



Influence of La/Al ratio on the structure and spectroscopy of Tm³⁺ doped Al₂O₃–La₂O₃–SiO₂ glasses



Xue Wang^{a, b}, Shuai Kang^{a, b}, Shaohua Fan^{a, b}, Shikai Wang^{a, **}, Chunlei Yu^a,
Danping Chen^a, Lili Hu^{a, *}

^a Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

^b University of Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

Lanthanum aluminosilicate (LAS) glasses with compositions (Tm₂O₃)_{0.8}–(Al₂O₃)_{12–x} (La₂O₃)_x–(SiO₂)_{87.2} (x = 0, 1.2, 4.5 mol%; La/Al = 0, 1/9, 3/5) were prepared via a sol–gel method combined with high temperature sintering. The total amount of Al₂O₃ and La₂O₃ was 12 mol%. The effect of the La/Al ratio on the structure and spectroscopic properties of Tm³⁺ has been studied in detail. The structure of Tm³⁺ doped LAS glasses was studied via ²⁷Al nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The spinning sideband patterns of the ²⁷Al NMR spectra showed that the population of Tm³⁺ ions in the vicinity of Al³⁺ decreased with an increase in the La₂O₃ concentration. FTIR and Raman spectra suggest that glasses with high La/Al ratios have less interconnected glass networks. The spectroscopic properties of Tm³⁺ ions were investigated via the Judd–Ofelt method using the measurement of absorption and emission spectra. Both the 1.8 μm fluorescence intensity and the relative intensity of up-conversion emission of Tm³⁺ ions decrease with an increase in the La/Al ratio. This indicates reduced cross relaxation between Tm³⁺ ions in glass with a high La/Al ratio. We conclude that the spatial distribution homogeneity of Tm³⁺ ions in LAS glass improves when the La/Al ratio increases.

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1. Introduction

In recent years, thulium-based fiber laser systems have been recognized as attractive alternatives to the high power laser sources which facilitate the generation of radiation in the 1.8–2.1 μm spectral region [1,2]. Lanthanum-alumina-silicate (LAS) glasses have high glass transition temperatures and beneficial mechanical and optical properties such as high Vickers hardnesses, Young's moduli and refractive indices, combined with excellent corrosion resistance [3,4]. Hence, LAS glass is a promising material for lasing ions.

Thulium-based fibers can be pumped efficiently by commercially available high power diode lasers, which emit at around 790 nm. An electron promoted to the excited state through the absorption of one pump photon has the energetic potential to release two laser photons because of cross-relaxation (CR) energy

transfer (³H₄, ³H₆ → ³F₄, ³F₄) between Tm³⁺ ions pumped with a 790 nm laser diode [5]. Thus, the glass composition must be synthesized carefully so as to favor the proximity of thulium ions, while not inducing much up-conversion emission. Therefore, bulk glasses with larger Tm³⁺ concentrations and less clustering are necessary. However, this cannot be achieved using pure SiO₂ as the host material due to its poor solvation of RE ions. The solubility of rare earth ions may be increased by co-doping with Al³⁺ or P⁵⁺ ions in silica glasses [6] or by introducing RE³⁺ ions into a M₂O–SiO₂ based glass that generally permits the formation of homogeneous amorphous phases [7].

It has been reported that Y³⁺ codoping into different Er³⁺-doped Al₂O₃ hosts in sol–gel processes can reduce the concentration quenching effect [8,9]. Ting et al. first obtained an increase in Er³⁺–Er³⁺ separation caused by Y³⁺ codoping in Er³⁺–Y³⁺-codoped TiO₂ films [8]. Nga et al. further confirmed that Y³⁺ codoping improves the dispersion of Er³⁺ in Er³⁺-doped SiO₂–Al₂O₃ glasses, leading to strong emission intensities [9]. Several studies have suggested that co-doping of the fiber core with another type of RE element can suppress concentration quenching of Er³⁺ ions

* Corresponding author.

** Corresponding author.

E-mail addresses: woshiwsk@163.com (S. Wang), hulili@siom.ac.cn (L. Hu).

[10–12].

