Journal of Non-Crystalline Solids 356 (2010) 2389–2392

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Preparation and magnetic properties of amorphous $EuTiO_3$ thin films

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ARTICLE INFO

Article history:
Received 15 October 2009
Received in revised form 7 April 2010
Available online 26 June 2010

Keywords:
Amorphous oxides;
Thin film;
Ferromagnetic interaction;
Conversion-electron Mössbauer spectroscopy

ABSTRACT

Amorphous $EuTiO_3$ thin films have been prepared by a pulsed laser deposition method, and their structural and magnetic properties have been investigated. High-resolution transmission electron microscope image and selected-area electron diffraction pattern as well as X-ray diffraction pattern confirm the amorphous nature of the thin films. ^{151}Eu conversion-electron Mössbauer effect measurements show that almost all of the europium ions are present as Eu^{2+} in the thin films. The amorphous $EuTiO_3$ thin film exhibits a positive Weiss temperature of 8.7 K, indicating predominant ferromagnetic interactions among Eu^{2+} ions. The signature of a ferromagnetic-like transition is observed at around 5.5 K.

1. Introduction

Magnetic properties of oxide and fluoride glasses containing transition-metal and/or rare-earth ions are interesting from a point of view of magnetism of solids where magnetic moments are randomly aligned. Spin glass (SG)-like magnetic transition of oxide and fluoride glasses has been extensively investigated so far [1–6]. In most insulating oxide and fluoride glasses, short-range antiferromagnetic (AFM) superexchange interactions via anions are dominant, as demonstrated by the negative values of Weiss temperature (θ_W) [4–6]. The random distribution of magnetic ions, as well as the prevailing AFM interactions among magnetic ions, causes geometrical frustration in the alignment of magnetic moments at low temperatures, eventually leading to the SG transition. On the other hand, there are only a few reports concerning amorphous insulating compounds with positive values of θ_W wherein ferromagnetic (FM) interactions are predominant [7,8]. Shoenes et al. [8] reported that a europium silicate glass with a composition of $Eu_{0.14}Si_{0.31}O_{0.55}$, in which Eu^{2+} ions accounted for 27% in cation ratio, was a paramagnet down to 1.5 K and had a positive θ_W of 1 K in contrast to most amorphous oxides, although no explanation for the origin of the positive θ_W was provided. Despite of the fascinating fact, the magnetic properties of Eu^{2+}-containing amorphous oxides have been rarely investigated since then. Further studies on amorphous oxide systems with high concentration of Eu^{2+} are thus necessary to understand the magnetic interactions.

Recently, we prepared borate, silicate, and borosilicate glasses with Eu^{2+} concentration of 10 to 45% (in cation ratio) by using a conventional melt-quenching method, and found that all the glasses thus obtained have positive θ_W values [9]. The result indicates that the FM interactions are predominant among Eu^{2+} ions in any oxide glass containing high concentration of Eu^{2+} ions. Besides, we have observed a para-ferromagnetic transition at around 2.2 K for oxide glasses containing 45% Eu^{2+}; it is the first report of insulating amorphous oxide showing a ferromagnetic transition. In this work, we focus on a binary europium titanate with the Eu^{2+} concentration of 50% in cation ratio, i.e., $EuTiO_3$. It is difficult to vitrify this compound by the conventional melt-quenching technique, but in the course of the research on thin film growth of crystalline $EuTiO_3$ using a pulsed laser deposition (PLD) [10,11], we accidentally found that the amorphization of $EuTiO_3$ could be achieved in the form of thin film through rapid cooling of the vapor phases.

In this paper, we particularly report on the structural and magnetic properties of the $EuTiO_3$ thin films prepared by PLD. The amorphous nature of the resultant thin film is confirmed by selected-area electron diffraction (SAED) analysis combined with high-resolution transmission electron microscope (HRTEM) observation as well as X-ray diffraction (XRD) analysis. The amorphous $EuTiO_3$ thin film exhibits a positive value of $\theta_W = +8.7$ K, which is the highest among the Eu^{2+}-containing amorphous oxides reported so far. We have also found the signature of a ferromagnetic-like transition at around 5.5 K for the amorphous $EuTiO_3$ thin films.

