glasses of both compositions. When the

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Table 1. Powder X-ray diffraction data for the phase compositions of glass-ceramic samples prepared at different temperatures

T*/°C	Composition **1**	Composition **2**
600	No crystalline phases were found	
650	$Sr_2B_2O_5$	$Sr_2B_2O_5$
700	$Sr_2B_2O_5$, SrB_2O_4	$Sr_2B_2O_5$, SrB_2O_4
750	$Sr_2B_2O_5$, SrB_2O_4	$Sr_2B_2O_5$, SrB_2O_4
800	$Sr_2B_2O_5$, SrB_2O_4, $SrFe_{12}O_{19}$	$Sr_2B_2O_5$, SrB_2O_4, $SrFe_{12}O_{19}$
850	$Sr_2B_2O_5$, SrB_2O_4, $SrFe_{12}O_{19}$	$Sr_2B_2O_5$, SrB_2O_4, $SrFe_{12}O_{19}$
900	$Sr_2B_2O_5$, SrB_2O_4, $SrFe_{12}O_{19}$	**

* The synthesis temperature of glass ceramic.

** The sample melts.

annealing temperature was increased to 700 °C, X-ray diffraction pattern showed lines of the second borate of composition SrB_2O_4. Beginning with 800 °C, X-ray patterns contained broadened lines corresponding to strontium hexaferrite.

For the glass of composition **1** annealed at 850 °C, the unit cell volume of $Sr_2B_2O_5$ is 494.3(7) Å^3 (a = 7.763(7) Å, b = 5.364(3) Å, c = 11.88(1) Å, α =92.6(1)°). According to the published data,[13] the unit cell volume of pure $Sr_2B_2O_5$ is 489.0 Å^3. An increase in the volume may be indicative of the replacement of boron with aluminum. The unit cell volume of SrB_2O_4 is 343.4(1) Å^3 (a = 11.952(4), b = 4.3375(4), c = 6.6245(7) Å), and it is virtually equal to that published in the literature[14] for pure SrB_2O_4 (343.3 Å^3).

For glass of composition **2** annealed at 850 °C, the unit cell volume of $Sr_2B_2O_5$ is 495.7(6) Å^3 (a = 7.783(9), b = 5.361(9), c = 11.892(8) Å, α = 92.6(1)°), and the unit cell volume of SrB_2O_4 is 345.9(5) Å^3 (a = 12.06(1), b = 4.337(7), c = 6.615(3) Å). Apparently, boron is partially replaced with aluminum in both borates.

In all cases, the unit cell parameters of hexaferrite are smaller (Table 2) than those of pure strontium hexaferrite (691.2 Å^3),[15] which is evidence that iron is replaced by aluminum. Taking into account the published data[11] for $SrFe_{12-x}Al_xO_{19}$, the unit cell volumes correspond to the replacement $x = 1.1\pm0.1$ for both compositions. Hence, the aluminum content in hexaferrite is much lower than that expected for the nominal composition, and excess aluminum is involved in strontium borates.

Scanning microphotographs of etched glass-ceramic samples are shown in Fig. 1. The samples were etched by keeping them in distilled water for ~1 h. Etching was accompanied by dissolution of strontium borates, and only hexaferrite particles remained on the sample surface. The composition of these particles was confirmed by X-ray microanalysis.

As can be seen, the hexaferrite particles have a hexagonal platelet shape similar to that observed earlier.[3,7–9] The size of hexaferrite particles increases, whereas the diameter to thickness ratio decreases as the annealing temperature increases (Table 3). At 800 °C, the particle anisotropy in a sample of composition **1** is higher than that in a sample of composition **2**, whereas at the maximal annealing temperature, the particles in a sample of composition **1** become less anisotropic.

Lines of hexaferrite are noticeably broadened even in the X-ray diffraction patterns of samples, which were synthesized at maximal temperature and characterized by the largest crystallite sizes. Apparently, this is evidence that the particles have somewhat different unit cell parameters, which is reasonable to relate to the difference in the degree of replacement of iron with aluminum. Therefore, the above-determined degrees of replacement are averaged over the samples.

The magnetic measurement data are given in Table 4. The saturation magnetization of the samples increases with increasing annealing temperature. The magnetization increases most substantially in a temperature range of 600—650 °C. Judging from the magnetization, it can be concluded that the major portion of hexaferrite crystallizes in this temperature range. Apparently, the absence of lines of a magnetic phase in X-ray diffraction patterns indicates that, in the temperature range 600—650 °C, this phase forms nanometer-size particles, which is below the

Table 2. Volumes and parameters of the hexagonal unit cell of $SrFe_{12-x}Al_xO_{19}$ in glass-ceramic samples

Sample composition	T* /°C	a	c	Unit cell volume/Å^3
		Å		
1	800	5.858(1)	22.91(2)	681.0(6)
1	850	5.854(1)	22.93(1)	680.4(4)
1	900	5.853(1)	22.93(2)	680.3(8)
2	800	5.845(2)	22.97(3)	679.8(4)
2	850	5.861(2)	22.962(5)	683.0(4)

* The synthesis temperature.

Table 3. Geometric characteristics of hexaferrite particles in glass ceramics

Glass composition	T*/°C	Diameter	Thickness	Diameter to thickness ratio
		nm		
1	800	250	60	4.2
1	900	380	130	2.9
2	800	400	110	3.6
2	850	450	140	3.2

* The annealing temperature.

