Hexaferrite submicron and nanoparticles with variable size and shape via glass-ceramic route

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Abstract. Strontium hexaferrite single domain particles embedded in the borate matrix were synthesized by the glass-ceramic method. The composites exhibit various morphologies depending on the initial glass composition and the thermal treatment conditions. The obtained materials contain magnetic particles with the average size ranging from tens to hundreds nanometers and with the magnetic properties changing from superparamagnetic to hard magnetic with record-high coercivities exceeding 10 kOe.

1. Introduction

M-type hexaferrites are characterized by pronounced single axis magnetocrystalline anisotropy and a high Curie temperature, which, in addition to the low fabrication costs, determines their wide application as hard magnetic materials [1]. Nowadays single domain hexaferrite particles are in the focus of an intense scientific activity. The interest in them lies in the fact that their magnetic behavior can be manipulated by varying the composition, size and aspect ratio of the particles.

One of the promising preparation methods of such finely dispersed particles is the glass-ceramic technique [2]. The initial glass contains chemical components mixed homogeneously on the atomic scale level. By application of a certain thermal treatment, it is possible to control nucleation and growth of the hexaferrite nanocrystals from the glass. In most cases the crystals are isolated from each other by the matrix phases that allow obtaining non-agglomerated single crystalline hexaferrite particles by dissolving the matrix.

2. Experimental

The glass samples were synthesized by melting a mixture of oxides in a platinum crucible at 1250°C for 2 h and quenching the melt between two steel rollers. The glass compositions used were 14SrO-6Fe₂O₃-12B₂O₃ (1) and 13SrO-5.5Fe₂O₃-4.5Al₂O₃-4B₂O₃ (2).

The samples of glass 1 were put into a cold furnace, then heated at 5 °C/min and taken out as soon as the desired temperature $T_{an}$ was reached. Glass 2 was annealed in two stages: first at 750 °C for 2 h, and then at 970 °C for 24 h with subsequent air quenching.

The hexaferrite powder was obtained by dissolving the borate matrix in hot 10 % acetic acid under ultrasonic treatment and subsequent precipitation in magnetic field.
The particle morphology was investigated using a LEO Supra 50VP scanning electron microscope. X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 diffractometer.

The DC magnetization as a function of magnetic field was measured using a Cryogenic S700 Squid magnetometer with a maximum applied field of 50 kOe at room temperature. The AC susceptibility was measured with a specially designed AC-susceptometer at 27 Hz and 1 Oe in the temperature range 18 – 290 K.

3. Results and discussion

3.1 Glass-ceramics 14SrO·6Fe₂O₃·12B₂O₃.

The dependence of saturation magnetization \( \sigma_s \) and coercive field \( H_c \) on the annealing temperature \( T_{an} \) is presented in Figure 1. The value of the saturation magnetization reflects the content of the ferromagnetic phase in the sample assuming the specific magnetization does not depend much on the particle size. After annealing at temperatures below 550 °C the samples show linear paramagnetic \( \sigma(H) \) dependence which suggests an absence of ferromagnetic phase. At \( T_{an} = 630-640 °C \) a noticeable amount of ferromagnetic phase forms, however the coercivity stays close to zero. Between 640 and 680 °C, \( \sigma_s \) and \( H_c \) abruptly increase which suggests the major quantity of the hexaferrite phase forms at these temperatures. The coercivity increases with the annealing temperature and reaches 6 kOe at \( T_{an} = 950 °C \). The presence of strontium hexaferrite phase was confirmed by XRD analysis. The hexaferrite particles reveal a plate-like shape (Figure 2). With increasing \( T_{an} \) from 680 to 950 °C, the particles mean diameter increases from tens to hundreds nm, their thickness to diameter ratio rises as well. The nanoparticles were also obtained in the colloidal solution by dissolving the borate matrix in diluted acetic acid.

At low temperatures, when the crystallization rate is slow, the formation of superparamagnetic material takes place. In Figure 3, the \( \sigma(H) \) plot is shown for the glass-ceramic sample, annealed at 570 °C for 20 h. No noticeable hysteresis is detected. The similar behavior is observed for the magnetic powder obtained by dissolving the matrix phases.

![Figure 1](image1.png)  
**Figure 1.** Saturation magnetization \( \sigma_s \) and coercive field \( H_c \) vs. annealing temperature for glass-ceramics 14SrO·6Fe₂O₃·12B₂O₃.

![Figure 2](image2.png)  
**Figure 2.** SEM micrographs of strontium hexaferrite particles obtained from glass-ceramics 14SrO·6Fe₂O₃·12B₂O₃ annealed at 680 °C (a), 740 °C (b), and 950 °C (c).
The AC susceptibility data of the superparamagnetic glass-ceramics are shown in Figure 4. The real part of the susceptibility has characteristic maximum at 185 K corresponding to the blocking temperature $T_B$. The imaginary part starts to rise below approx. 200 K indicating the appearance of hysteresis losses.

**Figure 3.** Magnetization $\sigma$ as function of magnetic field $H$ of glass-ceramics 14SrO-6Fe$_2$O$_3$-12B$_2$O$_3$ annealed at 570 °C for 20 h, and of corresponding powder.

**Figure 4.** AC susceptibility vs. temperature of glass-ceramics 14SrO-6Fe$_2$O$_3$-12B$_2$O$_3$ annealed at 570 °C for 20 h.

**Figure 5.** Magnetization vs. magnetic field of glass-ceramics 13SrO-5.5Fe$_2$O$_3$-4.5Al$_2$O$_3$-4B$_2$O$_3$ obtained as described in the text.
3.2 Glass-ceramics $\text{Sr}_3\text{Fe}_5\text{O}_{12-4}\text{Al}_2\text{O}_3-4\text{B}_2\text{O}_3$.

An important feature of the glass ceramic method is a possibility to substitute Fe atoms in the hexaferrite lattice by other elements simply varying the composition of the initial glass. It is known that partial substitution of Fe atoms by Al leads to a significant increase of coercivity. However to perform such substitution, temperatures over 1000 °C are usually required. That leads to an uncontrollable crystal growth, and large polydomain particles form. The mixture of components at the atomic level in the glass results in decrease of synthesis temperature, and on the other hand the non-magnetic matrix prevents particles from aggregation and intergrowth. In our previous work we reported the synthesis of Al-doped strontium hexaferrite with coercivities over 10 kOe [3]. Here we present a preparation of material with even higher $H_c$. The two-stage annealing of glass 2 results in submicron grained glass-ceramics with coercivity of 12.5 kOe. The corresponding hysteresis curve is shown in Figure 5. To our knowledge, this value of $H_c$ is the highest reported so far for hexaferrites.

4. Conclusions

In this short communication we have shown that glass-ceramic synthesis can provide a variety of magnetic materials based on strontium hexaferrite. The magnetic properties can be modified by changing the annealing conditions and initial glass composition. The hexaferrite particles crystallize in plate-like morphology and their diameter rise with increase of the annealing temperature. The particle thickness to diameter ratio also rises and these two factors result in the coercivity increase. At low temperatures very small superparamagnetic particles form. At intermediate temperatures, hexaferrite particles with diameter below 100 nm are obtained which already show coercivity of several kOe. The annealing at temperatures close to 1000 °C results in submicron hexaferrite grains with high coercivity, the aluminum doping leading to hexaferrite materials with record values of $H_c$ up to 12.5 kOe.

Acknowledgments

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References

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