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Magnetic properties of some gadolinium silica glass ceramics

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Glass-ceramics of $0.95SiO_2$-$0.05Na_2O$ composition containing up to 20% molar Gd_2O_3 were obtained by the sol-gel method and heat-treated at 250 °C, 500 °C and 1000 °C. The samples were studied using scanning electron microscopy (SEM), electron paramagnetic resonance (EPR) and magnetic susceptibility measurements. The electron micrographs show the modifications of the internal network structure of the studied samples with increasing the Gd_2O_3 concentration. The magnetic behavior of the xGd_2O_3 (1-x) ($0.95SiO_2$ $0.05Na_2O$) glass ceramics was assumed to be due to the presence of the Gd^{+3} ions. The EPR spectra recorded for these samples consist of a single broad absorption signal with the effective *g* - value of 2. These spectra prove that the Gd^{+3} ions exist in the host glass ceramic matrix predominantly as clustered species. The inverse magnetic susceptibility as function of temperature for the xGd_2O_3 (1-x) ($0.95SiO_2$ $0.05Na_2O$) glass ceramics indicates that the susceptibility per mole of magnetic ion follows a Curie-Weiss type behavior. The obtained paramagnetic Curie temperature values suggest the presence of weak ferromagnetic interaction between the Gd^{+3} ions.

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1. Introduction

Glasses containing rare-earth ions have been widely studied in the past decade due to their important applications in the field of optical telecommunication and laser technology. Some of these glasses were found to have interesting optical and magnetic properties [1,2]. Considerable interest was accorded to glasses containing gadolinium ions. The study of their magnetic behavior offered useful information concerning the distribution of the gadolinium ions in the host glass matrix and the nature of the magnetic interactions between these ions [3-6].

In the last years, the development of the sol-gel method [7] for preparing a large sort of materials has been offering the opportunity to study these rare-earth ions in glass-ceramics environment. Increased interest in glass-ceramics has resulted from their potential applications including coating on optical memory discs, electrooptic and magnetooptic devices. Different silicate systems become interesting in these circumstances.

The purpose of this paper was to study the magnetic properties of $xGd_2O_3(1\text{-}x)(0.95SiO_2\ 0.05Na_2O)$ glass-ceramics with x=0.05, x=0.10, x=0.15 and x=0.20, by means of magnetic susceptibility measurements and electron paramagnetic resonance. Scanning electron microscopy supplement the data that can be obtained.

2. Experimental

Samples of $xGd_2O_3(1\text{-}x)(0.95SiO_2\ 0.05Na_2O)$ composition were prepared starting from tetraethoxysilane (99.9 % purity) as source of silica and natrium and gadolinium nitrates.

The tetraethoxysilane was mixed with ethanol and water in molar ratio 1:3:1, and then stirred for an hour at room temperature. After this hydrolysis, the two nitrates were added to give a H_2O/tetraethoxysilane ratio of 20. This solution was stirred about an hour with a magnetic agitator and then dried at 60 °C.

The gel was again dried at 250 °C, crumbled and then pressed at 200 atm in the shape of discs with 22 mm diameter and approximately 1mm thickness. The samples were heat-treated in air under normal pressure and at different temperatures: 250 °C, 500 °C and 1000 °C for about 48 hours.

Magnetic susceptibility measurements were performed using a Weiss-type magnetic balance in the 80-300 K temperature range. The accuracy of the temperature control was better than ± 0.1 K over the whole temperature range and the overall accuracy of the measurements of the magnetic moment was less than ± 3 %.

The electron paramagnetic resonance (EPR) spectra were recorded on a 300EPS Bruker spectrometer, in X band, at room temperature on powder samples.

Microscopic examination of the samples was made with a Jeol JSM 5600-LV scanning electron microscope.

