Mid-infrared light emission characteristics of Ho$^{3+}$-doped chalcogenide and heavy-metal oxide glasses

YONG BEOM SHIN, JOO NYUNG JANG, JONG HEO
Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31 Hyojadong, Pohang, Kyungbuk, Korea

Received 2 June; accepted 15 August 1994

Emission characteristics of Ho$^{3+}$-doped heavy-metal oxide and chalcogenide glasses were investigated and compared with those of conventional oxide glasses. In addition to the fluorescence at approximately 1.2 μm ($^5I_6 \rightarrow ^5I_8$) and 2.0 μm ($^5I_7 \rightarrow ^5I_8$), another mid-infrared emission was observed at 2.9 μm from the transition $^5I_6 \rightarrow ^5I_7$. The calculated radiative transition probability and multiphonon decay rate of the latter transition using Judd–Ofelt analysis indicated that the occurrence of the 2.9 μm fluorescence was directly related to the low vibrational phonon energy of the host glasses.

1. Introduction
Heavy-metal oxide glasses generally refer to the family of glasses containing large amounts of heavy-metal cations such as bismuth and lead with none of the traditional glass-forming cations [1]. Most of the works on heavy-metal oxide glasses have been concentrated on the PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ system [2, 3] owing to its large glass-forming region, high refractive index, good transparency in the mid-infrared region together with the high chemical durabilities of the glasses. More recently, the structure of the glasses in this gallate system has also been investigated using vibrational [4] and NMR [5] spectroscopic techniques. Chalcogenide glasses, on the other hand, consist of one or more of group VI elements in the periodic table, namely S, Se and Te. Combinations with such elements as Ge, As, Sb and P produce glasses with highly covalent bond character. They are known to have large transmission windows in the mid-infrared wavelengths, good glass-forming abilities and stability against devitrification [6].

Doping of rare earths into heavy-metal oxide and chalcogenide glasses provides an opportunity to obtain fluorescence, and possibly laser action at longer wavelengths than presently available from silicate and phosphate glasses. Present silica-based solid-state lasers are operational only from the visible out to approximately 2 μm since the intrinsic phonon absorption bands extend from long wavelengths into the mid-infrared region [7]. Because of the extended infrared transmission out to 7 μm for heavy-metal oxide glasses and to 12 μm for chalcogenide glasses, these provide potential as host materials for enhanced efficiencies of fluorescence at mid-infrared wavelengths.
A wide variety of glasses doped with Ho$^{3+}$ have been prepared and their optical characteristics have been investigated [8–11]. For example, Reisfeld et al. [11] studied the absorption and emission characteristics of Ho$^{3+}$-doped germanate glasses. They have compiled the radiative transition probabilities, branching ratios and integrated emission cross-sections for several electronic transitions using calculations based upon the Judd–Ofelt theory. However, their main focus was on the light emission in the visible region of the spectrum and no experimental details have been provided on the fluorescences in the longer-wavelength region.

The present study is concerned with the synthesis and optical characterization of Ho$^{3+}$-doped chalcogenide and heavy-metal oxide glasses with emphasis on the optical phenomena associated with 2.0 $\mu$m and 2.9 $\mu$m fluorescences. Oscillator strengths, intensity parameters and several other laser parameters were calculated using Judd–Ofelt analysis and compared with previous results from different host glasses. Multiphonon relaxation associated with the transition responsible for the 2.9 $\mu$m fluorescence, which was not found from the conventional oxide-based materials, was also discussed.

2. Experimental procedures

2.1. Sample preparation

The composition of the host heavy-metal oxide glass was 56PbO–27Bi$_2$O$_3$–17Ga$_2$O$_3$ (mol%, denoted as EO glass hereafter), which was known to be one of the most stable glass-forming compositions [1, 2]. Starting materials used were PbO, Bi$_2$O$_3$ and Ga$_2$O$_3$ powders with purities over 99.9%. Ho$_2$O$_3$ 1.5 wt% was introduced to the mixture of the starting oxide powders. Melting was completed by heating the powders at the temperature of approximately 1390°C for 10 min using a platinum crucible and quenching on to the brass mould in air afterwards.

For chalcogenide glasses, Ge$_{30}$As$_{10}$S$_{60}$ (atom%, denoted as CH hereafter) was selected as a host composition with the addition of 0.5 wt% Ho$_2$S$_3$. Starting materials were Ge, As and S in their elemental forms with purities of 99.99%. Weighing was done inside a glove box filled with high-purity argon gas in order to minimize the incorporation of oxygen and moisture into the glasses. Silica ampoules containing the weighed amount of the starting materials were evacuated and sealed before melting. Melting was done by heating up to 1000°C for approximately 24 h using a three-zone rocking furnace. Ampoules containing the melts were then removed from the furnace and cooled in the air to form rod-shaped glasses.

2.2. Optical characterization

Absorption spectra of glasses were recorded using Perkin Elmer Lambda 19 UV/VIS/NIR spectrophotometer in the wavelength region of 190–2300 nm. Samples were optically polished to the thickness of approximately 1 mm and an undoped glass with the same thickness was used as a reference in order to remove the effect of host materials on the absorption spectra.

Fluorescence measurements were made through a monochromator and detector/lock-in amplifier arrangement controlled by a computer. A Ti-sapphire tunable laser, driven by an Ar$^+$ laser, was used as the pumping source. The pump wavelengths for Ho$^{3+}$ in EO and CH glasses were 903 nm and 905 nm, respectively. Fluorescence was detected by a liquid-nitrogen-cooled InSb detector and an LiTaO$_3$ pyroelectric detector. Judd–Ofelt analysis [12, 13] was used to calculate intensity parameters, radiative transition probabilities and branching ratios of various transitions among several energy levels in rare earths. Detailed descriptions of the analysis have been covered in numerous publications (for example, [11]), and therefore are not included. The reduced matrix elements $(||\mu^{(j)}||)$ were taken from data calculated for LaF$_3$ [14].