

Actual Composition and Structure of Manganese Ferrite Nanoparticles Dispersed in the Borate Glass Matrix

I. G. Vasilyeva*, L. S. Dovlitova**, V. I. Zaikovskii**, V. V. Malakhov**,
I. S. Edel'man***, A. S. Stepanov****, and Academician K. S. Aleksandrov****

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In recent years, ferrite nanoparticles have been considered as promising functional materials for high-density data storage devices [1–4]. Such materials can be prepared as thin films, dispersed powders, and composites [1, 4]. Manganese ferrite nanoparticles were crystallized from melts of potassium aluminum borate glass ($K_2O-Al_2O_3-B_2O_3$) with additions of iron(III) and manganese(II) oxides [5–9]. The particles were detected by X-ray diffraction and transmission electron microscopy [6–8]. Their size ranged from 5 to 50 nm depending on the synthesis conditions. The resulting glasses were transparent and exhibited the properties of magnetically ordered systems with high magnetization and Faraday effect values, including the remanent value, in relatively weak magnetic fields [8]. Efforts have been made to estimate the degree of clustering of magnetic ions by measuring the magnetic and optical properties of glasses [10–12]. However, the character of the change in these properties depended not only on the particle size. The measured integral properties of glasses are not unambiguously interpretable without knowledge of the actual composition and structure of ferrite nanoparticles, which determine the distribution of Mn and Fe cations over magnetic sublattices.

In this work, the actual composition and structure of ferrite nanoparticles dispersed in glass were determined for the first time by using the differential dissolution (DD) method and high-resolution transmission electron

microscopy (HRTEM). This task was challenging for small particles and their low content and nonuniform distribution in the glass matrix. In addition, determining the components of the glass itself in the ferrite against the background of the glass matrix is conjectural, although such a determination is mandatory for interpretation of the magnetic and optical properties of glass.

Glass samples with different oxide contents were prepared at the Vavilov State Optical Institute by the procedure described in [9]. A series of glasses of different composition was studied. In this work, we discussed the results of studying glasses with an overall content of Fe and Mn oxides of 3 wt % and the atomic ratio Mn/Fe = 0.86; i.e., the manganese content of the glass was nearly twofold higher than that required by the ferrite stoichiometry. The magnetic and magneto-optical characteristics of this sample ($M_H = 10 \text{ kOe} = 0.49 \text{ emu/g}$, $M_H = 2.0 \text{ kOe} = 0.39 \text{ emu/g}$, $\alpha_H = 2.0 \text{ kOe} = 7.35 \text{ deg/cm}$, $\alpha/M = 18.85$), as well as of the other samples synthesized by this technique, deviated noticeably from the analogous characteristics of massive manganese ferrite with regard to the content of the ferrite phase in glass. It was necessary to elucidate the nature of these deviations with the aim of improving the magnetic and magneto-optical properties of glasses.

Stoichiometry of manganese ferrite nanoparticles. The compositions of the matrix and nanoparticles were determined by the differential dissolution method [13, 14]. The analysis was carried out using a stoichiograph with an inductively coupled plasma atomic emission spectrometer as the detector. The flow-type dynamic dissolution condition was used; i.e., the composition and concentrations of the components of a solvent and its temperature are changed with time. Under these conditions, the individual phases constituting a multiphase sample go into solution one after another, which makes it possible to determine their stoichiometry and quantitative content. In so doing, no standard samples of the phases to be determined are required and the stoichiograph is calibrated against the standard solutions of the elements constituting the glass (except oxygen).

When the glass was dissolved in 0.1 M HCl, nanoparticles dispersed in the matrix were carried away from the reactor with the solvent flow as a colloid solution. Direct DD analysis did not allow us to determine

* Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

** Borekov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent'eva 5, Novosibirsk, 630090 Russia

*** Kirenskii Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

**** All-Russia Research Center, Vavilov State Optical Institute, ul. Babushkina 36/1, St. Petersburg, 192371 Russia

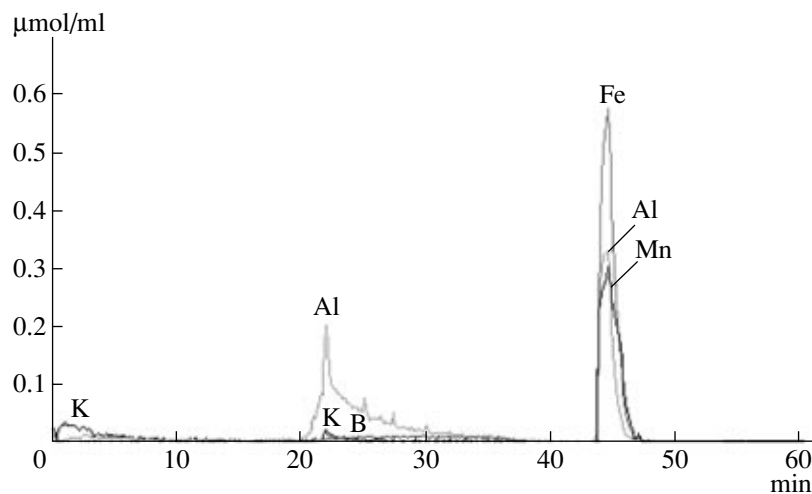


Fig. 1. Kinetic curves for dissolution of K, Al, B, Mn, and Fe from the concentrate in NaOH.

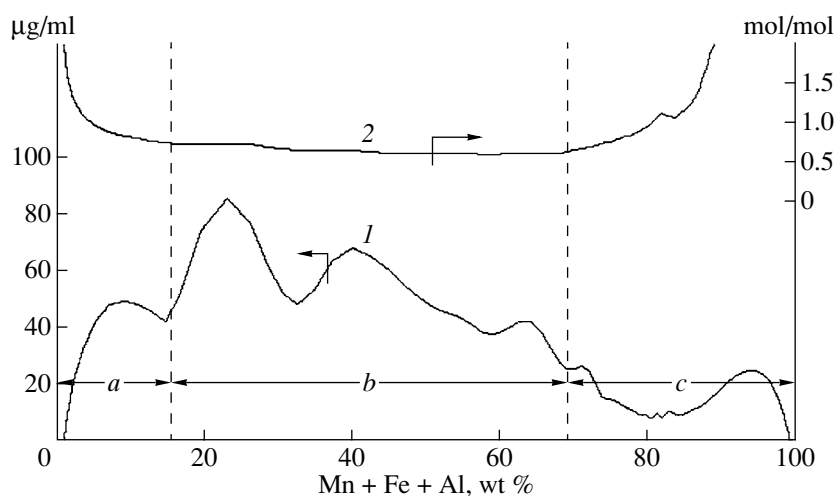


Fig. 2. (1) Kinetic curve for dissolution of the conglomerate of nanoparticles from the concentrate in the mixture of acids and (2) the Mn : Fe stoichiogram: the regions of dissolution of particles of composition $\text{Mn}(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_4$ with (a) $0.93 \geq x \geq 0.07$ and (b) $0 \geq x \geq 0.07$ and (c) the manganese oxide phase.

the composition of the nanoparticles since the matrix and the phases containing Fe and Mn were not completely separated. Therefore, in the detector, Fe and Mn were quantified simultaneously with the elements of the matrix (K, Al, and B), which was supported by the time-independent linear profile of the Mn/Fe stoichiogram. This problem was eliminated by preliminarily concentrating the nanoparticles. The concentrate was obtained by selectively dissolving the matrix in a static reactor in 0.1 M NaOH, in which the Fe and Mn oxide phases were insoluble.

The dry concentrate of nanoparticles (the concentrating factor was about 10) was analyzed by the DD method (Fig. 1). At the first stage of the flow-type dissolution (0–40 min, aqueous NaOH solution, pH 11, solution temperature increasing from 20 to 75°C),

residual amounts of the glass matrix components K, B, and Al dissolved from the concentrate. At the second stage, 40 min later, the solvent was replaced by a mixture of acids $\text{HCl} : \text{HNO}_3 : \text{H}_2\text{O} = 1 : 1 : 1$ at 75°C, in which the concentrate containing Fe, Mn, and some amount of Al completely dissolved. The quantitative data on the stoichiometric composition of the nanoparticles were extracted from analysis of the kinetic dissolution curves for Fe, Mn, and Al, as well as from the corresponding Mn : Fe, Mn : Al, and Al : Fe stoichiograms. It turned out that nanoparticles contained not only Fe and Mn but also Al. The entire conglomerate of nanoparticles is a mixture of spatially nonuniform phases of variable composition in the range from MnFe_2O_4 to MnAl_2O_4 , with the general formula $\text{Mn}(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_4$. The variable composition of phases