3. Results and discussion

The Fig. 1 presents the dependence of the inverse magnetic susceptibility as function of temperature, for some $xGd_2O_3(1\text{-}x)(0.95SiO_2\ 0.05Na_2O)$ glass-ceramic samples with x=0.05, x=0.10, x=0.15 and x=0.20, heat-treated at 1000 °C. The same dependence is shown in the figure 2 for the glass-ceramic samples with x=0.05, but heat-treated at 250 °C, 500 °C and 1000 °C.

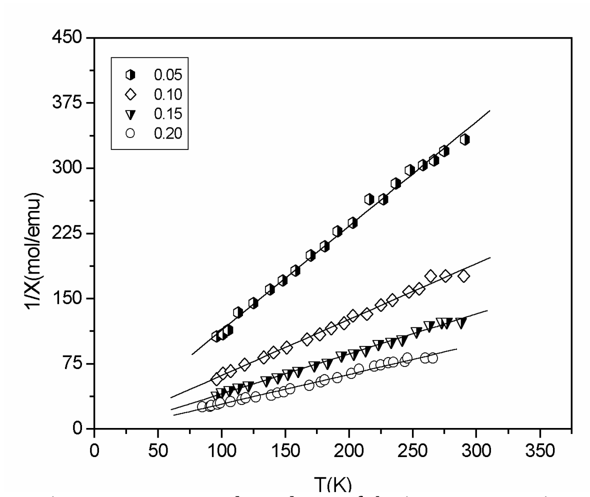

Fig. 1. Temperature dependence of the inverse magnetic susceptibility of the studied glass-ceramic samples heat-treated at 1000 °C.

The temperature variation of the reciprocal susceptibilities follow a Curie-Weiss behavior described by

$$\chi_m^{-1} = (T-\theta_p)/C_m \qquad (1)$$

where χ_m represents the molar magnetic susceptibility, T, the temperature, C_m is the molar Curie constant and θ_p is the paramagnetic Curie temperature. The solid lines in Figs. 1 and 2 depict the computer fit of experimental data according to Eq. (1).

The magnetic behavior of $xGd_2O_3(1-x)(0.95SiO_2\ 0.05Na_2O)$ glass-ceramic samples was assumed to be due to the presence of Gd^{3+} ions. The experimental magnetic susceptibilities were corrected taking into account the diamagnetic contribution of the $0.95SiO_2\ 0.05Na_2O$ host glass-ceramic matrix.

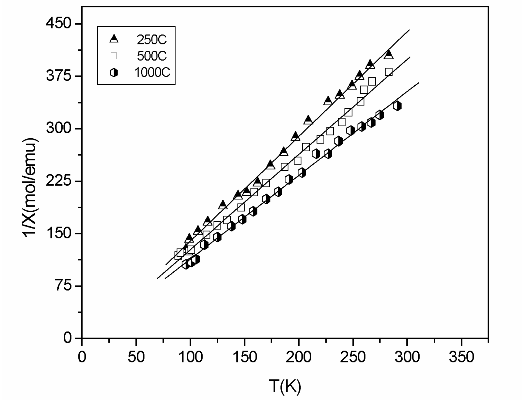

Fig. 2. Temperature dependence of the inverse magnetic susceptibility o f the glass-ceramic samples with x=0.05, heat-treated at 250 °C, 500 °C and 1000 °C.

The paramagnetic Curie temperature, θ_p, is a rough indicator of magnetic interaction between Gd^{3+} ions. The values obtained for θ_p for all the samples were small and positive ($2.4 \leq \theta_p \leq 16.8$ K) suggesting the presence of weak ferromagnetic interactions between the Gd^{3+} ions. Thus, at least a fraction of the Gd^{3+} ions is present in the host glass-ceramic matrix as coupled species. The augmentation of the Gd_2O_3 content, x, of the samples determines the increase of the θ_p values. This fact suggests the increase of the exchange interactions between the gadolinium ions.

