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Spectroscopy and XAFS analysis of Co-doped sulfide glasses

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Introduction

Because of the low phonon energy and high refractive index, rare-earth-doped chalcogenide glasses have received much attention in applications for fluorescence materials with high quantum efficiencies. Since the pioneering research by Reisfeld et al., extensive investigations have been performed on the rare-earth-doped chalcogenide glasses. However, it is strange that there are very few studies on the transition metal-doped chalcogenide glasses. We have investigated 3d transition metal-doped sulfide glasses for application to phosphors in mid-infrared region. Here we report the preparation, spectroscopic studies, and XAFS analysis on the Co-doped sulfide glasses in order to elucidate the environmental structure around the Co ions.

Experimental procedures

Glasses of the compositions, $60GaS_{3/2}\cdot10GeS_2\cdot30LaS_{3/2}$ and $70GeS_2\cdot30SbS_{3/2}$ were prepared by a conventional melting-cooling method using evacuated silica tubes. The used starting materials were metal elements and sulfur purified by distillation. Cobalt metal or sulfide was introduced into the starting batches. Absorption spectra were obtained with UV-visible-near infrared and IR spectrophotometers.

XAFS measurements at Co K-edge were performed at PF BL-7C with Si (111) double crystal monochrometer in a fluorescence mode. EXAFS functions were extracted by a standard method and curve-fitting analyses were performed with the program REX2000 supplied from Regaku Co. in order to obtain the structural parameters. Structural parameters of Co_9S_8 crystal were used as reference.

Results and Discussion

Figure 1 shows the absorption spectra of the Co-doped sulfide glasses. Absorption bands around 670 and 750 nm and a broad band consisting of at least three peaks were observed for the Ga_2S_3-GeS_2-La_2S_3 glass. The former two peaks were located around 750 and 820 nm for the GeS_2-Sb_2S_3 glass. The same bands were also observed in Co-doped ZnS crystal in which Co^{2+} ions sit at tetrahedral Zn^{2+} sites. It is supposed, therefore, that Co^{2+} ions also exist at tetrahedral sites in the glasses.

Figure 2 shows an example of the Fourier transforms of the k^3-weighted EXAFS functions and the curve-fitting of the reverse Fourier transform for the Co-doped $60GaS_{3/2}\cdot10GeS_2\cdot30LaS_{3/2}$ glass. The coordination number and bond distance were determined as 3.9 and 2.23 Å, respectively. The bond distance was slightly longer than that of the Co_9S_8 crystal, 2.15 Å. These results were well consistent with the spectral data.

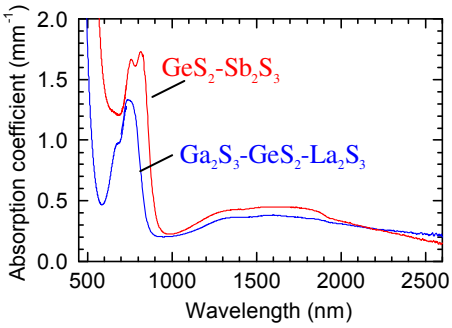

Fig. 1. Absorption spectra of Co-doped sulfide glasses.

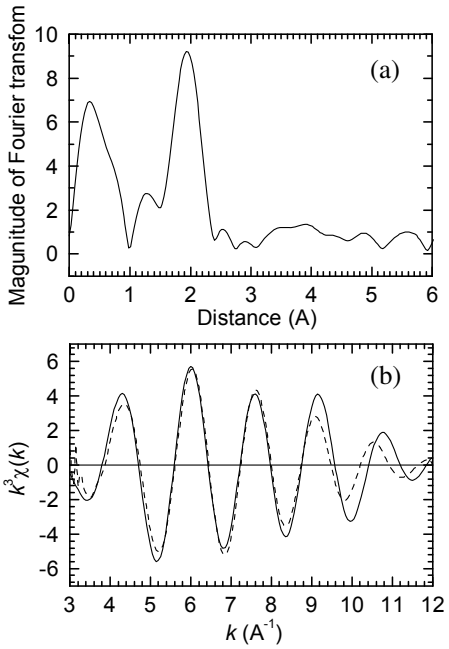

Fig. 2. (a) Fourier transform of Co K-edge XAFS function for the Co-doped Ga_2S_3-GeS_2-La_2S_3 glass and (b) curve-fitting (dashed line) of the reverse Fourier transform.

References

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