Available online at www.sciencedirect.com
ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 2363–2366
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

EPR and magnetic susceptibility studies of B_2O_3–Bi_2O_3–Gd_2O_3 glasses

I. Ardelean *, Lidia Griguta

Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania

Received 25 August 2006; received in revised form 15 March 2007

Abstract

Glasses of the $xGd_2O_3 \cdot (100 - x)[B_2O_3 \cdot Bi_2O_3]$ system with $0.5 \leqslant x \leqslant 10$ mol% were studied by electron paramagnetic resonance (EPR) and magnetic susceptibility measurements. Data obtained show that for low gadolinium oxide contents of the samples ($x \leqslant 3$ mol%) the Gd^{3+} ions are randomly distributed in the host glass matrix and are present as isolated and dipole–dipole coupled species. For higher gadolinium oxide contents of the samples ($x > 3$ mol%) the Gd^{3+} ions appear as both isolated and antiferromagnetically coupled species. The EPR spectra of the glasses reveal resonance sites with an unexpected high crystalline field in addition to the 'U' spectrum, typical for Gd^{3+} ions in disordered systems. This absorption line is due to Gd^{3+} ions that replace Bi^{3+} ions from the host glass matrix and could play the network unconventional former role in the studied glasses.

PACS: 61.43.Fs; 75.30.Hx; 75.50.Kj; 76.30.Kg

Keywords: Borates; Rare-earths in glasses; Electron spin resonance

1. Introduction

Glasses containing gadolinium ions are the subject of a great deal of interest due to their important optical and magnetic properties for technical applications. On the other hand, glasses that contain unconventional network formers like Bi_2O_3 so-called heavy metal oxide glasses, are intensively studied because of their special properties such as high refractive index, high density, high non-linear optical susceptibility which makes them suitable for optical uses, environmental guide-lines, and also for possible use in scintillation detectors for high energy physics [1–4].

A limited number of studies were devoted to the analysis of the rare-earth coordination structure by EPR measurements. In the last decade, oxide glasses such as borate [5,6], bismuthate [7,8], boro-tellurite [9], germanate, phosphate [10], and other oxide glasses [11] doped with gadolinium ions were studied by means of EPR and magnetic susceptibility measurements.

In order to extend the available information concerning the interesting class of the $B_2O_3 \cdot Bi_2O_3$ glasses containing gadolinium ions, in this work we investigated the $xGd_2O_3 \cdot (100 - x)[B_2O_3 \cdot Bi_2O_3]$ vitreous system with $0.5 \leqslant x \leqslant 10$ mol% by EPR and magnetic susceptibility measurements.

2. Experimental procedures

Glasses of the $xGd_2O_3 \cdot (100 - x)[B_2O_3 \cdot Bi_2O_3]$ system were prepared using pure reagent grade chemicals, H_3BO_3, $Bi(NO_3)_3 \cdot 5H_2O$ and Gd_2O_3 in suitable proportions. The mixtures were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace. The mixtures were introduced directly at 1200 °C in the pre-heated furnace. After 5 min the molten materials were quenched to room temperature by pouring on the stainless-steel plates.

EPR measurements were performed at room temperature using ADANI Portable EPR PS 8400-type spectrometer, in X frequency band (9.4 GHz) and a field modulation of 100 KHz. The microwave power used was 5 mW.

* Corresponding author. Fax: +40 264 591906.
E-mail address: arde@phys.ubbcluj.ro (I. Ardelean).

0022-3093/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2007.04.021

To avoid the alteration of the glass structure due to the ambient condition, samples of equal quantities were enclosed immediately after preparation in the tubular holders of the same caliber.

Magnetic susceptibility measurements were performed on a Faraday type balance in the 80–300 K temperature range. The sensitivity of the equipment was 10^{-7} emu/g.

3. Results

The EPR spectra recorded for the $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses are shown in Fig. 1. These spectra are due to the presence of Gd^{3+} ions in the $\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3$ host matrix and are relatively close to those previously reported for other oxide glasses containing gadolinium ions [5–14]. For low gadolinium concentrations in glass matrix the EPR spectra is characterized by prominent features with effective g_{eff} values of ≈6, ≈4.8, ≈2.87 and ≈2 and at higher concentration being superimposed on a broad resonance line shape that encompasses the prominent $g_{\text{eff}} \approx 2$ feature.

The dependence of the reciprocal magnetic susceptibility as a function of temperature for the $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses is presented in Fig. 2. The composition dependence of the paramagnetic Curie temperature (Θ_p) is shown in Fig. 3. The paramagnetic Curie temperature is a rough indicator of the magnetic interactions between Gd^{3+} ions. The Θ_p values were zero for the samples with $x \leqslant 3$ mol% (Curie type magnetic behavior) and small and negative ($\Theta_p \leqslant 11$ K) for those with $x > 3$ mol% (Curie–Weiss type magnetic behavior).

