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Comparative investigation of up-conversion luminescence in Tm^{3+}-doped oxide–chloride germanate and tellurite glasses

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Abstract

Tm^{3+}-doped oxide–chloride germanate and tellurite glasses have been synthesized by conventional melting method. Intense up-conversion luminescence emissions were simultaneously observed at room temperature in these glasses. The possible up-conversion mechanisms are discussed and estimated. However, in these Tm^{3+}-doped glasses, tellurite glass showed weaker up-conversion emissions than germanate glass, which is inconsistent with the prediction from the difference of maximum phonon energy between tellurite and germanate glasses. In this paper, Raman spectroscopy was employed to investigate the origin of the difference in up-conversion luminescence in the two glasses. Our results confirm that, besides the maximum phonon energy, the phonon density of host glasses is also an important factor in determining the up-conversion efficiency.

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1. Introduction

In recent years, the development of laser diode (LD) pumped up-conversion lasers is a promising concept towards all solid-state visible wavelength lasers [1]. Optical properties of trivalent lanthanide ions such as Er^{3+}, Ho^{3+}, Tm^{3+} and Nd^{3+} in glasses have been extensively studied to develop up-conversion visible or ultraviolet lasers, which can be operated at room temperature [1–6]. Tm^{3+} ion has stable excited levels suitable for emitting blue and ultraviolet up-conversion fluorescence. Recently, it was reported that a blue up-conversion 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 up-conversion in Tm^{3+}-doped glasses [9]. Host material for Tm^{3+} ion plays an important role in obtaining high-efficient up-conversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR) and thus achieves strong up-conversion luminescence [10,11]. However, in our present work, we found that germanate glass has higher maximum phonon energy than that of tellurite glass yet it possesses a better up-conversion luminescence. Hence, the consideration of maximum phonon energy alone may be not sufficient to explain the up-conversion efficiency. Raman scattering, which studies the interaction between photons and high frequency optical phonons caused by vibration of molecules and atoms in matter, is a nondestructive and convenient diagnostic tool for material characterization and

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analysis [12]. Compared with phonon side-band spectroscopy, Raman spectroscopy extracts more information including both phonon energy and phonon density. In this paper, the effect of phonon density on up-conversion luminescence properties in Tm^{3+}-doped oxide–chloride germanate and tellurite glasses have been investigated. Our results reveal that, besides the maximum phonon energy, the phonon density of host glasses is also an important factor in determining the up-conversion efficiency.

2. Experiments

The starting materials are reagent-grade $PbCl_2$, Nb_2O_5, Bi_2O_3, $ZnCl_2$, Na_2O, TeO_2 and high-purity GeO_2, Yb_2O_3, Tm_2O_3 and Er_2O_3 (>99.999%). The studied glasses were prepared in the compositions: (mol%) $60GeO_2$–$15Nb_2O_5$–$(24.95-x)PbCl_2$–$0.05Tm_2O_3$–xYb_2O_3 (GNPx) and $75TeO_2$–$20ZnCl_2$–$(4.95-x)Na_2O$–$0.05Tm_2O_3$–xYb_2O_3 (TZNx) (x=0.25, 0.5, 1, 1.5, and 2). Undoped oxide–chloride germanate and tellurite glasses were also prepared for measuring the Raman spectra. All these glasses were synthesized by conventional melting method. 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. The annealed samples were cut using a low-speed diamond saw and polished with 5-μm diamond paste. The polished samples have plate shapes with $20\times10\times1\ mm^3$ for optical measurements. The Raman spectrum was recorded on a FT-Raman spectrophotometer (Nicolet MODULE). In order to compare the stretching vibrations of the different composition samples as accurate as we can, the laser power level and scan frequency were fixed under the same condition. The visible up-conversion luminescence measurements were performed with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with the maximum power of 2 W. Blue luminescence decays were measured using a modulated 975 nm laser and a computer-controlled digitizing oscilloscope. The lifetime was calculated by fitting the exponential function to the decay data. All the measurements were performed at room temperature.

3. Results and discussion

The room temperature up-conversion luminescence spectra of GNP2 and TZN2 glasses in the wavelength region from 400 to 700 nm are shown in Fig. 1. Two emission bands centered at around 477 and 650 nm corresponding to the transitions $^1G_4\rightarrow{}^3H_6$ and $^1G_4\rightarrow{}^3H_4$ of Tm^{3+}, respectively, were simultaneously observed. Clearly, the red emission at 650 nm is much weaker than the blue emission at 477 nm in GNP2 and TZN2 glasses. It is also important to point out that the intense blue up-conversion fluorescence is bright enough to be observed by the naked eye at excitation power as low as 60 mW for GNP2 and TZN2 glasses. In frequency up-conversion process, the up-conversion emission intensity I_{up} increases in proportion to the nth power of infrared (IR) excitation intensity I_{IR}, that is, $I_{up}\propto I_{IR}^n$, where n is the number of IR photons absorbed per visible photon emitted. A plot of

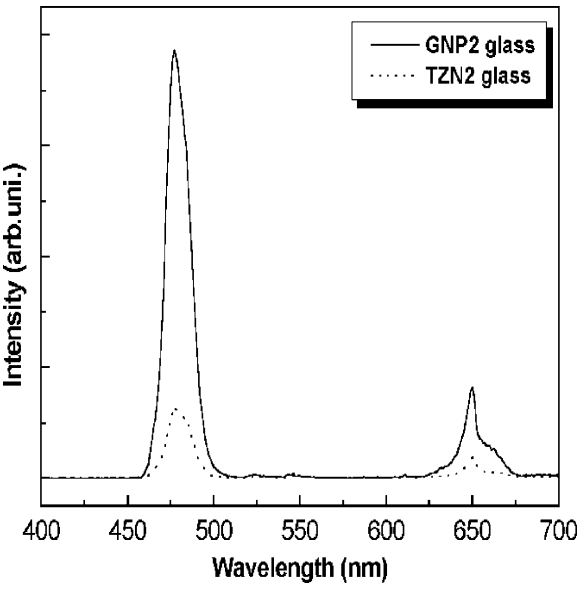

Fig. 1. The room temperature up-conversion spectra of GNP2 and TZN2 glasses under 975 nm LD excitation.

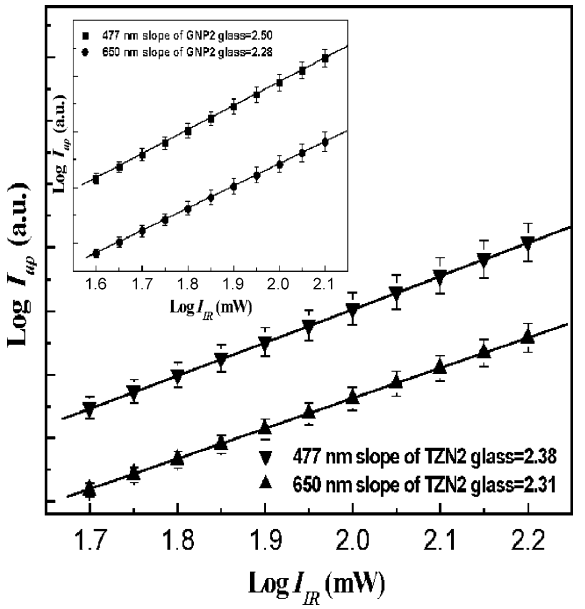

Fig. 2. Dependence of up-conversion fluorescence intensity on excitation power under 975 nm LD excitation for GNP2 and TZN2 glasses.