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Intense upconversion luminescence in ytterbium-sensitized thulium-doped oxychloride germanate glass

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Abstract

Structural and upconversion fluorescence properties in ytterbium-sensitized thulium-doped oxychloride germanate glass have been studied. The structure of oxychloride germanate glass was investigated by peak-deconvolution of Raman spectrum, and the structural information was obtained from the peak wavenumbers. The Raman spectrum investigation indicates that $PbCl_2$ plays an important role in the formation of glass network, and has an important influence on the upconversion luminescence. Intense blue and weak red emissions centered at 477 and 650 nm, corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3H_4$, respectively, were observed at room temperature. The possible upconversion mechanisms are discussed and estimated. Intense upconversion luminescence indicates that oxychloride germanate glass can be used as potential host material for upconversion lasers.

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Keywords: Rare-earth doped glasses; Optical materials; Optical spectroscopy; Upconversion emission

1. Introduction

It is known that some rare-earth ions can convert the wavelength of incident light to a shorter one via a multiphoton excitation process. And now, there is a great interest in such phenomena because of the possibility of infrared-pumped visible lasers and visible to ultraviolet light amplifiers. Optical properties of trivalent lanthanide ions such as Er^{3+}, Ho^{3+}, and Nd^{3+} in glasses have been extensively studied to develop upconversion visible or ultraviolet lasers which can

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be operated at room temperature [1–6]. Among the trivalent lanthanide ions, Tm^{3+} ion has stable excited levels suitable for emitting blue and ultraviolet upconversion fluorescence. It was reported that a blue upconversion of Tm^{3+} was discovered in fluorozirconate glass by co-pumping at both 676.4 and 647.1 nm using a krypton ion laser and by single wavelength pumping at 650 nm [7,8]. In addition, we found both blue and ultraviolet upconversion in Tm^{3+}-doped and Yb^{3+}/Tm^{3+}-codoped glasses [9,10]. Host material for Tm^{3+} ions plays an important role in obtaining high-efficient upconversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR) and thus achieves strong upconversion luminescence [11,12]. Though fluoride glasses have been studied due to low phonon energies, oxide glasses are more appropriate for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, bismuthate and germanate glasses combine high mechanical strength, high chemical durability, and temperature stability with good transmission in the infrared region, which make them promising materials for technological applications such as new lasing materials, upconverting phosphors, and optical waveguides [1,2,4,13,14]. To develop oxide glasses with extended infrared transmittance, large cations with low field strength, such as lead oxide, can be added.

As is known, glasses based on mixed oxide–halide systems combine the good optical properties of halide glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stability of oxide glasses [14]. So it is expected that oxychloride germanate should bring together the interesting properties of the two systems. Recently, many investigations have focused on oxyhalide tellurite glasses [15]. However, to the best of our knowledge, little attention has been paid to the study of Tm^{3+}-doped oxychloride germanate glass. In this paper, the structural and upconversion fluorescence properties of novel oxychloride germanate glass were investigated. Intense blue upconversion fluorescence has been observed, and the possible upconversion mechanisms are discussed and estimated.

2. Experimental details

The glass used in this work was synthesized by conventional melting and quenching method. The starting materials are reagent-grade $PbCl_2$, PbO, BaO, ZnO, K_2O and high-purity GeO_2 (>99.999%). The glass sample studied has the following composition: (mol%) $55GeO_2$–25 (BaO + ZnO + K_2O)–$20PbCl_2$–$0.05Tm_2O_3$–$1Yb_2O_3$ (GPClTY). Undoped (mol%) $55GeO_2$–25(BaO + ZnO + K_2O)–$20PbCl_2$ (GPCl) glass and $55GeO_2$–25(BaO + ZnO + K_2O)– 20PbO –$0.05Tm_2O_3$–$1Yb_2O_3$ (GPOTY) glass were also prepared. About 20 g batches of the well-mixed raw materials were melted at 1300 °C for 30 min in covered aluminium oxide crucibles in an electronic furnace with O_2 atmosphere. When the melting was completed, the liquid was cast into stainless-steel plate. The obtained glasses were annealed for several hours at the glass transition temperatures before cooling them to room temperature at a rate of 20 °C/h, and then were cut and polished carefully in order to meet the requirements for optical measurements.

The Raman spectrum was recorded on a FT-Raman spectrophotometer (Nicolet MODULE) within the range of 100–1000 cm^{-1}. Nd: yttritium–aluminum–garnet operating at 1064 nm was used as the excitation source and the laser power level was 500 mW.The upconversion luminescence spectrum was obtained with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with a maximum power of 2 W. In order to compare the luminescence intensity of GPClTY and GPOTY glasses as accurate as we can, the position and power (90 mW) of the pumping beam and the width (1 mm) of the slit to collect the luminescence signal were fixed under the same condition, and the sample was set at the same place in the experimental setup. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Upconversion fluorescence analysis

The room temperature upconversion luminescence spectra of GPClTY and GPOTY glass in the