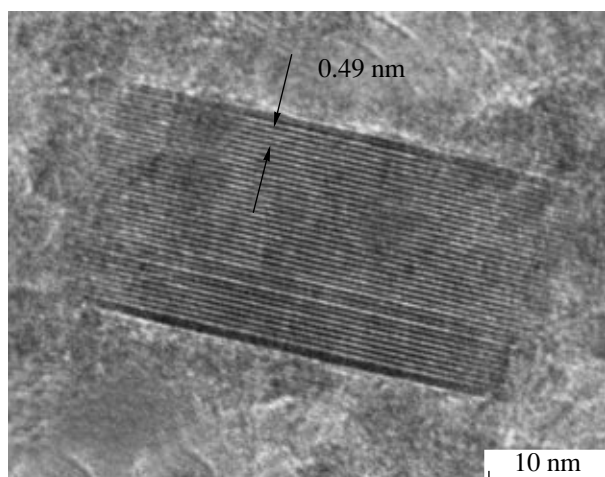


Fig. 3. HRTEM micrograph of a platelike MnFe_2O_4 particle.

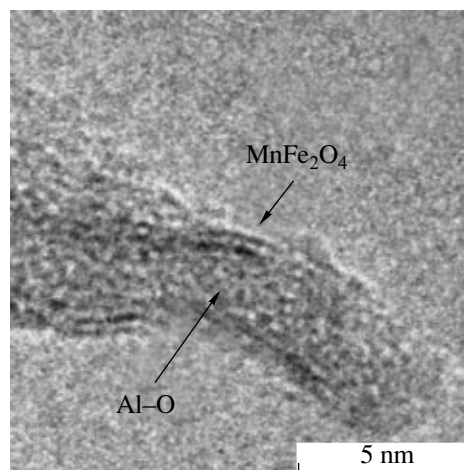


Fig. 4. HRTEM micrograph of a nanocomposite particle with alumina incorporated into the ferrite.

and the changing value of x were responsible for the fact that the contents of the phases were not exactly determined. About 77% of the conglomerate is accounted for by the phase with $0.07 \geq x \geq 0$ (Fig. 2, region *b*), and about 10% is due to the phase with $0.93 \geq x \geq 0.07$ (Fig. 2, region *a*). The nanoparticles also contain about 4% of the manganese oxide phase (Fig. 2, region *c*). Thus, as probed by the DD method, the manganese introduced into the glass charge in excess of the amount required by the ferrite stoichiometry was distributed over two phases, $\text{Mn}(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_4$ and MnO_x . The concentrate of nanoparticles contained about 9% of “free” aluminum (in the form of oxide), not incorporated in the above phases but present in the concentrate bulk.

Structure of manganese ferrite nanoparticles.

The HRTEM micrographs were obtained on a JEOL JEM-2010 microscope with a lattice resolution of 0.14 nm and an accelerating voltage of 200 kV. An EDAX spectrometer with a Si(Li) detector was used to determine the elemental composition of the samples by energy dispersive X-ray analysis (EDX).

According to HRTEM, the initial glass and the concentrate prepared from this glass are dominated by spherical particles 10 nm in size, along with well-faceted platelike crystals 30–50 nm in size. Figure 3 shows the HRTEM micrograph of a separate platelike particle from the concentrate of nanoparticles. There can be seen the close packing of atomic packets in the lattice with the interplanar spacing $d_{(111)} = 0.49$ nm, which is consistent with the structure of the cubic spinel MnFe_2O_4 . According to HRTEM, the smallest particles contain severely distorted doubled atomic packets of a spinel (Fig. 4). Between these packets, amorphous regions are located, which, according to EDX, consist mainly of aluminum and oxygen. Such layered objects, 2–3 nm thick, are nanocomposite units of the material under consideration.

Comparison of HRTEM and DD data allows us to conclude that large structurally perfect ferrite nanoparticles do not contain aluminum or contain only minute amounts, whereas the smallest nanocomposite particles with a distorted structure contain relatively large amounts of aluminum in the oxide form. It is evident that the substitution of aluminum for iron in the manganese spinel brings about structural stresses and their relaxation leads to the formation of the observed nanoheterogeneous state of particles. Thus, we have presented the first experimental evidence for the nanosize effect of incorporation of aluminum into the manganese ferrite composition. Our findings directly support the earlier hypothesis that aluminum acts as a diamagnetic diluent in exchange coupling of Fe and Mn paramagnetic ions [10–12], which is invoked to explain anomalous magnetic and optical properties. The DD and HRTEM data on the actual composition of ferrite particles and their quantitative contents make it possible to refine the experimental magnetic and optical parameters of glasses. At the same time, such diagnosis of glasses at different stages of their preparation is necessary for controlling the phase composition and stoichiometry of ferrite nanoparticles with the aim of producing glasses with predictable properties.

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