Magnetic studies of TeO$_2$ - Fe$_2$O$_3$ glass systems obtained by the sol-gel method

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Abstract. Glass of the xFe$_2$O$_3$/(1-x)TeO$_2$ systems with x = 0.03-0.40 were obtained by sol-gel method and studied by magnetic susceptibility measurements. The temperature dependence of the reciprocal magnetic susceptibility follows a Curie law till 10 mol% Fe$_2$O$_3$ and over this concentration follows a Curie-Weiss law with the negative paramagnetic Curie temperature. The main result coming out from this behaviour is: at concentrations lower than x = 10 mol% Fe$_2$O$_3$ iron ions are isolated or participate at dipolar interactions and at concentrations larger than 10 mol% Fe$_2$O$_3$ a higher part of iron ions participates at superexchange magnetic interactions.

1. Introduction

Glasses are materials that have an unlimited theoretical variety of compositions. This is the reason why their properties are very different, fact that leads to a large area of applications of glasses and these applications are opened at new concepts.

During recent years, there has been increasing interest in the synthesis, structure and properties of heavy metal oxide glasses containing TeO$_2$, due to their high refractive index (n), n ≈ 2, high IR transparency, high non-linear third order optical susceptibility (50 times higher than the one of SiO$_2$ systems) [1-3].

The processing route mainly adopted for producing tellurite glasses is a melting and quenching technique, which is difficult to produce homogeneous multicomponent tellurite glasses due to their relatively high volatility, limited stability and ready contamination by crucibles. Sol-gel process is an attractive alternative to overcome these drawbacks [4].

The sol-gel method is a particularly attractive way of synthesizing these materials, since it offers a possibility of control over the microstructure and composition of the host matrix and the opportunity to prepare homogenous glasses with large heavy metals ions concentrations [5].

The study of the properties of tellurite glasses with iron ions represents an important thing due to the possibility of those existing in the valence state Fe$^{2+}$ and Fe$^{3+}$ [6], which determinates the magnetic properties of interest due to the antiferromagnetic behaviour.

In this present work we proposed to prepare and to study magnetic behaviour of iron ions in the tellurite glass systems obtained by the sol-gel method.
2. Experimental
A tellurite glass systems containing iron oxide was prepared by using the sol-gel method. The samples were obtained in the system: tellurium tetraethoxide /acetic acid /ethanol /water /iron nitrate. Tellurium tetraethoxide (85% Alfa Aesar) and iron nitrate (99.9% Alfa Aesar) were used as precursors. For the precursors reactivity control acetic acid were used.

Samples with the xFe$_2$O$_3$(1-x)TeO$_2$ composition (where x = 0.03, 0.05, 0.10, 0.20, 0.30, 0.40) were obtained.

In order to perform the magnetic susceptibility measurements, powder samples were pressed at a pressure of 10 atm. Pieces detached from these pressed samples were weighted and were used for magnetic measurements. Magnetic susceptibility measurements were performed in the 80-300 K temperature range using a Weiss type magnetic balance.

3. Results and discussion
The temperature dependence of the inverse magnetic susceptibility, $\chi^{-1}$, is presented in figure 1 for the studied tellurite glass systems containing iron ions. The collapse of data to straight lines indicates that the susceptibility per mole of magnetic ion follows a Curie-Weiss type behaviour [7]:

$$\chi^{-1} = \frac{T - \theta_p}{C}$$

where $\chi$ represents the molar magnetic susceptibility, $T$, the temperature, $C$ is the molar Curie constant and $\theta_p$ is the paramagnetic Curie temperature. By fitting the experimental data according to equation (1), we determined the values of $C$ and $\theta_p$.

The paramagnetic Curie temperature, $\theta_p$, is a rough indicator of magnetic interaction between iron ions.

![Figure 1](image)

**Figure 1.** The temperature dependence of $\chi^{-1}$ for xFe$_2$O$_3$(1-x)TeO$_2$ glasses with (a) 3 ≤ x ≤ 10 mol% and (b) 20 ≤ x ≤ 40 mol%.

