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Fabrication of Sm^{2+}-doped macroporous aluminosilicate glasses with high alumina content

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Abstract

Macroporous Al_2O_3–SiO_2 glasses doped with Sm^{2+} have been prepared from a sol–gel system containing aluminum *sec*-butoxide, tetramethoxysilane, samarium chloride hexahydrate, poly(ethylene oxide), nitric acid, and water. Monolithic gels having interconnected macropores and skeletons are formed by inducing the phase separation parallel to the gelation. The use of aluminum *sec*-butoxide preheated at 80 °C as the starting material enables the incorporation of Al^{3+} into the gel skeleton up to 20 mol% in cation ratio. The maximum amount of Al^{3+}, i.e., 20 mol%, is twice as large as that reported in our previous study, where aluminum *sec*-butoxide was diluted with *sec*-butanol prior to the hydrolysis. Heat-treatment of Sm^{3+}-doped $20AlO_{3/2} \cdot 80SiO_2$ macroporous glass under the reducing atmosphere converts Sm^{3+} to Sm^{2+}, which is confirmed by the appearance of intense emission peaks attributed to 4f–4f transitions of Sm^{2+}.

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1. Introduction

Interference of multiply-scattered light occurs in random media where a large refractive index contrast exists on the length scale comparable to light wavelength. The interference effect brings about various fascinating phenomena such as coherent backscattering and photon localization [1–4]. One interesting phenomenon is an optical memory effect, which is observed in random media doped with photoreactive species such as Sm^{2+} [5]. When such a medium is irradiated with a monochromatic light, a three-dimensional interference pattern is created inside the medium. The interference pattern varies with the wavelength and the incident angle of laser beam, and is memorized by the space-selective photobleaching. This means that the information about the incident light is stored in the form of spatial modulation of optical absorbance within the medium. Most of the photoreactive random media reported so far consist of fine particles including ZnS nanocrystals and ground glasses [5,6]. However, for the practical applications, monolithic structures are rather suitable. In this point of view, porous monoliths are promising as random media, in which the scattering strength can be tuned by manipulating the sizes of pores [7,8].

A sol–gel method combined with a phase separation is one of the smart and convenient techniques for the fabrication of porous media [9,10]. The macroporous morphology is formed via the development of a transient structure of phase separation parallel to the hydrolysis and condensation of metal alkoxides and subsequent freezing of the structure by the sol–gel transition. By controlling the relative rate of phase separation to the sol–gel transition, one can tune the sizes of pores and skeletons systematically. Based on this concept, we recently fabricated

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Sm^{2+}-doped Al_2O_3–SiO_2 macroporous monoliths under the coexistence of aluminum *sec*-butoxide, $Al(OC_4H_9)_3$, and tetramethoxysilane, $Si(OCH_3)_4$ [11,12]. $Al(OC_4H_9)_3$ is a very viscous liquid at room temperature. Thus, for reproducible sample preparation, one needs to reduce the viscosity of $Al(OC_4H_9)_3$ by some pretreatment, such as diluting or heating. In our previous study, the dilution was selected as the pretreatment; $Al(OC_4H_9)_3$ was mixed with *sec*-butanol with the volume ratio of 1:2 prior to the hydrolysis. However, the addition of *sec*-butanol inevitably facilitates the fragmentation of gel skeletons during the phase separation, due to the dilution of metal alkoxides. Under such a diluted condition, it is hard to fabricate a macroporous monolith with a high content of Al^{3+}. Consequently, the concentration of Al^{3+}, defined as the molar ratio of Al^{3+} to the sum of Al^{3+} and Si^{4+}, is limited to 10 mol% at most, although the presence of Al^{3+} is effective for the reduction of Sm^{3+} to Sm^{2+} in silica-based glasses [13–15].

In this study, another pretreatment has been selected to fabricate macroporous aluminosilicate glasses containing samarium ions; $Al(OC_4H_9)_3$ is preheated at 80 °C instead of being diluted with *sec*-butanol. The preheating of $Al(OC_4H_9)_3$ allows the preparation of macroporous monoliths even if the Al^{3+} concentration is increased up to 20 mol%. We also have demonstrated that the conversion of Sm^{3+} to Sm^{2+} is achieved in macroporous $20AlO_{3/2} \cdot 80SiO_2$ glasses by the heat-treatment under the reducing atmosphere.