CR can easily occur when the distance between two Tm^{3+} ions decreases. This process reduces the population of Tm^{3+} at the ${}^3\text{H}_4$ energy level and increases the quantity of ions at the ${}^3\text{F}_4$ energy level and the 1.8 μm emission intensity [13,14]. Therefore, emission spectra can be used to investigate the spatial distribution of Tm^{3+} ions when La_2O_3 is added to silica glass. The effect of the La/Al ratio on the spectroscopic characterization of Tm^{3+} ions was studied using absorption and emission spectra. The structures of glasses were studied systematically via ${}^{27}\text{Al}$ MAS NMR, FTIR and Raman spectroscopy. Co-doping with La^{3+} is found to be an effective way to homogenize the spatial distribution of Tm^{3+} ions in this glass.

2. Experiments

Glasses with compositions $(\text{Tm}_2\text{O}_3)_{0.8}(\text{Al}_2\text{O}_3)_{12-x}(\text{La}_2\text{O}_3)_x(\text{SiO}_2)_{87.2}$ ($x = 0, 1.2, 4.5$ mol %) (simplified as TLAS1, TLAS2 and TLAS3, respectively) were prepared via a sol-gel method combined with high temperature sintering. Tetraethoxysilane (TEOS), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ were chosen as the precursors. Hydrochloric acid and deionized water were added to sustain the hydrolysis reaction. The analytically pure reagents were weighed and then stirred for 24 h at 30 °C to form homogeneous and clear doping sols. The sol was heated from 70 °C to 1100 °C to produce dry gel powders in which organics were nearly all decomposed. Then the powder was sintered in vacuum at 1750 °C for 3 h to form glass.

The glass was polished into chips 2 mm thick for optical property measurements. NMR measurements were carried out at a magnetic field strength of 11.7 T. ${}^{27}\text{Al}$ magic angle spinning (MAS)-NMR spectra were acquired at a resonance frequency of 130.3 MHz, using a Bruker Avance III HD 500 MHz NMR spectrometer equipped with a 4 mm MAS-NMR probe operated at a rotor frequency of 12.0 kHz. A typical pulse length was 0.95 μs (30° solid flip angle) and the relaxation delay was 0.2 s. The number of accumulated transients is 102400. Chemical shifts are referenced to a 1 M aqueous solution of $\text{Al}(\text{NO}_3)_3$. Fourier transform infrared spectroscopy (FTIR) was performed using a Nexus FT-IR Spectrometer and a Thermo Nicolet spectrophotometer. The absorption spectra were recorded using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrophotometer in the range of 250–2000 nm. The up-conversion emission spectra of the Tm-doped glass were measured with an Edinburgh FLS920 type spectrometer using a Xenon arc lamp (150 W) as the excitation source. The emission spectra were measured using an Edinburgh FLS920 type spectrometer with an 808 nm laser diode as its excitation source. The fluorescence lifetime was measured via pulsed 808 nm LD excitation using the instrument FLSP 920. All measurements were conducted at room temperature.

3. Results and discussion

3.1. Raman and FTIR spectra

The room temperature Raman and FTIR absorption spectra of TLAS glasses are shown in Fig. 1(a) and Fig. 1(b), respectively. Raman spectroscopy studies of silicate glasses show the formation of orthosilicate structural units, silicon–oxygen stretching vibrations of tetrahedral silicate units, symmetric stretching vibrations of silicate tetrahedra, inter-tetrahedral Si–O–Si linkages, and the structural unit Q_n^{Si} , where Q represents the tetrahedral unit and n is the number of bridging oxygens (BO) per tetrahedron [15]. The broad bands of the Q_n units with $n = 4, 3, 2, 1,$ and 0 are centered around 1200, 1100, 950, 900, and 850 cm^{-1} respectively [16]. These values shift to lower wavenumbers replacing the Si by Al atom as a

