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Structural relaxation of densified GeS_2 glass by thermal annealing

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Introduction

Thermal relaxation behavior of densified GeS_2 glass was examined to elucidate the mechanism of permanently densification phenomenon of GeS_2 glass. The fast and slow relaxation processes were found to occur in the thermal relaxation process of the densified GeS_2 glass by the analyses of density relaxation curves. In the present study, therefore, the recovery of Ge-S bond length during the thermal annealing was examined by Ge-K EXAFS measurement.

Experimental

Permanent densification of GeS_2 glass was carried out under 6 GPa at 270°C with a 6-8-type multi-anvil high-pressure apparatus. Thermal treatments of densified GeS_2 glass were carried out in vacuo at several temperatures for a total time of 128h. The densities of the samples were measured by the Archimedes method using CCl_4 as an immersion liquid. The EXAFS measurements of the glasses thermally treated at 100°C and the reference crystal, β-GeS_2, were conducted with a transmission mode by using the EXAFS facility at BL-10B. The Si(311) double crystals were used as a monochromator. Analyses of the collected EXAFS data were performed by using the Sakane program.

Result and Discussion

The relaxation-function was plotted against the annealing time in Fig. 1. The relaxation-function is defined by

$$\Phi(T, t) = (\rho(T, t)-\rho_\infty) / (\rho_0-\rho_\infty), \quad (1)$$

where ρ_∞ and ρ_0 are the densities of the undensified glass and the unrelaxaed glass before thermal annealing, respectively, and $\rho(T, t)$ is the density after annealing at T K for t hours.

As can be seen from this figure, the samples treated below 150°C can be fitted by two straight lines which have different slopes. This means that the thermal relaxation process of the permanently densified GeS_2 glass has two relaxation processes which have different activation energies. For convenience, The two relaxation processes are referred to as the fast- and slow-process. For the samples treated above 200°C, the fast-process has already completed in the present time scale.

The Ge-S bond lengths obtained by analyzing the Ge-K EXAFS oscillation curves were plotted against the annealing-time in Fig. 2. The Ge-S bond length keeps a constant value during the fast-process, and then slightly decreased at the beginning of the slow process. The decreased value keeps constant during the slow-process.

As a result, it was found that the recovery of the Ge-S bond length occurs at the beginning of the slow-process.

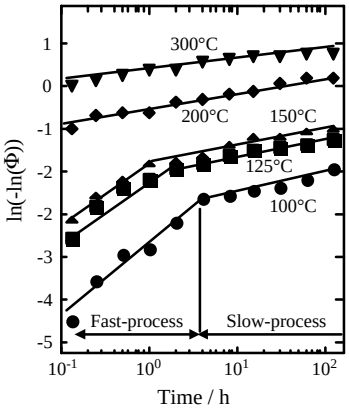

Fig. 1. Relaxation-function was plotted against annealing-time in thermal relaxation of permanently densified GeS_2 glasses.

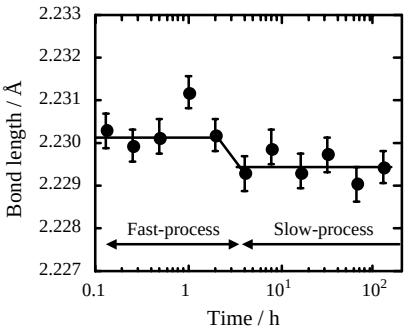

Fig. 2. Relationship between annealing-time and Ge-S bond length.

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