Short Communication

Microstructure and magnetic character of terbium borate glass

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Microstructure and magnetic character of 30 $Tb_2O_3 \cdot 70\ B_2O_3$ glass have been examined by means of high-resolution transmission electron microscopy and magnetization measurements. Although no trace of crystalline phases was observed in the electron diffraction pattern, the transmission electron micrograph revealed that there exist clusters, the size of which is about 1 nm, in the present glass. The magnetization measurements showed that this glass is paramagnetic at room temperature. However, the magnetization is high enough for the glass to adhere to a permanent magnet in the Nd–Fe–B system at room temperature.

Mikrostruktur und magnetisches Verhalten von Terbiumboratgläsern

Mikrostruktur und magnetisches Verhalten eines 30 $Tb_2O_3 \cdot 70\ B_2O_3$-Glases wurden mit Hilfe hochauflösender Elektronentransmissionsmikroskopie und Magnetisierungsmessungen untersucht. Obwohl kein Anzeichen von kristallinen Phasen in dem Elektronenbeugungsbild beobachtet wird, zeigt das Gefügebild der Durchstrahlungselektronenmikroskopie, daß in dem untersuchten Glas Nester existieren, deren Größe etwa 1 nm ist. Die Magnetisierungsmessungen zeigten, daß dieses Glas bei Raumtemperatur paramagnetisch ist. Die Magnetisierung ist jedoch für das Glas hoch genug, daß es bei Raumtemperatur an dem Dauermagneten des Systems Nd–Fe–B haften bleibt.

1. Introduction

Since transparent materials with high magnetization are expected to exhibit Faraday and Volgt effects to a large extent, they can be used as optical isolators or switching devices utilizing optical bistability. One candidate of such materials is an inorganic glass containing a large amount of rare-earth ions. The Faraday effect has been observed for rare-earth borate [1], phosphate [2], silicate [3] and other multicomponent glasses [4 to 7]. Although these materials are inferior to ferrite single crystals because of their smaller degree of Faraday rotation, they possess superior character since they are transparent in the visible light region. Among the rare-earth borate glasses, terbium borate glass has the largest Faraday rotation angle [1]. In this communication, the microstructure and magnetization of 30 $Tb_2O_3 \cdot 70\ B_2O_3$ glass are studied. It has been found that this glass adheres to a permanent magnet in the Nd–Fe–B system [8] and that the glass contains clusters of about 1 nm.

2. Experimental and results

Glass with 30 $Tb_2O_3 \cdot 70\ B_2O_3$ composition was prepared by using Tb_4O_7 and B_2O_3 as starting materials. They were mixed thoroughly and melted in a platinum crucible at 1450 °C for 1 h in air. The melt was quenched in two ways; it was poured on an iron plate and quenched by being pressed with the other iron plate, or rapidly quenched by falling onto a twin-roller made of stainless steel and rotating at 3000 rpm. The resultant samples were transparent and colorless. The samples were subjected to magnetization measurements and transmission electron microscopic (TEM) observation. The magnetization measurements were performed on the bulk sample at room temperature by using the Faraday method. After the bulk sample was put into a silica tube and held between two electromagnets, the external field was applied up to $1.01 \cdot 10^6$ A/m (12.7 kOe). The transmission electron microscopy was carried out on the glass foil obtained by the twin-roller method. For this measurement, the ultra-high voltage electron microscope of the Research Center, Osaka University, Osaka (Japan) was utilized.

Figure 1 shows the magnetization curve of the 30 $Tb_2O_3 \cdot 70\ B_2O_3$ glass at room temperature. The relation between the magnetization and the external field is linear, indicating that this sample is paramagnetic at room temperature. The susceptibility was determined to be $1.71 \cdot 10^{-6}$ m^3/kg from the slope of the line by using the least squares fitting. The magnetic moment per Tb^{3+} ion is 9.3 in units of Bohr magneton, derived from the susceptibility value by using the Curie-Weiss law:

$$\varkappa = N M^2/[3 \mu_0 k (T-\theta)] \quad (1)$$

where N is the number of Tb^{3+} ion, M is the magnetic moment of Tb^{3+} ion (in Wb m), μ_0 is the magnetic permeability of vacuum (in kg m/C^2) k is the

Received January 22, 1992.

