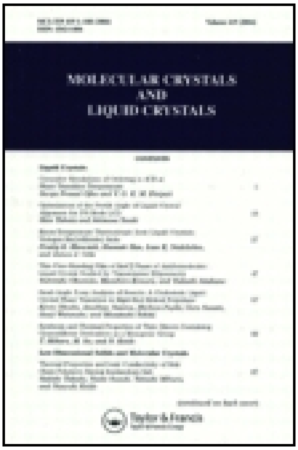

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Preparation of Core-Shell Structured Superfine-Particle Dispersed Glasses

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Preparation of Core-Shell Structured Superfine-Particle Dispersed Glasses

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A sol-gel method has been used to prepare particle-dispersed glasses containing superfine (less than 30 nm in diameter) particles of cuprous oxide Cu_2O. The X-ray diffraction spectrum of the bulk material and the absorption spectra of thin (less than 1 μm thick) films show that partial reduction induced by an exposure to H_2 produces core-shell-structured (Cu_2O core and Cu shell) superfine-particle-dispersed glasses. Those glasses are stable in a dry atmosphere.

<u>Keywords:</u> sol-gel method; core-shell structure; superfine particle; X-ray spectrum; absorption spectrum; cuprous oxide

INTRODUCTION

Super-fine-particle-dispersed systems have received much attention because of their characteristic optical properties such as high fluorescence emissivity[1] and non-linearity[2]. Superfine-particle-dispersed systems in which the particles are either metals or semiconductors show a high third-order optical non-linear susceptibilities[3]. If the superfine particles have a core-shell structure, its non-linearity is theoretically expected to be greatly enhanced[4]. However, superfine particles are generally very unstable because of their high surface energy. Particles should therefore be held in matrices in advance and be modified their surface later. A superfine-particle-dispersed glass prepared by a sol-gel method is porous and thus provides a good reaction field when it is exposed to a reactive gas.

This paper introduces a sol-gel method to fabricate the core-shell structured superfine-particle dispersed glasses thus described both as a bulk and a film in

EXPERIMENTAL. Then, it describes their properties in RESULTS and DISCUSSION.

EXPERIMENTAL

Selection of Materials

Dispersed nano-particles should be stable in the atmosphere and allowed to react at high temperatures. Metal sulfide or oxide is a promising starting material which provides the following partial reduction. Gold and silver are good for their stability at atmospheric conditions. However, their ions easily changed into metal atoms when exposed to hydrogen sulfide or oxygen at elevated temperatures for the sake to make a compound nano-crystals. Copper is also stable in dry air and less stable at high temperatures. In case of reduction, cupric(Cu^{2+}) compounds tend to change first into cuprous(Cu^{+}) compounds. Therefore it is very hard to fabricate an expected core-shell structure by using cupric compound. Furthermore, a sol-gel matrix is damaged by exposure to hydrogen sulfide at elevated temperatures. For these reasons, we decided to prepare nano-particles consisting of a cupric oxide (Cu_2O) core and a copper shell by using the procedure explained below.

Preparation of Bulk Material

A dispersion of Cu^{2+} in tetraethoxysilane (TEOS) was poured into a Teflon petri dish and left several days to cast. The resultant wet gel was heated, at the rising up rate of 0.5 ℃/min., to 150 ℃ in order to make a dry gel body. This gel was then heated under nitrogen atmosphere up to 800 ℃ for 2 hr to prepare a Cu_2O particle-dispersed system[5,6]. Then the product was exposed to H_2 at 500 ℃ for 15 min. to reduce only the surface of the Cu_2O particles. The X-ray radial distribution spectra of the products were measured before and after the reduction.

A bulk product had many cracks due to the heat treatment at 800 ℃. This would make precise measurements of optical properties very difficult - especially measurement of third order non-linear susceptibilities by using a degenerate four-wave mixing method[7]. We also worried that the reduction might not be uniform and would occur only at the particles located on and near the surface of the bulk material. Therefore we made thin films by using the data obtained for the bulk materials.

