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Synthesis of magnetic glass ceramics containing fine $SrFe_{12}O_{19}$ particles

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The magnetic glass ceramics with the particles of $SrFe_{12}O_{19}$ having various aspect ratios was obtained by the crystallisation of oxide glass precursors in different chemical systems.

The M-type strontium hexaferrite is a promising material for developing high-density data storage devices and permanent magnets due to its high magnetocrystalline anisotropy and chemical stability.[1,2] Finely dispersed $SrFe_{12}O_{19}$ with advanced characteristics can be formed *via* devitrification of oxide glass.[3–5] The chemical composition of the precursor oxide glass affects on its physical and chemical properties; and, hence, the process of its crystallisation. One can expect that a wide variation in the glass composition will extend possibilities to control the size and aspect ratio of the particles, as well as their magnetic properties. Therefore, it is important to investigate new chemical systems and compositions appropriate for material formation. Here, we consider magnetic glass ceramics in the $SrO–B_2O_3–Fe_2O_3$, $SrO–B_2O_3–Fe_2O_3–Bi_2O_3$ and $SrO–SiO_2–Fe_2O_3$ systems.

Glass compositions were chosen after investigations of phase equilibrium in the areas of the $SrFe_{12}O_{19}$ existence.[6,7] The oxide ratio in the glass corresponded to the following compositions: $SrFe_{12}O_{19}$ + 8SrB_2O_4 (I), $SrFe_{12}O_{19}$ + 12$Sr_2B_2O_5$ (II), $SrFe_{12}O_{19}$ + 12$SrB_{1.5}Bi_{0.5}O_4$ (III), $SrFe_{12}O_{19}$ + 12$SrSiO_3$ (IV).

Precursors were prepared from reagent grade chemicals (SiO_2, Fe_2O_3, Bi_2O_3, H_3BO_3 and $SrCO_3$) by heat treatment at 600–800 °C for 24 h in pellets. The pellets were melted in a platinum crucible at 1200–1500 °C using plasmotron Alplas-2.2 flame. The melt was quenched between two copper plates.

The glass samples were heated for 2 h to the annealing temperatures in the range 600–1275 °C and the samples were air quenched after annealing for 2 h.

Glass-ceramic samples I, II and IV obtained at high annealing temperatures contained two phases denoted in their nominal phase compositions. At low annealing temperatures, the samples contain some intermediate crystalline and amorphous phases in addition.

Samples III contained several phases even at high annealing temperatures. Iron was found to be distributed between $SrFe_{12}O_{19}$, $BiFeO_3$ and $Sr_5BiFeB_yO_z$. Besides, the fourth phase of SrB_2O_4 was present.

The magnetisation at H = 720 kA m^{-1} (M) and coercive force (H_c) of glass-ceramic samples I are shown in Figure 1. The

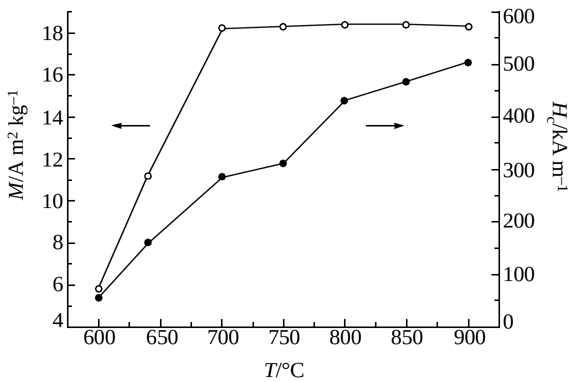

Figure 1 Magnetisation at 720 kA m^{-1} (M) and coercivity (H_c) for glass-ceramic samples $SrFe_{12}O_{19}$ + 8SrB_2O_4 *vs*. annealing temperature.