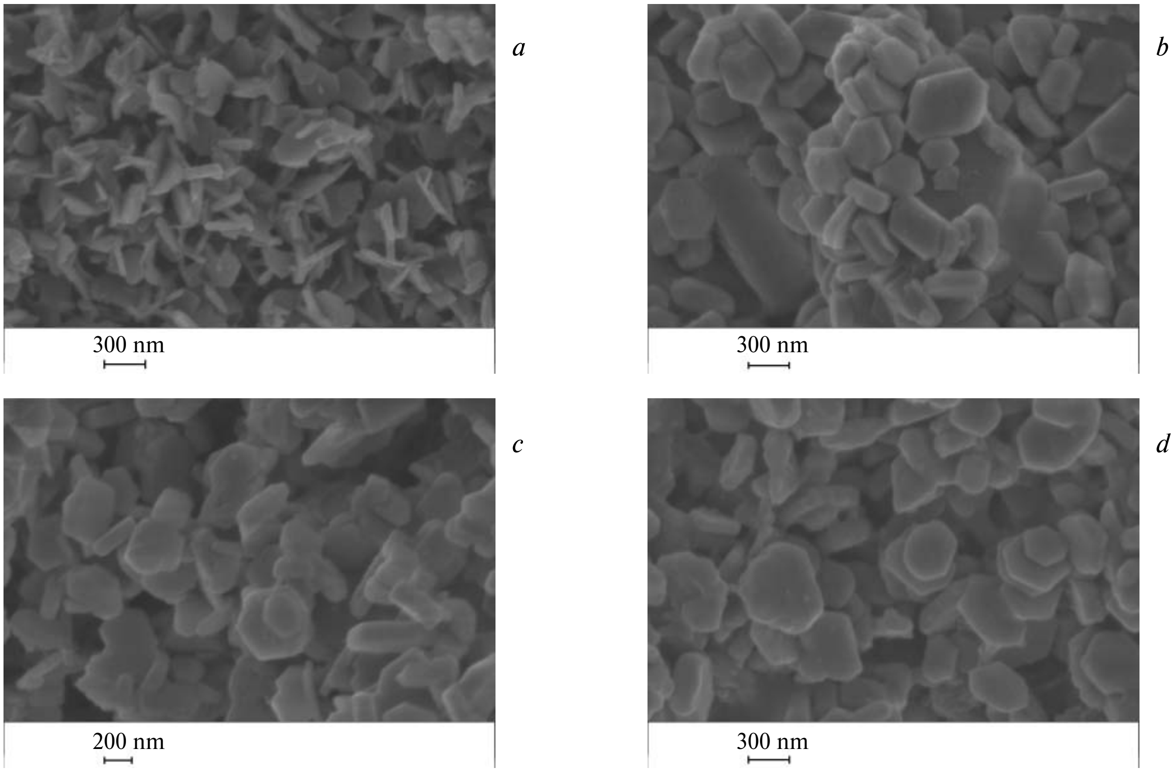

Fig. 1. Scanning microphotographs of glass-ceramic samples of compositions **1** (*a*, *b*) and **2** (*c*, *d*) synthesized at 800 (*a*, *c*), 850 (*d*), and 900 °C (*b*). Hexaferrite particles have a hexagonal platelet shape.

Table 4. Coercive forces and saturation magnetizations of glass-ceramic samples of compositions **1** and **2**

Composition	T*/°C	H_c/kA m^{-1}	M_s/A m^2 kg^{-1}
1	600	10	3.2
1	650	295	17.8
1	700	310	19.0
1	800	430	16.7
1	900	580	18.3
2	600	50	4.3
2	650	290	16.1
2	800	440	14.9
2	850	475	15.8

* The annealing temperature.

resolution limit of the electron microscope used in the present study.

Beginning with the annealing temperature of 700 °C, a slight nonmonotonic change in the magnetization was observed, which is attributable to the influence of two opposite factors. An increase in the annealing temperature leads to an increase in the portion of the crystalline phase of hexaferrite, resulting in an increase in the magnetization. At the same time, a change in the annealing temperature can be accompanied by a change in the aluminum content in the hexaferrite phase, and an increase in the aluminum content should lead to a decrease in the magnetization.

For samples of composition **1**, the coercive force increases with increasing annealing temperature and is 580 kA m^{-1} at 900 °C. This is the highest known value compared to hexaferrite particles prepared earlier by glass crystallization. For samples of composition **2**, the maximal coercive force is somewhat smaller (475 kA m^{-1}).

The coercive force of a single-domain particle with uniaxial magnetic anisotropy taking into account its shape is estimated by the equation:

$$H_c = 0.48[2K_1/\mu_0 M_s + (N_\perp - N_\parallel)M_s],$$

where K_1 is the magnetocrystalline anisotropy constant of the compound, M_s is the saturation magnetization, $N_\parallel$ and $N_\perp$ are the demagnetizing factors parallel and perpendicular to the easy magnetization axis.[3] For a thin plate, a sphere, and a rod, the $N_\parallel - N_\perp$ difference is –1, 0, and 0.5, respectively, *i.e.*, the particles characterized by a smaller diameter to thickness ratio have a higher coercive force.

At the maximal temperature, the hexaferrite particles prepared from the glass of composition **1** are characterized by the smallest diameter to thickness ratio compared to particles prepared from other samples, the aluminum content being approximately the same. As a consequence, the former particles are characterized by the largest coercive force.

To summarize, we prepared glass ceramics containing submicron particles of aluminum-doped strontium hexaferrite and characterized by high coercive forces.

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