2. Experimental

Amorphous $EuTiO_3$ thin films were deposited on silica glass substrates by the PLD method. Polycrystalline $EuTiO_3$ was prepared by the solid-state reaction at 1200 °C under a flowing gas of 95 vol.% Ar + 5 vol.% H_2 and used as a target for PLD. The silica glass substrate and high-density target were set in a vacuum chamber with a base pressure of 10^{-6} Pa. A KrF excimer laser operating at a wavelength of 248 nm, a repetition frequency of 10 Hz, and an energy of 180 mJ was focused on the target. The film deposition was performed at room

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doi:10.1016/j.jnoncrysol.2010.05.014

temperature under the base pressure (~10^{-6} Pa). The thickness of the resultant thin film was estimated to be about 160 nm by a surface profiler (Alpha-Step IQ, KLA-Tencor). The molar ratio of Eu to Ti in the thin film was determined to be 1:1.01 by Rutherford backscattering measurements and subsequent analysis with the simulation program SIMNRA.

XRD analysis with Cu Kα radiation (Rint2500, Rigaku) and SAED analysis combined with HRTEM observation (JEM-2100F, JEOL) were carried out to identify the amorphous nature of the resultant films. For the HRTEM observation, the cross-sectional specimen was prepared by an Ar ion milling at 5 kV using a liquid-nitrogen-cooling system. In order to examine the valence state and local environment of Eu ions, ^{151}Eu conversion-electron Mössbauer (CEM) spectroscopy was performed at room temperature using $^{151}Sm_2O_3$ with activity of 1.85 GBq as a 21.5 keV γ-ray source. The velocity calibration was done with the magnetic hyperfine spectrum of α-Fe foil obtained using ^{57}Co-doped Rh as a 14.4 keV γ-ray source. Utilizing the CEM spectrum of EuS with rock-salt structure, the full width at half maximum (FWHM) of Eu^{2+} absorption peak in cubic symmetry was estimated to be about 2.5 mm/s in our experimental setup, which is comparable to the reported value [12]. The magnetic measurements were carried out with a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL). The magnetic susceptibility χ was measured as a function of temperature T (2 K<T<300 K) under an external magnetic filed H of 100 Oe, while the magnetization M as a function of H (−5 T<H<5 T) was obtained at 2 K.

3. Results and discussion

3.1. Structural characterization: XRD analysis, TEM observation, and CEM spectroscopy

Fig. 1(a) shows the XRD pattern for the $EuTiO_3$ thin film prepared by the PLD method. No sharp diffraction peaks ascribed to crystalline phases are observed, indicating the amorphous nature of the thin film. A broad peak around $2\theta = 20°$ and a shoulder around $2\theta = 30°$ arise from the silica glass substrate and thin film, respectively. The amorphous nature was further corroborated by HRTEM image and SAED pattern, as depicted in Fig. 1(b).

Fig. 2 displays the room-temperature ^{151}Eu CEM spectrum for the amorphous $EuTiO_3$ thin film. The spectrum mainly consists of two peaks with isomer shifts of about −13 and 0.5 mm/s relative to EuF_3, which are assigned to the absorptions due to Eu^{2+} and Eu^{3+}, respectively [13]. The absorption is much more intense for Eu^{2+} than for Eu^{3+}, and the absorption area of the former is about 97% of the total absorption area. Given that the Debye temperature (θ_D) for Eu^{2+} is lower than that for Eu^{3+} (e.g., $\theta_D = 145$ K and 261 K for Eu^{2+} and Eu^{3+} in a fluorozirconate glass, respectively [14]), it is expected that at least 97% of Eu ions are present as the divalent state in the amorphous thin film. A close look at Fig. 2 reveals that the Eu^{2+} absorption band is split due to the quadrupole interactions between the electric field gradient and the electric quadrupole moment of ^{151}Eu nucleus [13]. Therefore, we have analyzed the Eu^{2+} absorption band with the method developed by Shenoy and Dunlap [15]. The γ-ray resonance energy between excited and ground states is given by

$$R(I_Z^*, I_Z) = eV_{ZZ}\left[Q_e P(I^*, I_Z^*) - Q_g P(I, I_Z)\right] + \delta, \quad (1)$$