2. Experimental procedure

Glasses with the compositions of $xAlO_{3/2} \cdot (100 - x)$-$SiO_2$ (x; 0–30 in mol%) doped with 3 wt% Sm_2O_3 were prepared by using $Al(OC_4H_9)_3$ (Tokyo-kasei, Japan), $Si(OCH_3)_4$ (Shin–Etsu Chemical Co., Japan), and $SmCl_3 \cdot 6H_2O$ (Mitsuwa's Pure Chemicals, Japan) as sources of inorganic components. Poly(ethylene oxide) [PEO; $HO(–CH_2CH_2–O–)_nH$, Aldrich, USA] with an average molecular weight of 10000 was used as a water-soluble polymer to induce the phase separation, and nitric acid as a catalyst for hydrolysis and condensation.

Samples were prepared as follows. First, $Si(OCH_3)_4$ was dissolved in 10 ml of 2 M nitric acid aqueous solution (2 M HNO_3aq) in the presence of PEO and $SmCl_3 \cdot 6H_2O$ at 0 °C. Then, $Al(OC_4H_9)_3$ preheated at 80 °C was added to the mixture with vigorous stirring. After stirring for 30 min, the resultant solution was poured into a glass container. The container was sealed and kept at 60 °C. The gelation time was monitored by tilting the container to find the time when the bulk fluidity of the solution was lost. After gelation, the wet gel was aged at the same temperature for 24 h, and dried at 60 °C for the evaporation of the solvent. The dried gel thus obtained was sintered at 1000 °C for 2 h in air. Some of the sintered samples were reheated at 1000 °C for 1 h under flow of a reducing gas of 50 vol.% N_2, 47.5 vol.% Ar, and 2.5 vol.% H_2.

A scanning electron microscope (SEM; S-2600N, Hitachi Ltd., Japan) was used to observe the macroscopic morphology of the dried gels. The size distribution of pores was measured for the dried gels by mercury porosimetry (PORESIZER9320, Micromeritics Co.). The fluorescence spectra before and after the heat-treatment in a reducing atmosphere were measured at room temperature with a fluorescence spectrophotometer (Hitachi-850) using the 488 nm line of an Ar^+ laser as the excitation light.

3. Results and discussion

A relation between the calculated starting composition and the resultant gel morphology is shown as a ternary diagram in Fig. 1(a). Three end components of the triangle are Al_2O_3, 2 M HNO_3aq, and PEO, and the compositions are expressed in terms of mass percent. Here, the weight of Al_2O_3 was calculated by assuming that $Al(OC_4H_9)_3$ was completely hydrolyzed and condensed. In the diagram, the resultant gel morphologies are classified into three different types; nanoporous gel (represented by closed circle), particle aggregate (open circle), and interconnected macropore (crossed circle). The morphology of nanoporous gel refers to the structure without micrometer-sized pores, i.e., transparent or translucent gels, while that of particle aggregates consists of micrometer-sized particles. The morphology of interconnected macropore, which is the one we aim to obtain, is characterized by the bicontinuous structure in which both the gel skeletons and the macropores are highly continuous. In the diagram, the nanoporous gels are obtained when the PEO content is zero or very low (around the left side of the triangle), or high (right side of the triangle). Also, the starting solutions become

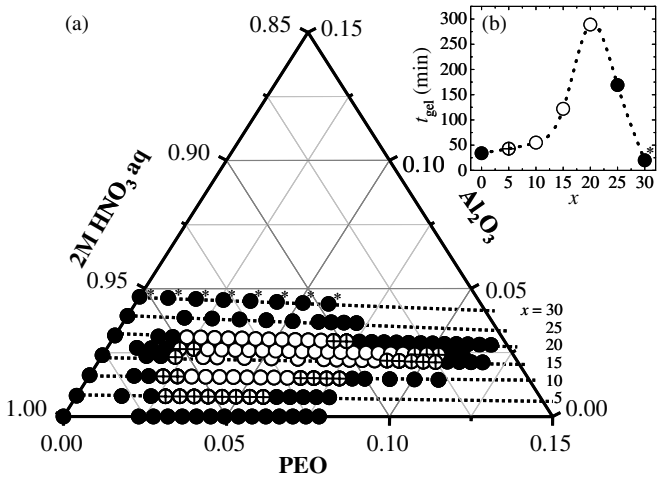

Fig. 1. (a) Relationship between starting composition and resultant gel morphology. (●) Nanoporous gel; (○) Particle aggregate; (⊕) Interconnected macropore. Dashed lines indicate the composition ranges containing the same amount of Al^{3+}. When $x = 30$, the solution is not completely homogeneous after stirring for 30 min, which is indicated by (∗). (b) Gelation time (t_{gel}) as a function of alumina concentration (x) for the set of samples prepared under the condition that PEO content is fixed at 0.6 g. Symbols are the same as in (a), and the dashed line is guide for the eyes.