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Environmental effect on the magnetic properties of Fe ions in glasses and ceramics

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Abstract

The effect of the environment on the magnetic properties of Fe-ions in a sodium germanate glass, a sodium silicate glass, and in the same devitrified glasses has been studied. In the four samples investigated, the inverse magnetic susceptibility (χ^{-1}) follows a Curie–Weiss law behavior with a negative Curie temperature θ_p indicating an antiferromagnetic interaction in the four samples. The measurements also revealed that $|\theta_p|$ in both glass matrices is relatively low (<10 K) while in the crystalline samples it increased by 4-fold in the silicate and by about 20-fold in the germanate. The molecular field coefficients γ_m are negative for all four samples. The γ_m values for the Fe-germanate glass and the crystalline sample are 3 and 10 times larger than the corresponding values for Fe-silicate. These results reflect a stronger exchange interaction in the germanate (glass and crystalline) than the silicate samples. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Magnetic properties of disordered materials containing transition metal ions have been extensively studied in the past for both practical and fundamental reasons [1–6]. Specifically, oxide glasses containing Fe_2O_3 exhibit interesting optical, magnetic and electrical properties that are important for practical applications [7–11]. However, little work has focused on a comparative study of the magnetic properties of Fe-ions in different environments and in glass and glass ceramic obtained by heat treatment of the parent glass. The samples we have investigated in the present work are sodium silicate and sodium germanate glasses doped with a moderate amount

of Fe_2O_3 . These samples are part of a series of sodium silicate and sodium germanate glass samples that have been studied by means of X-ray photoelectron spectroscopy (XPS) [14,15]. The XPS technique has been used to analyze the Fe 3p core level spectra in order to obtain the number of ferric and ferrous ions present in the glasses. Other thermal and physical properties of these glasses have been measured such as thermal expansion coefficient and density.

In the present study, we report the magnetization measurements of the 0.05 Fe_2O_3 -doped sodium germanate and sodium silicate glasses and the glass ceramics obtained by heat treatment of the parents glasses at their respective crystallization temperatures. The objective is to compare the magnetic properties of Fe-ions in (i) two glassy environments with different types of atoms, (ii) the glass and the glass ceramic with the same type of atoms and (iii) two crystalline environment with different type of atoms. The inverse susceptibility

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versus temperature data has been used to calculate the Curie temperature, θ_p , and the effective magnetic moment, μ_{eff} . These parameters qualitatively describe the strength of the magnetic interaction, and can be recapped as a molecular field coefficients γ_m describing the environment around the magnetic ions.

2. Experimental procedure

The glass composition prepared had the formula $(0.65)\text{SiO}_2-(0.30)\text{Na}_2\text{O}-(0.05)\text{Fe}_2\text{O}_3$ and $(0.65)\text{GeO}_2-(0.30)\text{Na}_2\text{O}-(0.05)\text{Fe}_2\text{O}_3$. Analytical grade powders of Fe_2O_3 , Na_2CO_3 , GeO_2 and SiO_2 in the required stoichiometric ratios, were melted in a platinum crucible at 1300 °C for 2 h. The melt was cast into preshaped graphite-coated steel molds yielding glass rod specimens.

The chemical compositions of the samples were determined by inductive coupled plasma spectroscopy (ICP). The glass composition was analyzed at least twice and the estimated relative uncertainty in the ICP technique is about 5%. Differential thermal analysis (DTA) was performed at a heating rate of 10 °C/min using a Stanton Redcroft DTA model 673-4. Quartz was used as a reference material since the α - β transition helps to establish the exo/endothemic directions and the transformation occurs at a known temperature (573 °C), thus confirming the accuracy of the temperature scale of the DTA trace. The glass was then heat treated for 2 h at the crystallization temperature (T_x), determined from the DTA trace with heating and cooling rates of 1 °C/min. See Table 1 for T_g and T_x values.

The magnetization data (M versus H and M versus T) were recorded using a computer-con-

trolled variable temperature vibrating sample magnetometer PAR-4500/150A. The temperature-measuring sensor was a calibrated carbon glass resistor located near the specimen. The system was calibrated using pure nickel standard. The overall accuracy in the temperature measurements is better than 1% throughout the range, while that of the magnetization measurements is estimated to be approximately 5%.

3. Results

The dc magnetic susceptibility (χ) was calculated by choosing a specific value of the applied magnetic field of 2 T and measuring M at different temperatures. Then χ is simply M/H . The inverse dc magnetic susceptibility χ^{-1} in the temperature range 2.5–70 K is shown in Figs. 1(a) and (b) for the glasses and the glass ceramic samples, respectively. The glass samples reveal a linear behavior down to about 10 K, below which the data of the germanate glass show an upward curvature, while the data of the silicate glass show a slight downward curvature.