The temperature dependence of the reciprocal magnetic susceptibility follows a Curie law till x ≤ 10 mol% Fe$_2$O$_3$ and over this concentration follows a Curie-Weiss law with the negative paramagnetic Curie temperature. This fact suggest that at concentrations lower than x = 10 mol% Fe$_2$O$_3$ iron ions are isolated or participates at dipolar interactions and at concentrations x > 10 mol% Fe$_2$O$_3$ a higher part of iron ions participates at superexchange magnetic interactions. The nature of these superexchange magnetic interactions is antiferromagnetic because $\theta_p$ has a negative value.

Also, we have calculated Curie molar constants, the magnetic moment and molar fractions of Fe$^{3+}$(x$_1$) and Fe$^{2+}$(x$_2$) ions in studied samples (table 1).
Table 1. Curie molar constants, magnetic moment and molar fractions of Fe$^{3+}$($x_1$) and Fe$^{2+}$($x_2$) ions.

| $x$ [mol% Fe$_2$O$_3$] | $C_M \times 10^2$ [emu/mol] | $\mu_{\text{eff}}$ [µB] | $x_1$ [mol% Fe$_{2}\text{O}_3$] | $x_2$ [mol% Fe$_{2}\text{O}_3$] |
|-----------------------|-----------------------------|-----------------|-----------------|-----------------|
| 3                     | 21.85                       | 5.50            | 1.7             | 1.2             |
| 5                     | 37.10                       | 5.42            | 2.4             | 2.5             |
| 10                    | 73.26                       | 5.39            | 4.3             | 5.6             |
| 20                    | 143.87                      | 5.35            | 8.1             | 11.7            |
| 30                    | 215.61                      | 5.35            | 14.0            | 19.0            |
| 40                    | 285.30                      | 5.33            | 15.2            | 24.8            |

We observe that the magnetic moment decrease from 5.50 µ$_B$ at 3 mol% Fe$_2$O$_3$ to 5.33 µ$_B$ for 40 mol% Fe$_2$O$_3$. Knowing that the magnetic moments of Fe$^{3+}$ and Fe$^{2+}$ ions in free state are $\mu_{\text{Fe}^{3+}} = 5.92$ µ$_B$ and $\mu_{\text{Fe}^{2+}} = 4.90$ µ$_B$ and giving the fact that in many paramagnetic salt [8] and in oxide glasses [9] the magnetic moments of Fe$^{3+}$ and Fe$^{2+}$ ions are equal to the ones in free state, we assume that in all the studied samples these iron ions coexist [10-12].

The data presented in table 1 permitted the calculation of the amount of the iron ions in their 3+ ($x_1$) and 2+ ($x_2$) valence state. Given that in both valence states iron ion is magnetic, we calculated the amount of Fe$^{3+}$ and Fe$^{2+}$ ions by solving the equations:

$$
\begin{align*}
&x_1\mu_{\text{exp}}^2 = x_1\mu_{\text{Fe}^{3+}}^2 + x_2\mu_{\text{Fe}^{2+}}^2, \\
&x = x_1 + x_2
\end{align*}
$$

Thus, in the studied samples, iron ions are found in both valence states and at concentrations lower than $x = 10$ mol% iron ions are isolated or participate at dipolar interactions and at concentrations $x > 10$ mol% Fe$_2$O$_3$ a higher part of iron ions participates at superexchange magnetic interactions. The nature of these superexchange magnetic interactions is antiferromagnetic.

4. Conclusion

Tellurite glass systems doped with iron ions have been prepared by the sol-gel method and magnetic behaviour of these systems were studied. The temperature dependence of the reciprocal magnetic susceptibility follows a Curie law for low concentrations of magnetic ions ($x \leq 10$ mol % Fe$_2$O$_3$), iron ions are isolated or participate at dipolar interactions, respectively a Curie- Weiss law for high concentrations of magnetic iron ions ($x > 10$ mol % Fe$_2$O$_3$), a part of iron ions participates at superexchange magnetic interactions for the xFe$_2$O$_3$(1-x)TeO$_2$ (where $x = 0.03\div0.40$) system.

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