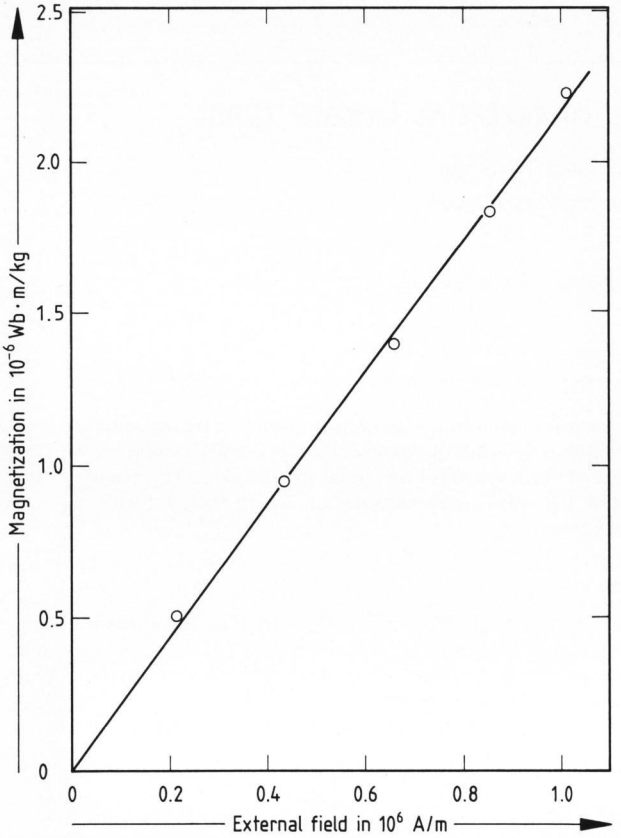

Figure 1. The magnetization curve of $30\,Tb_2O_3 \cdot 70\,B_2O_3$ glass at room temperature.

Boltzmann constant (in J/K), T is the absolute temperature (in K) and with the assumption that θ is negligibly small compared with the room temperature. It is reasonable to assume that θ is much lower than room temperature because the superexchange interaction among rare-earth ions is generally very weak. For example, a very small value of θ was obtained for BaF_2-NaPO_3 glasses bearing a large amount of terbium or dysprosium ions [6]. The value of the magnetic moment obtained experimentally is almost identical with the theoretical one, i.e., 9.72, which is obtained by

$$M = g\,[J\,(J+1)]^{1/2}, \qquad (2)$$

where g is the Lande g factor and J is the total angular momentum. In other words, the superexchange interaction among Tb^{3+} ions is very weak in the present glass. Although this glass is paramagnetic at room temperature, it adheres to a permanent magnet in the Nd–Fe–B system [8] because of relatively high magnetization of this glass as well as very large maximum energy product of the neodymium iron boride permanent magnet used.

The electron diffraction pattern of the $30\,Tb_2O_3 \cdot 70\,B_2O_3$ glass is shown in figure 2. Only the halo pattern is observed, indicating that the sample is judged to be amorphous from the electron

Figure 2. Electron diffraction pattern of the $30\,Tb_2O_3 \cdot 70\,B_2O_3$ glass.

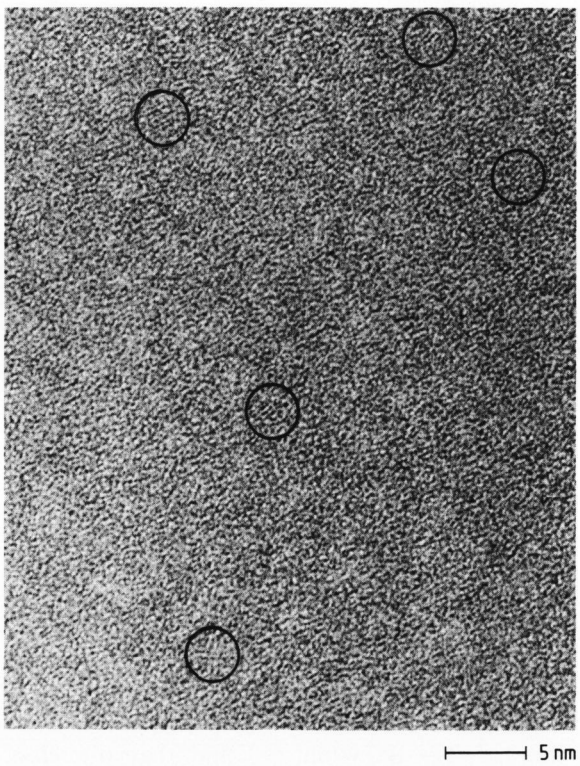

Figure 3. High-resolution electron micrograph of the $30\,Tb_2O_3 \cdot 70\,B_2O_3$ glass.

diffraction photograph. Figure 3 shows an electron micrograph of the $30\,Tb_2O_3 \cdot 70\,B_2O_3$ glass. The magnification is $2.15 \cdot 10^6$ times. The photograph shows that in this glass there exist clusters which are observable as somewhat ordered structure. Some of them are indicated by circles in the photograph. The size of the clusters is about 1 nm. This structure, i.e., the assemblage of clusters of about 1 nm, is very

similar to those revealed in amorphous WO_3 [9] and amorphous silicon [10] by using high-resolution electron microscopy. The composition and the structure of the clusters in the present glass are unclear at present. Further investigation on the structure of the present glass is in progress.

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The authors would like to thank Professor M. Shiga and Dr. H. Wada, Department of Metal Science and Technology, Kyoto University, Kyoto (Japan), for the magnetization measurements and for suggestions on many aspects of the present work.

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