In Fig. 1(b) we present similar data for the crystallized samples. The χ^{-1} versus T graph of the devitrified germanate glass, curves downward and deviates markedly from linear behavior below 30 K. However, for the crystallized silicate sample, the data show an upward curvature and deviates slightly from linear behavior below 15 K. In all cases, the high temperature ($T > 30$ K) magnetic susceptibility data follows a Curie–Weiss behavior: $\chi = C(T - \theta_p)^{-1}$, where C is the Curie constant, and θ_p is the Curie temperature. The Curie temperature θ_p is an indicator to the type of the exchange interaction and roughly estimates its

Table 1
Thermal and magnetic parameters for the samples used in this study

Sample	$T_g \pm 2$ (°C)	$T_x \pm 2$ (°C)	$\mu_{\text{eff}} \pm 0.2$ (μ_B)	θ_p (K)	γ_m ($\text{erg}^{-1} \text{Oe}^2 \text{g}$)
Crystallized germanate	–	–	6.2	–188	–26 700
Germanate glass	475	617	5.8	–11.25	–2900
Crystallized silicate	–	–	5.4	–17.7	–2460
Silicate glass	455	694	5.6	–4.1	–1070
Fe^{2+} (free ion)	–	–	5.4	–	–
Fe^{3+} (free ion)	–	–	5.9	–	–

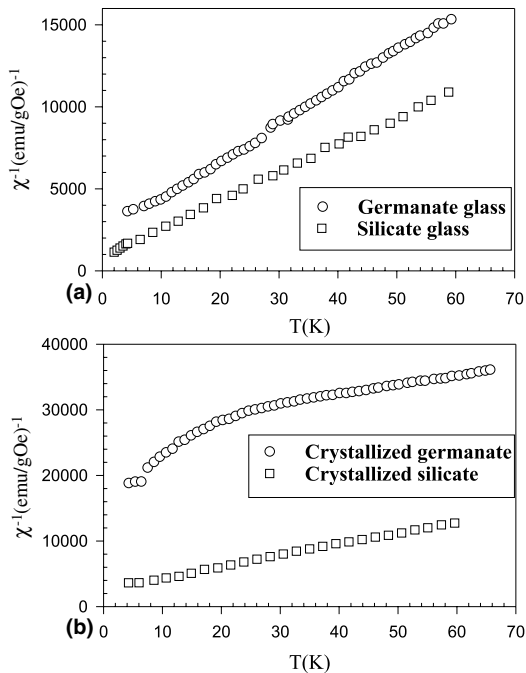


Fig. 1. Variations of the inverse susceptibility with temperature for (a) the glass samples, and (b) the crystallized samples.

strength. A negative θ_p value reflects antiferromagnetic interaction. The θ_p values for the four samples are listed in Table 1.

The effects of the environment can be clearly illustrated using the molecular field theory. The Curie temperature and the magnetic susceptibility can be used to calculate the molecular field coefficient γ_m as $\chi'_m = \theta_p / (T - \theta_p)$. The results are shown in Figs. 2(a) and (b) for the glasses and the glass ceramic samples, respectively. The γ_m values for the glass samples are almost constant down to about 10 K. The corresponding values for the crystalline samples are constants down to about 25 K. The temperature independent part of γ_m for the four samples are listed in Table 1.

4. Discussion

The iron silicate glass has been investigated by Mossbauer and neutron diffraction techniques [14]. The Mossbauer spectra of the glass sample

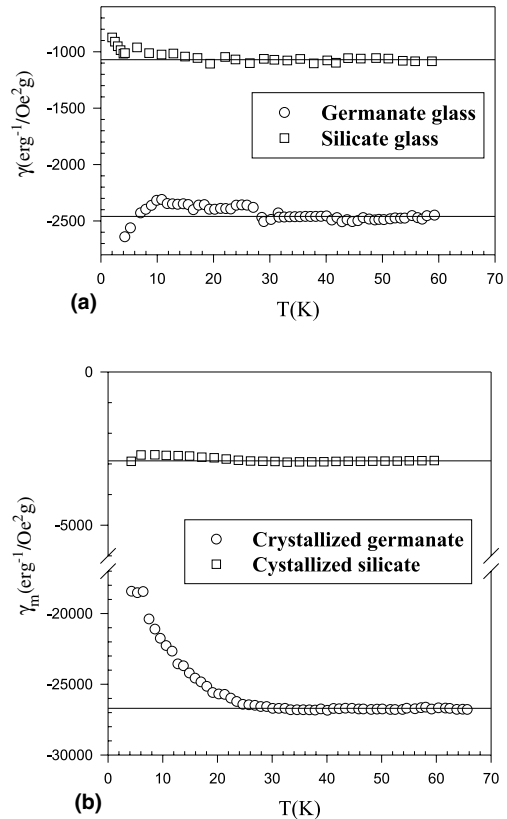


Fig. 2. Changes in the molecular field coefficient with temperature for (a) the glass samples, and (b) the crystallized samples.