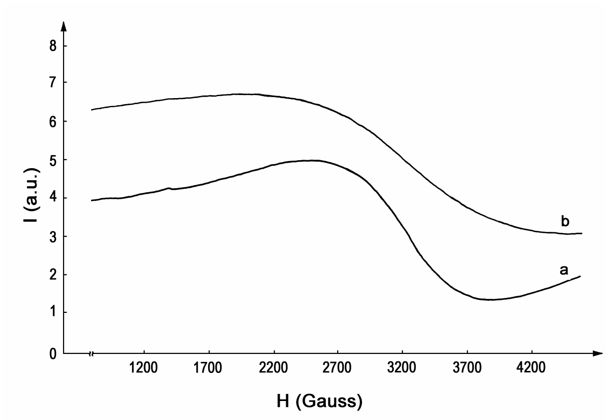

Fig. 3. EPR spectra of the $xGd_2O_3(1-x)(0.95SiO_2\ 0.05Na_2O)$ samples with x=0.05 (a) and x=0.15 (b) heat-treated at 1000 °C.

The effective magnetic moment per gadolinium ion, μ_{eff}, was calculated from the experimentally determined C_m values. These magnetic moment values were found in the range of $7.03 \div 8\mu_B$, close to that for the free gadolinium ion ($\mu_{eff} = 7.98\mu_B$ (i.e., [4])).

Some representative EPR spectra recorded for the $xGd_2O_3(1-x)(0.95SiO_2\ 0.05Na_2O)$ samples, namely those for the samples heat-treated at 1000 ^oC, are shown in Fig. 3. These spectra are due to the presence of Gd^{3+} ions in the studied samples. The spectra consist of a single broad absorption signal with the effective g-value of 2, where $g = h\nu/\mu_B H$, h is the Planck constant, ν is the microwave frequency, μ_B is the Bohr magneton and H is the value of the external applied magnetic field at the resonance line position. The EPR spectra shows that the Gd^{3+} ions are present in the studied samples as clustered species [3-6,8] in agreement with the magnetic susceptibility data. Increasing the gadolinium content of the samples determine the broadening of the EPR signal. This is due to (i) the increase of the degree of local structural disorder in the host glass-ceramic matrix [9] and/or (ii) the increase of the distribution range of the size of clusters present in the studied glass-ceramics.

The electron micrographs of the glass-ceramics samples with x=0.10 and x=0.20 are shown in Fig. 4 (a) and (b). These micrographs point out structural changes that occur with increasing the gadolinium content.

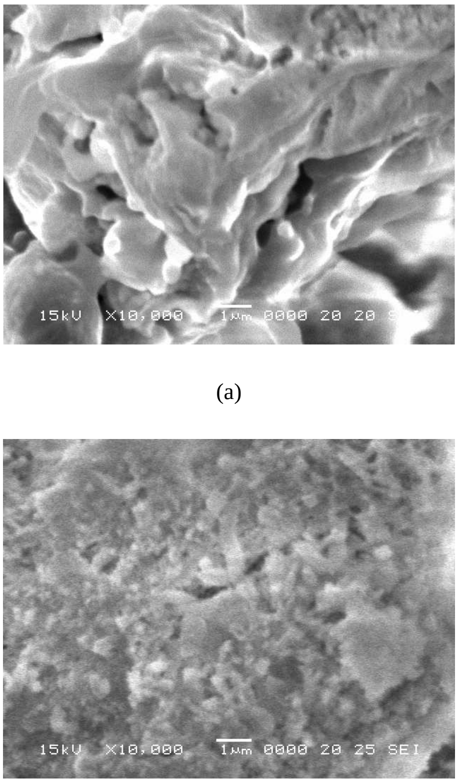

Fig. 4. SEM micrographs of the glass-ceramic samples heat-treated at 1000 °C with x=0.10 (a) and x=0.20 (b).

4. Conclusions

The study of the $xGd_2O_3(1\text{-}x)(0.95SiO_2\ 0.05Na_2O)$ glass-ceramics obtained by the sol-gel method show that their magnetic properties are determined by the presence of the Gd^{3+} ions as clustered species. The compositional evolution of the EPR data suggests that the gadolinium ions play a network modifier role in the studied sample. SEM micrographs support these assertions.

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