# Spectroscopic properties of $Tm^{3+}$–$Ho^{3+}$ codoped $SiO_2$–$Al_2O_3$–CaO–SrO glasses

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## Abstract

$Tm^{3+}$–$Ho^{3+}$ codoped $50SiO_2$–$10Al_2O_3$–$25CaO$–$15SrO$ glasses with good thermal stability are prepared by a melt-quenching method. Efficient emission of $Ho^{3+}$:$^5I_7$ is observed upon excitation with an 800 nm laser. The sample doped with 1 mol% $Tm_2O_3$ and 0.1 mol% $Ho_2O_3$ presents a broadband spectrum with a full width at half-maximum of 345 nm. The sample doped with 1 mol% $Tm_2O_3$ and 0.7 mol% $Ho_2O_3$ has the maximum emission intensity of Ho:$^5I_7$ to $^5I_8$. With increased $Ho_2O_3$ content, the fluorescence intensity ratio of emission from Ho:$^5I_7$ to that from Tm:$^3F_4$ linearly increases. The emission cross-section and energy-transfer efficiency are also calculated. The maximum emission cross-section of the transition from Ho:$^5I_7$ to $^5I_8$ is $3.72 \times 10^{-21}$ $cm^2$ at 2065 nm. When the sample is doped with 1 mol% $Tm_2O_3$ and 1 mol% $Ho_2O_3$, the transfer efficiency from $Tm^{3+}$ to $Ho^{3+}$ is 0.954. The emission cross-section, energy-transfer constants, and fluorescence efficiency in $50SiO_2$–$10Al_2O_3$–$25CaO$–$15SrO$ glass are larger than those in silicate glasses without alkali ions, indicating that $50SiO_2$–$10Al_2O_3$–$25CaO$–$15SrO$ glass is a favorable glass host for 2 μm lasers.

## 1. Introduction

Laser sources operating at 2 μm wavelength have many features with potential applications, such as the monitoring of atmospheric pollutants, medical surgery, high-resolution spectroscopy of low-pressure gases, and eye-safe laser radar [1–3]. Thus, researchers are searching for efficient, compact, and cheap sources of laser radiation at this wavelength. Among such sources, $Tm^{3+}$- and $Ho^{3+}$-doped glass lasers have great potential [4–7]. Drawing rare-earth doped glass into fibers is an effective way of producing laser output. Accordingly, complete knowledge of the spectroscopic properties of $Tm^{3+}$ and $Ho^{3+}$, as well as the thermal stabilities of laser materials, is necessary.

Unlike thulium ions, $Ho^{3+}$ cannot be directly pumped by a readily available, high-power, and low-cost diode laser source. To solve this problem, $Ho^{3+}$-doped glasses are sensitized by $Tm^{3+}$, $Er^{3+}$, or $Yb^{3+}$ [8–10]. Compared with the other two sensitizers, $Tm^{3+}$ has low energy loss, and laser output is realized using $Tm^{3+}$–$Ho^{3+}$ codoped fibers [6,11].

Compared with other kinds of glasses, silicate glasses have many advantages, including low cost, stable thermal properties, excellent mechanical properties, and low thermal expansion coefficient. A mode-locked laser using Tm–Ho codoped fiber has been reported [12]. However, most of the investigated silicate laser glasses contain alkali metal ions, which are harmful to 2 μm emission compared with alkaline earth ions [13]. Thus, in the present study, the host glass is $SiO_2$–$Al_2O_3$–CaO–SrO.

## 2. Experimental

The studied silicate glasses are composed (in mol%) of $50SiO_2$–$10Al_2O_3$–$25CaO$—$15SrO$–$1Tm_2O_3$–$xH_2O_3$ (where $x=0$, 0.1, 0.2,

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0.4, 0.7, and 1), with the corresponding samples denoted as S0, S0.1, S0.2, S0.4, S0.7, and S1, respectively. The mixed powders are melted at 1470 °C for 1 h, cast on a preheated steel plate, and annealed for several hours at 750 °C. During melting, oxygen is induced into the molten glass for 0.5 h to eliminate the hydroxyl group. Annealed glasses sized $10 \times 10 \times 1$ mm$^3$ are fabricated and polished for optical property measurements.

Refractive index and density are measured by the prism minimum deviation method and Archimedes method using distilled water as immersion liquid respectively. Absorption spectra are recorded with a PerkinElmer Lambda 900 UV/VIS/NIR spectrophotometer. Infrared transmittance is measured with a Thermo Scientific Nicolet spectrophotometer. Emission spectra are measured with an Edinburg FL920 type spectrophotometer. All measurements are carried out at room temperature.

## 3. Results and discussion

### 3.1. Thermal stability

The differential scanning calorimetry (DSC) curve of S0 is shown in Fig. 1. The glass transition temperature ($T_g$) and onset crystallization temperature ($T_x$) are 765 and 1039 °C, respectively. The temperature difference $\Delta T = T_x - T_g$ is used to determine the stability of a glass against devitrification [14]. $\Delta T$ of S0 is 274 °C, indicating its suitability for fiber drawing.