4. Discussion

The EPR spectra, illustrated in Fig. 1, show resonance signals at $g_{\text{eff}} \approx 6$, $g_{\text{eff}} \approx 2.87$ and $g_{\text{eff}} \approx 2$ which is a characteristic of the so-called 'U' spectrum of Gd^{3+} ions in disordered materials [12–15]. EPR spectra of rare-earth ions in glasses are generally very anisotropic and sensitive to variations in ligand field from site to site [15]. Most of the authors consider the mentioned absorption features ($g_{\text{eff}} \approx 6$, $g_{\text{eff}} \approx 2.87$, $g_{\text{eff}} \approx 2$) to be generated by Gd^{3+} ions disposed in cubic, octahedral or tetraehedral sites with moderate distortions. In these sites the gadolinium ions experience a relatively weak crystalline field and they are characterised by a coordination number higher than six [5–9,12–14]. The difference between Gd^{3+} EPR spectra of $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses and the 'U' spectrum is the occurence of an asymmetric absorption line with $g_{\text{eff}} \approx 4.8$. This line indicates a relatively strong crystal field with an orthorhombic symmetry and is associated with gadolinium ions with a coordination number lower than six. This location for Gd^{3+} is unusual being known

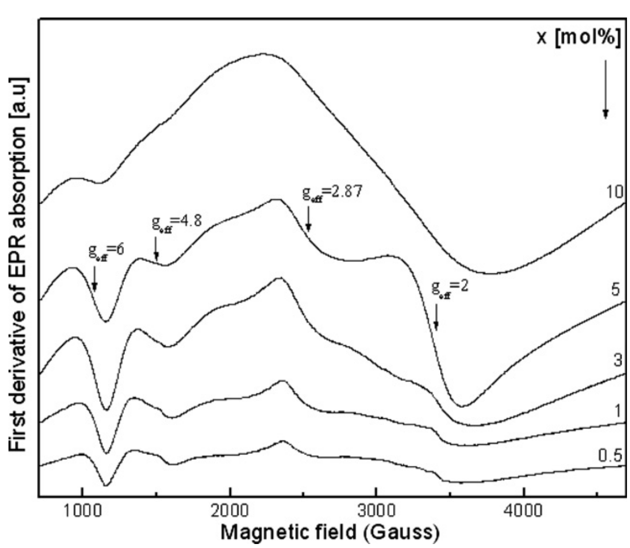

Fig. 1. EPR spectra of $x\text{Gd}_2\text{O}_3 \cdot (100 - x) \cdot [\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses.

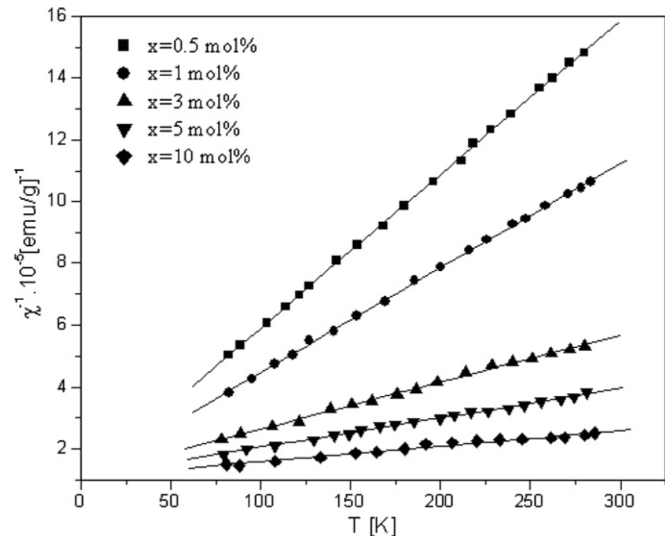

Fig. 2. The temperature dependence of the reciprocal magnetic susceptibility for $x\text{Gd}_2\text{O}_3 \cdot (100 - x) \cdot [\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses.

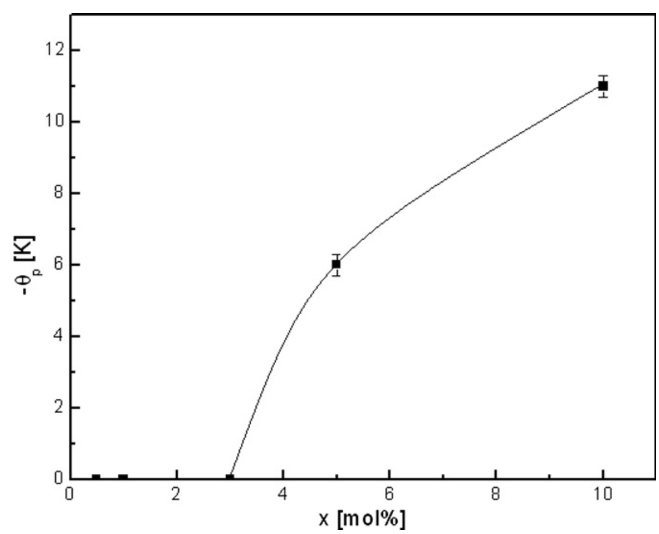

Fig. 3. The composition dependence of the paramagnetic Curie temperature. The solid line is a guide for the eye.