consequence of the weaker Al–O bond. In Fig. 1(a) there is a broad band centered at about 1050 cm^{-1} in TLAS1 and TLAS2 glasses, which indicates that there is a distribution of Q_n units, most of which are Q_3 units. The main band is shifted to 980 cm^{-1} in TLAS3 glass, which indicates that most of the Q_n units are Q_2 units. Comparing Raman spectra of the TLAS1 and TLAS2 glasses, the broadening of the Q_3 band toward higher wavenumbers indicates the possible presence of Q_4 in TLAS1. However, the Q_3 band of TLAS2 glass extends towards both lower and high wavenumbers. This suggests that both Q_2 and Q_4 units may have been present when La_2O_3 was added to the silica glass. The band at 800 cm^{-1} is characterized by the vibrations of Si and Al atoms on a tetrahedral cage of oxygen. Such vibrations exist only in a highly polymerized network [17]. The 800 cm^{-1} band intensity decreases as the La/Al ratio increases. This indicates a decrease in polymerized SiO_4 and AlO_4 tetrahedra. The relative intensity of the 600 cm^{-1} band suggests the presence of three-membered SiO_4 ring structures [18]. The intensity of this band also decreases with increasing La/Al ratio. Therefore, Raman spectra of TLAS series glasses suggest that a less interconnected glass network is formed as the La/Al ratio increases.

For FTIR absorption spectra, the shoulder peak at 950 cm^{-1} can be attributed to the stretching vibration of terminal Si–O[−] groups [19]. As suggested by Handke et al., termination of Si–O[−] groups is generated by breaking Si–O–Si units via the introduction of network modifiers [20]. The relative intensity of the Si–O[−] groups in Fig. 1(b) increases with the La/Al ratio. This increases the population of Si–O–RE (RE = Tm, La) in TLAS3 glasses. Hence, La^{3+} ions can depolymerize the network structure of TLAS glass. FTIR spectra are in good agreement with the Raman spectra. According to the Raman and FTIR absorption spectra of TLAS glasses, TLAS glass develops a less interconnected glass network when the La/Al ratio is increased.

3.2. ${}^{27}\text{Al}$ NMR spectroscopy

Fig. 2 shows the ${}^{27}\text{Al}$ MAS NMR spectra of both TLAS glasses with three different La/Al ratios. The spectra are characterized by three principal resonances at chemical shifts of 50, 30, and 0 ppm, which represent aluminum species with coordination numbers of four, five, and six (Al(4), Al(5), and Al(6)), respectively [21,22]. The ‘central’ 1/2 to −1/2 transition of ${}^{27}\text{Al}$ NMR signals are significantly broadened by paramagnetic interactions between the ${}^{27}\text{Al}$ and the electron spins of the Tm ions. In Fig. 2, it is shown that an increase in the La/Al ratio leads to an obvious increase in the fraction of Al(4) species, along with a significant decrease in the amount of Al(6). In Fig. 2, sidebands from the central’ 1/2 to −1/2 transition are observed at chemical shifts of 210, 118, −23, −182, and −295 ppm for TLAS1. Sidebands from the central’ 1/2 to −1/2 transition are also observed at chemical shifts of 118 and −23 ppm for TLAS2 and TLAS3. It is found that the number of sidebands decreases as the La/Al ratio in TLAS glasses increases. It is known that interaction between Al^{3+} and Tm^{3+} ions leads to the formation of sidebands in ${}^{27}\text{Al}$ MAS NMR spectra [23,24]. The decrease in spinning sideband patterns in the ${}^{27}\text{Al}$ MAS NMR spectrum indicates that the population of Tm^{3+} ions around Al^{3+} and the interaction between Tm^{3+} and Al^{3+} ions decreases with an increase in the La/Al ratio.

According to the results of Raman, FTIR and NMR spectra of TLAS glasses, with increase of La/Al ratio, the Q_2 units (SiO_4 tetrahedron with two bridging oxygen) increases, AlO_4 unit increases, AlO_6 unit decreases, and more La^{3+} and Tm^{3+} ions can coordinate with Si–O– and form LaO_6 and TmO_6 polyhedra [25,26]. In TLAS1 glass, most of the second coordinating layer of Tm^{3+} is Al^{3+} , while it can be either Al^{3+} or Si^{4+} in TLAS3 glass. Therefore, compared with TLAS1 glass, the spatial distribution of Tm^{3+} ions in TLAS3 glass is more homogenous.

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