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Effect of Al_2O_3 on phase separation of SiO_2–Nd_2O_3 glasses

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Abstract

The immiscibility boundary and the critical point of SiO_2–Nd_2O_3 system glass were determined as a function of Al_2O_3 addition. The critical temperature of the immiscibility boundary was observed to decrease with the addition of Al_2O_3. Using the regular solution model, the observed decrease of the immiscibility boundary was directly related to the decrease of the concentration fluctuation of Nd_2O_3 in SiO_2. It is concluded that the Al_2O_3 addition to Nd_2O_3 containing silica glass is beneficial in decreasing the concentration quenching effect, deterioration of the optical efficiency due to clustering of rare earth element, because Al_2O_3 addition diminishes the concentration fluctuation of Nd_2O_3 in silica glass.

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Keywords: Aluminosilicates; Silica; Silicates; Phases and equilibria; Fluctuations

1. Introduction

Oxide glasses doped with rare earth (Re) elements have been investigated extensively as they are useful as lasers and optical amplifiers [1,2]. Among various oxide glasses, SiO_2 glass can be a good host for rare earth oxides because of its high transparency, low coefficient of thermal expansion, and excellent chemical durability [3–7]. However, the low solubility of rare earth oxides in SiO_2 causes concentration quenching of fluorescence. For example, in SiO_2–Nd_2O_3 system glass, even at a few hundreds ppm of Nd_2O_3, formation of Nd–O–Nd bonding occurs [8–10] and leads to nonradiative relaxation due to energy transfer between Nd ions [11], resulting in deterioration of the optical efficiency of amplifiers and lasers [12–18].

In order to increase the solubility of rare earth ions in SiO_2 glass, Al_2O_3 is often added to Re_2O_3–SiO_2 glass [19–22]. Various models have been put forth to explain why Al_2O_3 increases the solubility. Arai et al. investigated the effect of Al_2O_3 addition to Nd_2O_3–SiO_2 glasses prepared by the plasma chemical vapor deposition (CVD) by electron-spin-eco-envelope-modulation (ESEEM), and suggested that Al ions are located preferentially around Nd ions to form the solvation shell [23]. Sen et al. stated, by using the NMR spin-lattice relaxation technique, that Nd clusters were broken up with Al co-doping, and that homogeneous distribution of Nd ions in Nd_2O_3–Al_2O_3–SiO_2 glasses can be obtained when the amount of Al co-doping reaches 10 times of the amount of Nd [8]. Sen [9] also observed, by using the Nd and Al extended X-ray absorption spectroscopy (EXAFS), that Nd–O–Si and Nd–O–Al bonds were formed at the expense of Nd–O–Nd bonds on Al_2O_3 addition. He suggested that Nd ions compensate for the charge of $[AlO_4]^{-1}$ units. Laegsgaard [24] proposed a microscopic model for the dissolution of Er ions in SiO_2 with Al co-doping and explained why 10 Al ions for one Nd are needed while only three Al ions are needed for the charge balancing. On the other hand, Monteil et al. [25] stated that Al co-doping modifies rare earth local structure, and that rare earth ions are preferentially located in Al-rich domain. These previous models attempt to explain how

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concentration quenching is diminished, mainly qualitatively, by suggesting a unique structure which can cause the break-up of Nd clustering.

The present authors consider that alumina's effect on the Re_2O_3–SiO_2 systems is similar to its effect on many other oxide systems. Many Re_2O_3–SiO_2 systems exhibit liquid-in-liquid (or glass-in-glass) immiscibilities [26–28]. Al_2O_3 addition is known to suppress the immiscibility tendency of many silicate and borosilicate glass systems [29–34]. The present authors consider that Al_2O_3 addition can lower the immiscibility boundaries of SiO_2–Nd_2O_3 system glasses also, and that this trend, rather than a particular glass structure, is the source of the homogeneous distribution of neodymium ions. The purpose of the present paper is to investigate the effect of Al_2O_3 addition on the immiscibility behavior of the SiO_2–Nd_2O_3 glass system, which is considered a typical SiO_2–Re_2O_3 glass system, and offer an alternative explanation for the reason why Al_2O_3 addition can decrease the clustering of rare earth oxides.