Preparation of Films

Thin glass films were prepared on a clean synthesized quartz-glass plate by the procedure shown below.

$$\underset{\text{sol solution}}{\text{Cu}^{2+}\ \&\ \text{TEOS}} \xrightarrow[\text{Stirring}]{} \xrightarrow[\text{Dipping}]{} \xrightarrow[150\,^\circ\text{C},\ 2\ \text{hr}]{\text{Air}} \xrightarrow[800\,^\circ\text{C},\ 2\ \text{hr}]{\text{N2}} \text{A} \xrightarrow[100\text{-}500\,^\circ\text{C}]{\text{H2}} \text{B}$$

TABLE I Composition of sol solutions (molar ratio) with respect to TEOS

Solution No.	$Cu(NO_3)_2$	HNO_3	H_2O	C_2H_5OH
(a)	0.02	0.01	7	10
(b)	0.02	0.01	10	10
(c)	0.04	0.01	4	10
(d)	0.04	0.01	7	10
(e)	0.04	0.01	10	10
(f)	0.04	0.01	15	10
(g)	0.04	0.01	20	10
(h)	0.04	0.01	30	10
(i)	0.04	0.1	7	10

The contents of the Cu^{2+} & TEOS sol solutions we prepared are listed in Table I. The change of the contents is due to differentiate the mobility of Cu ions in each film. To prepare films reproducibly, the room temperature and humidity during dipping were maintained at 23°C and 35%. Efforts were also made to keep the atmosphere clean in order to prevent dust particles from being nucleation centers when nano-particles were formed. Each of the films ((a) to (i) in Table I) was transparent in the central area where its thickness on both sides of the substrate was between 0.1 and 0.5 µm. At the edges, however, where the films were 0.5 to 1.0 µm thick, each film had many cracks. The absorption spectrum of each sample was measured both at a central area and at a rough edge area by using a conventional spectrometer (Hitachi 330). Very small flakes were scratched off the films and observed by using a transmission electron microscope (Hitachi H-9000).

RESULTS and DISCUSSION

Bulk

The X-ray radial distribution spectra measured before and after the reduction are shown in Figs. 1(a) and 1(b). The particle diameters shown in the figures were estimated using Scherrer's equation. It is natural to consider that particles are reduced from their surface. Therefore, the core-shell structured superfine particles shown in the inset in Fig. 1(b) are expected to have been formed. This X-ray spectrum of the partially reduced one is identical to the one measured after the sample had been kept in a desiccator for three months.

Film

Absorption spectra of the samples were measured after the films had been

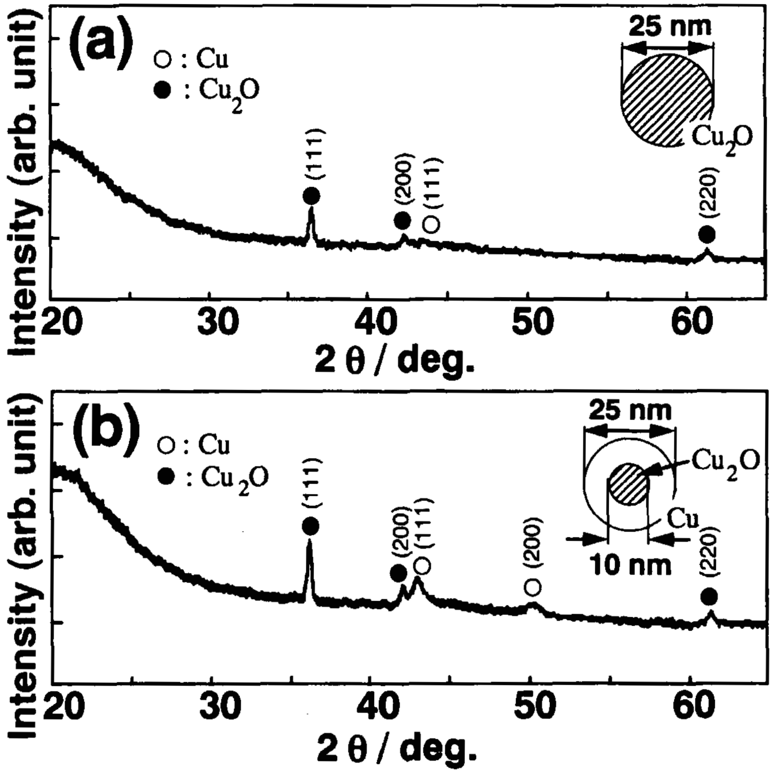

FIGURE 1 The X-ray radial distribution pattern of a Cu/TEOS system measured (a) before and (b) after reduction. The inset figures show particle sizes estimated from diffraction peak positions and widths.