where e is the elementary charge, V_{zz} is the electric field gradient in the direction z, Q_e and Q_g are the excited- and ground-state nuclear quadrupole moments, respectively, I^* and I are the excited- and ground-state nuclear spins, respectively, I_z^* and I_z are the z projections of excited- and ground-state nuclear spins, respectively, and δ is the isomer shift. $P(I^*, I_z^*)$ and $P(I, I_z)$ are written as

$$P(I, I_Z) = \sum_{N=0}^{4} a_N(I, I_Z)\eta^N, \quad (2)$$

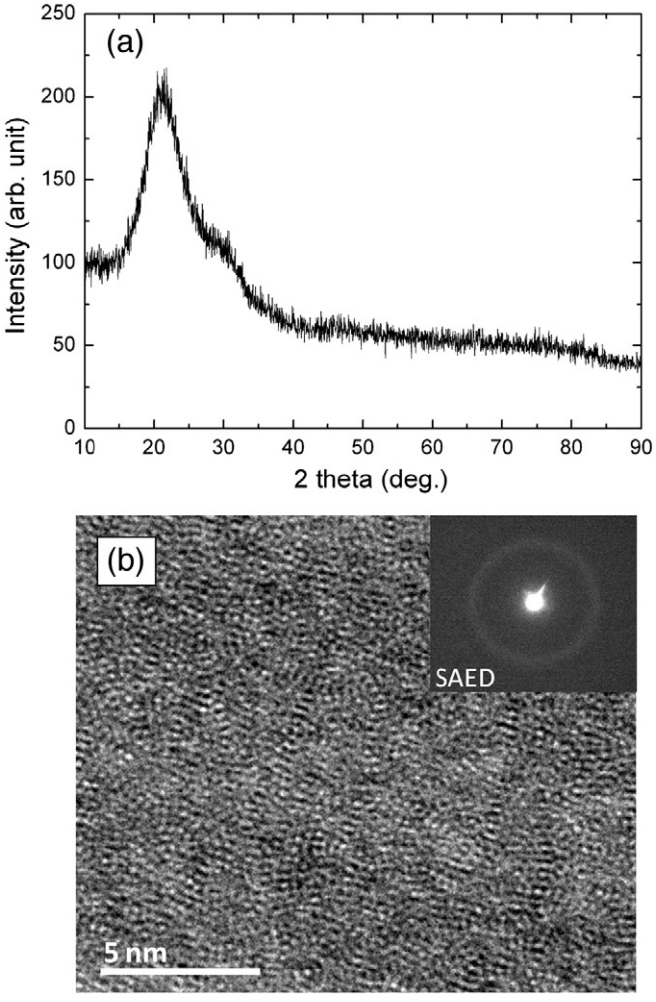

Fig. 1. (a) XRD pattern of amorphous $EuTiO_3$ thin film prepared by the PLD method. (b) HRTEM observation of the amorphous $EuTiO_3$ thin film. The inset shows the SAED pattern.

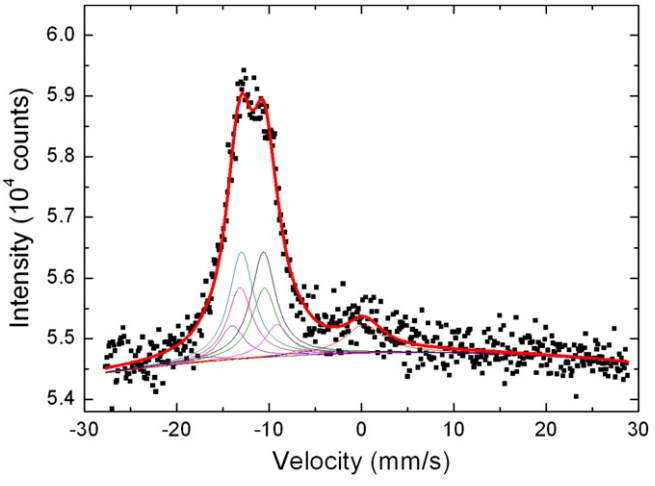

Fig. 2. ^{151}Eu CEM spectrum measured at room temperature for the amorphous $EuTiO_3$ thin film. The closed squares represent the experimental data, and the solid line is the fit of theoretical curve using Eqs. (1)–(3). The component lines corresponding to the 12 transitions are also shown for the Eu^{2+} absorption peak at around −12 mm/s.