2. Experimental procedure

Nd_2O_3–SiO_2 glasses with various concentrations of Al_2O_3 additions were prepared by melting. Composition ranges of the glasses were Nd_2O_3 2.5–40 mol%, Al_2O_3 0–15 mol% with the balance SiO_2. (All the glass compositions are expressed in mol%, unless specified otherwise). Batch materials used in glass melting were sol–gel-derived high purity silica powder from Nippon Kasei Chemical Co., Ltd. (MKC® silica PS400L), Nd_2O_3 powder from Sigma-Aldrich (99.9% purity) and reagent-grade Al_2O_3 powder from Fisher Scientific. The batch was mixed using an alumina mortar and pestle. Approximately, 50 mg of the mixture was put in a 90%Pt–10%Rh boat (ca. 10 mm × 10 mm × 5 mm) and melted for 1 h at 1750 °C in air. A small batch was used for ease of melting and quenching. The melted glass was quenched by putting it into water together with the boat. Similar glasses were heat-treated also at 1600 °C before water quenching. To prepare these samples, the glass was melted at 1750 °C for 1 h and then cooled down to 1600 °C in the furnace, and held for 1 h at 1600 °C and then quenched in water.

The surfaces of samples were polished with a SiC polishing paper (600 grit) and then with CeO_2 particles. The polished samples were washed with alcohol, neutral detergent in water, alcohol again and finally with water in an ultrasonic cleaner.

To observe the microstructures of phase separation, scanning electron microscope (SEM) images of the polished surface coated with thin gold film were taken with a JEOL-840 SEM and at least three spots of the sample were examined. For identification of each phase composition of a phase-separated glass, elemental analyses were also carried out using the same SEM instrument. The probe diameter in this case was approximately 1 μm in diameter. For phase-separated samples, SEM images showed a two phase structure as shown in Fig. 1. Darker colored particles are considered to be on the sample surface whereas the light colored particles appear to be inside the sample. Volume fraction of separated phases were determined by first selecting only the particles on the surface as shown in Fig. 2(a) and (b) and evaluating the area fraction of the dark part and the white part as shown in Fig. 2(b), using analySIS FIVE (Olympus). The tie lines of phase separation ware estimated using the obtained volume fraction.

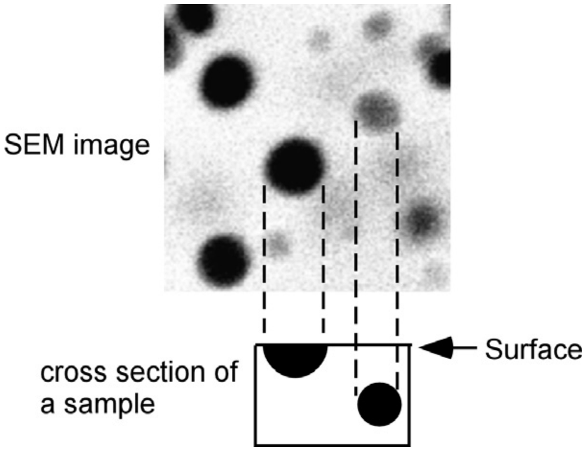

Fig. 1. Dark and light black spherical phases in a SEM image of a phase-separated sample.

For selected samples, X-ray diffraction analyses (XRD) with a Siemens D5000 Diffractometer were made to confirm that the glass samples are amorphous. Electron microprobe analyses with a CAMECA SX 100 of a sample were made to see whether the nominal compositions are close to the real glass compositions. For this purpose, rhyolite glass was used as the SiO_2 standard, Nd_2PO_4 was used as the Nd_2O_3 standard, and kyanite was used as the Al_2O_3 standard. The spot size probed with electron beam was about 5 μm in diameter, and 13 data points were selected randomly.

3. Results

3.1. XRD analysis and electron microprobe analysis

Fig. 3 shows the results of XRD measurement for selected SiO_2–Nd_2O_3–Al_2O_3 ternary glass powder samples. Since the sample quantities were small, some diffraction signal originates from the plastic sample holder employed (e). To make sure that a crystalline peak, if any, can be detected with the employed small quantity of the sample, a similar quantity of copper powder sample was measured (f). There was no crystalline peak observed in the prepared ternary glass samples while a peak was observed in the same quantity of copper powder, indicating that the sample quantity is adequate for peak detection. Table 1 shows the result of electron microprobe analysis for $85SiO_2$–$7.5Nd_2O_3$–$7.5Al_2O_3$ glass. The difference between nominal and analyzed compositions was 1.2–1.5 mol% for SiO_2 and Nd_2O_3 while it was 0.3 mol% for Al_2O_3.