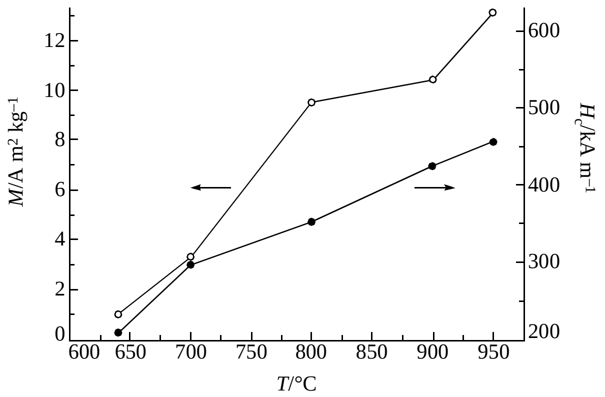

Figure 2 Magnetisation at 720 kA m^{-1} (M) and coercivity (H_c) for glass-ceramic samples $SrFe_{12}O_{19}$ + $12Sr_2B_2O_5$ *vs.* annealing temperature.

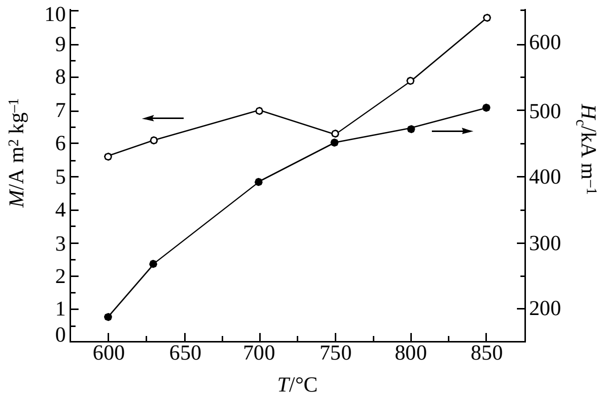

Figure 3 Magnetisation at 720 kA m^{-1} (M) and coercivity (H_c) for glass-ceramic samples $SrFe_{12}O_{19}$ + $12SrB_{1.5}Bi_{0.5}O_4$ *vs.* annealing temperature.

magnetisation of the samples increases with annealing temperature and, starting from 700 °C, saturates at about 18 A m^2 kg^{-1}, which corresponds to the crystallisation of the total amount of $SrFe_{12}O_{19}$. The coercive force of the samples increases up to 850 °C and reaches 504 kA m^{-1}.

The SEM and TEM data show that $SrFe_{12}O_{19}$ forms hexagonal platelet particles. Geometric characteristics of the particles are presented in Table 1. The particle size for composition I increases with annealing temperature, while the aspect ratio decreases from 5 to 2.6.

The magnetisation and coercive force of glass-ceramic samples II are shown in Figure 2. The magnetisation continuously increases with annealing temperature, which corresponds to the crystallisation of a $SrFe_{12}O_{19}$ phase in a wide temperature range, as shown by XRD measurements. The coercive force of the samples continuously increases and reaches 456 kA m^{-1}. The aspect ratio for the $SrFe_{12}O_{19}$ particles of composition II is considerably higher than that for glass ceramics I, *e.g.*, it is equal to 7.4 at 800 °C.

Hence, the lower coercive force for composition II can be explained by the higher aspect ratio of the particles, which determines demagnetising factors $N_\parallel$ and $N_\perp$. The dependence of H_c on $N_\parallel$ and $N_\perp$ is given by $H_c = 0.48[2K_1/M_s + (N_\parallel - N_\perp)M_s]$.[8]

Figure 3 shows the magnetisation and coercive force for glass-ceramic samples III obtained at different temperatures. The magnetisation of the glass-ceramic samples increases with annealing temperature to about 10 A m^2 kg^{-1}. The coercive force raises from 188 to 504 kA m^{-1} under the same conditions.

An increase in the annealing time at 850 °C from 2 to 4 or 8 h does not result in magnetisation changes, while the coercive force of the samples decreases to 476 and 440 kA m^{-1}, respectively.

