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Magnetic behaviour of europium ions in some tellurite glasses obtained by the sol-gel method

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Abstract. In the paper, tellurite glasses doped with europium ions have been prepared by the sol-gel method and were studied by magnetic susceptibility measurements. The authors found that $\text{xEu}_2\text{O}_3(1-x)\text{TeO}_2$ system shows a Curie-Weiss type magnetic behaviour. The magnetic europium ions are present in the host glass matrix in both their $2+$ and $3+$ valence states. The magnetic interactions between the europium ions are antiferromagnetic.

1. Introduction

Tellurite glass systems containing different rare earth oxides have attracted a great attention in the last years because of their interesting properties such as low glass transition temperature, high refractive index (in the range from 1.85 to 2.2), high transmittance from ultraviolet to near infrared, high non-linear third order optical susceptibility (50 times higher than the one of SiO$_2$ systems) [1-3]. Due to these properties tellurium glasses are ideal materials for applications in many important fields like telecommunication technology, laser and optical fibre technology, optical device technology, etc. [4, 5].

The tellurium oxide (TeO$_2$) is a conditional glass former. The main structural units present in the structure of the tellurium glasses are the TeO$_4$ trigonal bipyramids, or if we take into account the $5s^2$ lone pair of tellurium atoms (E), a distorted TeO$_4$E bipyramid. In this bipyramid, the two equatorial oxygen atoms are separated from the tellurium atoms by distances shorter than the sum of the covalent radii of oxygen (0.73 Å) and tellurium atoms (1.35 Å), and the two axial oxygen atoms by distances longer than value (figure 1) [6, 7].

![Figure 1. Model for the TeO$_4$ structural unit.](image-url)
The type and the concentration of network modifying ions modifies the structure of the host glass matrix [8].

The traditional processing route adopted for producing tellurite glasses consists in mixing and melting appropriate amounts of the component oxides followed by the quenching of the melts. This technique presents some important disadvantages such as the difficulty to produce homogeneous multicomponent tellurite glasses due to their relatively high volatility, limited stability and contamination by crucibles. These disadvantages impair the optical properties of the tellurite glasses. The intensification of the investigation of different properties of the tellurite glass systems containing different metal ions (mainly rare earth or transitional metal ions) started in the last years, due to the development of sol-gel process. The sol-gel method is an attractive alternative to offer advantages of a better control of physical and chemical properties of the target materials [9].

The goal of this paper was to study the magnetic behaviour of europium ions in the tellurite glass systems obtained by the sol-gel method.

2. Experimental

A tellurite glass systems containing europium oxide was prepared by using the sol-gel method. The samples were obtained in the system: tellurium tetraethoxide (Te(OEt)₄) /acetic acid (CH₃COOH) /ethanol (EtOH) /water (H₂O) /europium nitrate (Eu(NO₃)₃). Tellurium tetraethoxide (85% Alfa Aesar) and Eu(NO₃)₃ (99.9% Alfa Aesar) were used as precursors. For the precursors reactivity control acetic acid were used.

Samples with the xEu₂O₃(1−x)TeO₂ composition (where x = 0.07, 0.11, 0.15) 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, $\chi^{-1}$, for the studied tellurite glass system containing europium ions is presented in figure 2. The data collapse to straight lines indicating that the magnetic susceptibility follows a Curie-Weiss type behaviour:

$$\chi^{-1} = (T - \theta_p) / C$$

(1)

where $C$ is the Curie constant and $\theta_p$ is the paramagnetic Curie temperature.

![Figure 2. Temperature dependence of $\chi^{-1}$ for xEu₂O₃(1−x)TeO₂ glasses.](image)

The temperature dependence of the reciprocal magnetic susceptibility follows a Curie-Weiss law with negative paramagnetic Curie temperatures. Because the obtained paramagnetic Curie temperatures, $\theta_p$, present negative values, the nature of these superexchange magnetic interactions is
presumed to be antiferomagnetic. The paramagnetic Curie temperatures, the molar Curie constants, the magnetic moment per europium ion and the Eu\(^{2+}/\text{Eu}^{3+}\) ions fractions are presented in table 1.

**Table 1.** Paramagnetic Curie temperature, molar Curie constants, magnetic moment per europium ion and the Eu\(^{2+}/\text{Eu}^{3+}\) ratio for xEu\(_2\)O\(_3\)\((1-x)\text{TeO}_2\) glasses.

| x \([\text{mol\% Eu}_2\text{O}_3]\) | \(-\theta_p\) [K] | \(C_M\) [emu/mol] | \(\mu_{\text{eff}}\) [\(\mu_B\)/atom] | Eu\(^{2+}/\text{Eu}^{3+}\) |
|---|---|---|---|---|
| 7 | 40 | 0.17 | 3.2 | 0.11 |
| 11 | 160 | 0.37 | 3.6 | 0.14 |
| 15 | 165 | 0.58 | 3.9 | 0.19 |

In general, the europium ions appear in oxide glasses in two valence states, namely Eu\(^{2+}\) and Eu\(^{3+}\). The magnetic moments of the free Eu\(^{3+}\) and E\(^{2+}\) ions are \(\mu_{\text{Eu}^{3+}} = 3.4\ \mu_B\) and respectively, \(\mu_{\text{Eu}^{2+}} = 7\ \mu_B\) [10]. Consequently, the magnetic properties of the samples studied can be explained by the presence of both Eu\(^{3+}\) and Eu\(^{2+}\) ions, as well as by the occurrence of superexchange magnetic interactions between the europium ions. Due to these interactions the occurrence of Eu\(^{3+}\)–Eu\(^{2+}\), Eu\(^{3+}\)–Eu\(^{3+}\) and respectively, Eu\(^{3+}\)–Eu\(^{2+}\) pairs is possible.

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

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

(2)

We note that the \(x_2/x_1\) ratio increases with increasing the europium ion content of the samples.

Figure 3 shows the variation of the paramagnetic Curie temperatures with respect to the europium oxide content of the samples.

**Figure 3.** The variation of the paramagnetic Curie temperatures with respect to the europium oxide content of xEu\(_2\)O\(_3\)\((1-x)\text{TeO}_2\) glasses.

The increase of \(\theta_p\) value shows the intensification of the superexchange magnetic interactions between europium ions with the increase of their amount. A certain reduction of the \(\theta_p\) value at high concentrations of the content of europium ions can be due to interactions between pairs of europium ions with different valences (Eu\(^{3+}\)–Eu\(^{2+}\)) which are weaker than the interactions between the same valent ions (Eu\(^{2+}\)–Eu\(^{2+}\) or Eu\(^{3+}\)–Eu\(^{3+}\)).

Thus, in the studied samples, europium ions are found in both valence states, they interacting with each other through a superexchange mechanism. These interactions are of antiferomagnetic nature. Magnetic behaviour of the studied samples is probably mictomagnetic [11], the europium ions being present as both isolated and coupled species.
4. Conclusion
Tellurite glasses doped with europium ions have been prepared by the sol-gel method and were studied by magnetic susceptibility measurements. The obtained data for the $x$Eu$_2$O$_3$$(1-x)$TeO$_2$ (where $x = 0.07 \div 0.15$) system show a Curie-Weiss type magnetic behaviour. The magnetic europium ions are present in the host glass matrix in both their 2+ and 3+ valence states. The magnetic interactions between the europium ions are antiferomagnetic.

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