have shown that both Fe^{2+} and Fe^{3+} were present in the glass and that the ratio $[\text{Fe}^{2+}]$ to $[\text{Fe}_{\text{total}}]$ was 14.5%. The M versus H data obtained for the two glass samples have also been reported elsewhere [12,15]. The data for the Fe-doped silicate and Fe-doped germanate glasses were fitted to a Brillouin function in order to obtain the number of Fe^{2+} and Fe^{3+} ions present in the glass sample. The $[\text{Fe}^{2+}]$ to $[\text{Fe}_{\text{total}}]$ ratio obtained from the best fit to the data was found to be about 42% for both glass samples. The ratio $[\text{Fe}^{2+}]$ to $[\text{Fe}_{\text{total}}]$ was also determined from the analysis of the Fe 2p core level XPS spectra and was found to be about 43% in both glasses [12,13]. A good agreement is found between the XPS and the magnetic measurements done on the two glass samples. However, the ratio $[\text{Fe}^{2+}]/[\text{Fe}_{\text{total}}]$ determined by Mössbauer technique for the Fe-silicate glass is found to be much

lower than the one determined by magnetization or XPS analyses. It should be noted that the value of the concentration of Fe^{2+} obtained by Mössbauer technique is affected by the observed weak signal and its broad full width at half maximum. The Fe-germanate glasses are being analyzed by Mössbauer and neutron techniques. The results of the analyses will be presented elsewhere. The downward curvature seen in χ^{-1} versus T graph for the silicate glass sample can be qualitatively explained by Simpson's model [16]. Similar behavior has been seen in iron phosphate and manganese phosphate [4] and in iron borate glasses [5]. The Curie temperature θ_p is found to be negative for the glass and the crystallized samples indicating an antiferromagnetic exchange interaction between Fe-ions in the four samples. This would imply that heat treating the glass does not affect the type of exchange interaction in both the silicate and the germanate samples. The Curie temperature in the both glass samples is smaller in magnitude than their corresponding values in the crystallized samples. This would indicate that the magnetic exchange interaction in the glass sample is weaker than that in the crystalline sample. This might be due to the bond disorder in the glassy state that weakens the magnetic exchange interaction.

Also, θ_p for the germanate glass and glass ceramic are consistently higher than that of the silicates, implying a stronger antiferromagnetic exchange interaction in the Fe-doped germanate samples.

The low temperature inverse magnetic susceptibility data of the crystallized germanate sample showed gradual downward deviation from linear behavior below 25 K. The downward curvature of the inverse susceptibility is reminiscent of ferrimagnetism in which unequivalent spins Fe^{2+} and Fe^{3+} are arranged antiferromagnetically. In the case of the crystallized silicate sample the inverse magnetic susceptibility data curves upward reflecting antiferromagnetic behavior. This is qualitatively reflected in the values of the effective magnetic moment (μ_{eff}), where μ_{eff} in the germanate is much larger than μ_{eff} in the silicate. The effective magnetic moments of iron ions, calculated from the high temperature slope of the inverse

magnetic susceptibility versus temperature are listed in Table 1.

It is also noted that the theoretical values of the magnetic moment of isolated Fe^{2+} and Fe^{3+} ions are 5.4 and 5.9 μ_B , respectively, [17]. The calculated values for the glass are higher than that of the crystallized sample, however, they are all between the above two theoretical values, except for the crystallized germanate sample.

The changes in γ_m with temperature are shown in Figs. 2(a) and (b) for the glass and the crystallized samples, respectively. The coefficient is negative revealing antiferromagnetic exchange interaction present in the four samples investigated. The absolute value of the coefficient γ_m (at $T > 30$ K) for Fe-germanate glass is about 3 times the value of the Fe-silicate glass. The crystallized samples showed drastic enhancement both in the magnitude and in the overall behavior of γ_m . Moreover, the value of $|\gamma_m|$ in the crystallized silicate has increased by 3-fold, while in the crystallized germanate, it showed an order of magnitude higher than the value for the glass sample. The position of the peak (Figs. 2(a) and (b)) is shifted to a lower temperature in the crystallized germanate. The data for the crystallized silicate sample showed a downward turn behavior, while the glass sample showed an upward curvature. The magnetization difference between the Fe-silicate and the Fe-germanate bulk glasses and their glass ceramics counterparts, might be partly due to fine precipitates commonly seen in crystalline or glass ceramics rich in Fe-ions.

5. Conclusion

We have produced crystalline samples (glass ceramic) by heat-treating two glass samples having the composition $(0.65)\text{SiO}_2-(0.30)\text{Na}_2\text{O}-(0.05)\text{Fe}_2\text{O}_3$ and $(0.65)\text{GeO}_2-(0.30)\text{Na}_2\text{O}-(0.05)\text{Fe}_2\text{O}_3$. The interaction in all samples is antiferromagnetic, since θ_p is negative, and stronger in the crystalline samples, with smaller μ_B and larger θ_p . Heat treatment at the corresponding crystallizing temperatures of both glass samples affected the structure of the materials and the local environment surrounding the magnetic ions. The crystal-

lized samples showed drastic enhancement in the magnitude and in the overall behavior of γ_m . The crystallized silicate absolute value has increased by 3-fold, while the crystallized germanate showed an order of magnitude increase. Moreover, the position of the peak is shifted to a lower temperature in the crystallized germanate. The crystallized silicates showed a down turn behavior, while the glass sample showed an upward curvature.

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