### 3.2. Absorption spectra and Judd–Ofelt analysis

The room-temperature absorption spectra of all samples are measured from 300 nm to 2500 nm. The spectra of all Tm–Ho codoped samples are similar, and the absorption intensity is proportional to the mole fractions of rare-earth ions. For example, the absorption spectra of S0 (Tm singly doped) and S1 (Tm–Ho codoped) are shown in Fig. 2. The absorption bands corresponding to the transitions are labeled. An obvious absorption band exists at around 790 nm, which indicates that the glass can be efficiently excited at 800 nm. The absorption
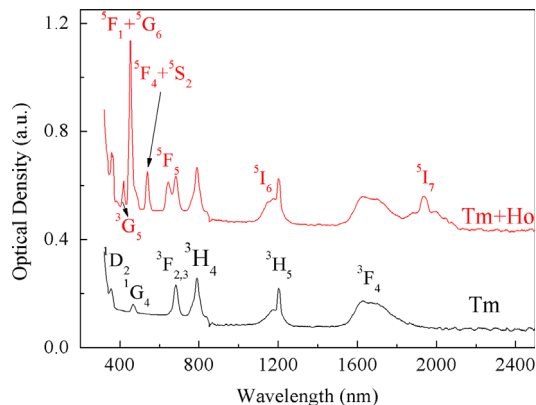


Fig. 1. DSC of 50SiO$_2$–10Al$_2$O$_3$–25CaO–15SrO glass.



Fig. 2. Absorption spectra of 50SiO$_2$–10Al$_2$O$_3$–25CaO–15SrO glasses doped with 1 mol% Tm$_2$O$_3$ (black) and codoped with 1 mol% Tm$_2$O$_3$ and 1 mol% Ho$_2$O$_3$ (red).

band of Tm:$^3F_4$ is close to that of Ho:$^5I_7$, indicating high-efficiency energy transfer (ET) from Tm:$^3F_4$ to Ho:$^5I_7$.

The Judd–Ofelt theory is widely used to evaluate spectroscopic properties of rare-earth-doped glasses. The Judd–Ofelt parameters indicating the local environment and bond property of rare-earth ions can be calculated based on the absorption spectra. $\Omega_2$, $\Omega_4$, and $\Omega_6$ of Ho$^{3+}$ in S1 are $4.63 \times 10^{-20}$, $2.08 \times 10^{-20}$, and $0.97 \times 10^{-20}$ cm$^2$, respectively. The Judd–Ofelt parameters of Ho$^{3+}$ in our glass and other common glasses are listed in Table 1. The fluoride glass host yields comparatively small $\Omega_2$, whereas germanate, tellurite, and silicate glasses show relatively large $\Omega_2$, as shown in Table 1. $\Omega_2$ is sensitive to covalent bonding, so oxide glasses have a larger degree of covalent bonding than that of fluoride glass. $\Omega_2$ of Ho$^{3+}$ is larger in S1 than in a previously reported silicate glass [15]. This difference is due to the variation in the local environment of Ho$^{3+}$ in different glasses. Different species of modifying elements tend to be distributed in modifier-rich regions, so the modifier ions significantly influence Judd–Ofelt parameters. The silicate glasses in this study do not contain alkali ions, so the distortion around Ho$^{3+}$ ion is larger than that around silicate with alkali ions, thereby resulting in a larger $\Omega_2$ [13].

Judd–Ofelt parameters can be used to calculate the transition probability $A$ and radiative lifetime $\tau_{rad}$. These two parameters can be determined by the following expressions:

$$A = 1/\tau_{rad} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \left[ \frac{n(n^2+1)^2}{9} S_{ED} + n^3 S_{MD} \right], \quad (1)$$

$$S_{ED} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle S, L, J || U^{(\lambda)} || S', L', J' \rangle|^2, \quad (2)$$

$$S_{MD} = \left( \frac{\hbar}{2mc} \right)^2 |\langle S, L, J || L + 2S || S', L', J' \rangle|^2, \quad (3)$$

where $m$ and $e$ are the mass and charge of the electron, $n$ is the refractive index, $J$ is the total angular momentum at the ground state, $|U^{(\lambda)}|$ is the reduced matrix element insensitive to the host environment, and $S_{ED}$ and $S_{MD}$ are the line strengths for electric and magn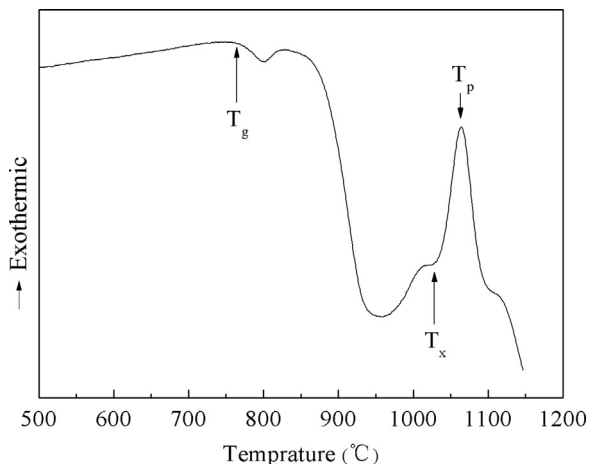etic dipole transitions, respectively. Only when $S = S'$