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A pulsed EPR study of clustering of Yb^{3+} ions incorporated in GeO_2 glass

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Abstract

The structural aspects of clustering of Yb^{3+} ions and the paramagnetic behavior of these clusters have been investigated in GeO_2 glasses doped with 140–1100 ppm by weight of Yb_2O_3 using time-domain electron paramagnetic resonance (EPR) spectroscopic techniques. The echo-detected EPR (EDEPR) spectra of Yb^{3+} ions and their unusual dependencies on microwave power and magnetic field have been found to be indicative of the formation of clusters of these rare earth ions in GeO_2 glass that behave as non-Kramers type spin systems. The magnetic field and concentration dependence of phase relaxation rates of Yb^{3+} in these glasses further substantiate such a scenario and indicate the formation of clusters of Yb^{3+} ions. A comparison of the EDEPR spectra with calculated cw-EPR line shapes yields a semi-quantitative measure of the typical cluster size of $\geqslant 3$ Yb atoms and intra-cluster Yb–Yb distances of 3.5–4.0 Å in these glasses at doping levels of $\geqslant 350$ ppm of Yb_2O_3.

1. Introduction

Glasses doped with rare-earth (RE) ions have found important technological applications in recent years as solid-state lasers and more importantly as optical fiber amplifiers for optical telecommunication networks. However, clustering of the dopant RE ions even at doping levels of a few hundred to a few thousand parts per million (ppm) due to their low solubility in silicate and germanate glasses severely limit the ability of making compact devices which would require high concentration of these ions. Such a limitation is a consequence of the fact that clustering of RE ions gives rise to cross relaxation between excited ion-pairs within a cluster that results in non-radiative de-excitation of the ion-pair which in turn drastically lowers the gain of the amplifier [1,2]. Our understanding of the intermediate-range structural aspects of RE clustering in glasses including cluster size and intra-cluster RE–RE distances has remained largely qualitative in spite of the extensive structural studies of RE-doped glasses using a variety of spectroscopic techniques in the recent past [3–10].

Recently, advanced time-domain electron paramagnetic resonance (EPR) methods were shown by us to be promising in obtaining indirect structural information on the spatial distribution of dopant paramagnetic centers in glasses [4]. Here we report the results of an electron spin echo (ESE) study of GeO_2 glasses doped with Yb^{3+} ions. Yb has been chosen as a model RE ion since Yb-doped glasses have shown significant potential in recent years as candidates for high-power fiber laser and amplifier applications in the 1 μm wavelength region [11,12]. GeO_2 is a 'fully polymerized' host glass similar to SiO_2 where all oxygen atoms are 'bridging', i.e. linked to two Ge atoms [13]. Dopant RE ions in such glasses are expected to be significantly clustered even at very low doping levels of a few hundred ppm due to the lack of optimum coordination environments that presumably would require non-bridging oxygens [6].

The echo-detected EPR (EDEPR) spectra of Yb^{3+} ions in the Yb-doped GeO_2 glasses have been analyzed in conjunction with electronic spin-lattice and phase relaxation rate measurements to understand the nature of Yb clusters in these glasses. Preliminary comparisons between calculated cw-EPR line shapes and experimental

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