heated at 800 ℃ for 2 hours, but before the reduction (at stage A described in Preparation of Films). At the transparent area in the films (a) to (i), only the absorption of Cu^+ [8] was observed. This indicates that transparent films are too dense for the ions to move and form a nano-particle. At the edge area, absorption peaks at 330 and 440 nm assigned to Cu_2O particles [6] were observed as depicted by curve A in Fig. 2 in the case of sample(g). Gradual reductions under the conditions depicted in the right part in Fig. 2 resulted in the absorption wavelength changing as shown by curves B, C, and D in the figure. Curve D is the same as the one reported for copper nano-particles[9]. The width of the peak at 570 nm in curve D indicates that the mean diameter of the Cu particles is about 5 nm. As expected theoretically [10], composite structured nano-particles absorb wavelengths different from those absorbed by elementary particles consisting of the composite. Therefore, the observed shifts are direct proof for the formation of core-shell structured particles.

Transmission electron microscope observation showed that the superfine particles were actually formed and dispersed uniformly in the edge area of the

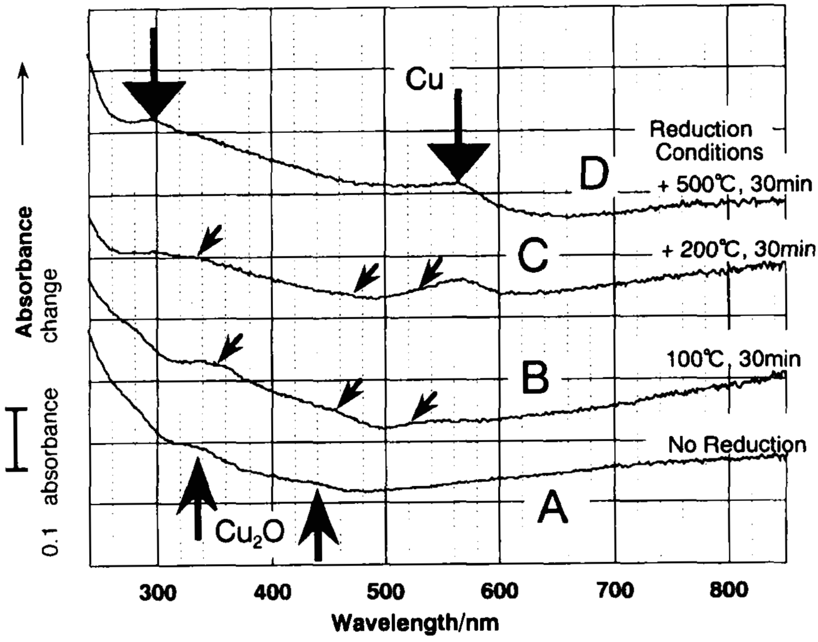

FIGURE 2 Absorbance change due to reduction

films. Most of the particles were 5 - 10 nm in diameter. However, our magnification (x 50K) was too low to observe clearly the structure in particles. No obvious particle growth was observed in transparent area in any of the films from (a) to (i). This is in accordance with the results obtained when measuring the absorption spectra. When these samples were kept in a desiccator for a month, their absorption spectra did not change.

CONCLUSIONS

A sol-gel method was used to prepare bulk and thin-film glasses containing dispersions of superfine Cu_2O particle. The X-ray diffraction spectrum from the bulk material and the absorption spectra of the thin films show that the partial reduction induced by an exposure to H_2 produces core-shell-structured (Cu_2O core and Cu shell) superfine-particle-dispersed glasses. In films, nano-particles grew only around the edges of the films. Those particles are stable in a dry atmosphere.

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