In the samples obtained by heat treatment at 850 °C for 2 and 8 h, $SrFe_{12}O_{19}$ platelet particles are characterised by average sizes of 150×450 and 180×560 nm, respectively. Apparently, in the latter case, more particles can have a size exceeding a monodomain critical size that results in the H_c decrease.

Magnetic parameters for glass-ceramic samples IV are shown in Figure 4. A magnetic phase arises at 700 °C. The magnetic response of the sample annealed at this temperature corresponds to 20% of the theoretical for the $SrFe_{12}O_{19}$ + $12SrSiO_3$ composite and increases to ~30% at 950 °C. The coercive force grows from ~0 to 376 kA m^{-1} in the annealing range 700–950 °C. At 1000 °C, the magnetisation sharply rises about three times and then grows slowly with increasing temperature, while H_c remains nearly constant (~400 kA m^{-1}).

The geometric characteristics of the $SrFe_{12}O_{19}$ particles are shown in Table 1. The average particle size for the sample annealed at 1000 °C is 50×260 nm. With a further growth of the annealing temperature, the particle size constantly increases, while the aspect ratio initially grows slightly (1100 °C) and then decreases by a factor of about 4.

The local minimum of the coercive force at 1100 °C can be explained by a higher aspect ratio of particles at this temperature. For the samples annealed at 1150–1250 °C, the size of some particles exceeds a monodomain critical size that has to lead to a decrease in H_c, while the low aspect ratio results in an increase in H_c. Compensation of these factors may explain minor changes in the coercive force for these samples.

In conclusion, it was shown that $SrFe_{12}O_{19}$ crystallised as plate-like particles with the aspect ratio dependent on the glass chemical composition and thermal treatment conditions. With increasing annealing temperature, the particle size increased, while the aspect ratio demonstrated a tendency to decrease. The particles were obtained with an aspect ratio from 1.4 to 7.4 and mean size ranging from tens to hundreds of nanometres. The thicker grains were characterised by a higher coercive force.

Table 1 Geometric characteristics of the $SrFe_{12}O_{19}$ particles obtained at different temperatures from $SrFe_{12}O_{19}$ + $8SrB_2O_4$, $SrFe_{12}O_{19}$ + $12Sr_2B_2O_5$ and $SrFe_{12}O_{19}$ + $12SrSiO_3$ glasses.

Glass composition	Annealing temperature/°C	Diameter/nm	Thickness/nm	Aspect ratio
$SrFe_{12}O_{19}$ + $8SrB_2O_4$	700	50	10	5.0
	800	390	120	3.2
	850	420	160	2.6
	900	470	180	2.6
$SrFe_{12}O_{19}$ + $12Sr_2B_2O_5$	800	810	110	7.4
$SrFe_{12}O_{19}$ + $12SrSiO_3$	1000	260	50	5.2
	1100	710	110	6.4
	1150	840	510	1.6
	1250	1200	830	1.4

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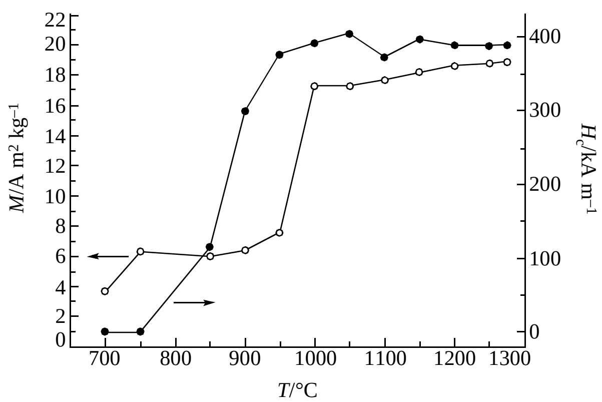

Figure 4 Magnetisation at 720 kA m^{-1} (M) and coercivity (H_c) for glass-ceramic samples $SrFe_{12}O_{19}$ + $12SrSiO_3$ *vs.* annealing temperature.

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