Judd-Ofelt Parameters of Sm$^{3+}$-doped Alkali Telluroborate Glasses

Vu Phi Tuyen*

Graduate University of Science and Technology - VAST, Hanoi, Vietnam

Received 15 January 2016
Revised 22 February 2016; Accepted 21 March 2016

Abstract: Alkali borotellurite glass (ABTe) doped with concentration of 0.5 mol% Sm$^{3+}$ ions was prepared by melting method. The absorption, luminescence spectra and lifetime of ABTe:Sm$^{3+}$ have been measured at room temperature. The results were analyzed using Judd–Ofelt (JO) theory, that gives the $\Omega$ intensity parameters, transition probabilities ($A_g$), calculated branching ratios ($\beta_c$), measured branching ratios ($\beta_{meas}$) and stimulated emission cross-sections ($\sigma_{sp}$) for $^4G_{5/2}\rightarrow^4H_J$ transitions.

Keywords: Alkali borotellurite glass, Judd-Ofelt theory.

1. Introduction

Samarium with 4f$^5$ electron configuration usually exists in triply ionized (Sm$^{3+}$), which is a quite popular rare earth element. The optical properties of Sm$^{3+}$ ions doped glasses have been extensively investigated due to their wide applications in many optical devices like: lasers, sensors, high-density memories, undersea communications and optical amplifiers [1,2]. Recently there have been many reports on optical properties of Sm$^{3+}$ doped glasses to which TeO$_2$ component was added. Besides, the authors also gives the application prospects of these glasses [1-4].

In this work, the optical properties of Sm$^{3+}$ in borotellurite glass with co-former B$_2$O$_3$ and TeO$_2$ (TeO$_2$-B$_2$O$_3$-Na$_2$O-CaO-Al$_2$O$_3$-Sm$_2$O$_3$) being a low phonon energy and high refractive index material [1-4] have been investigated by using Judd-Ofelt theory. The different types of network modifier like Na$_2$O, CaO and Al$_2$O$_3$ were added to borotellurite glass to improve their chemical durability and alter the physico-chemical properties. Al$_2$O$_3$ has received significant consideration as the most likely useful matrix composition due to its high solubility of the RE$^{3+}$ ions.

2. Experiments

Alkali-borotellurite glass (ABTe) with the composition of 44.5TeO$_2$+30B$_2$O$_3$+5Al$_2$O$_3$+10Na$_2$O +10CaO+0.5Sm$_2$O$_3$ was prepared by conventional melt quenching. The optical absorption spectrum

*Tel.: 84-1299958668
Email: tuyenvuphi@yahoo.com

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was obtained between wavelengths 300 and 2000 nm using Jascco V670 spectrometer. The photoluminescence spectrum was recorded by Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd-Ofelt parameters

Absorption spectra of the ABTe:0.5 mol%Sm$^{3+}$ glass in two regions of wavelength 350–500 nm and 900–1700 nm are showed in Fig. 2. The observed 13 absorption bands were assigned to transitions from the $^6H_{5/2}$ ground state to the $^6H_{5/2}$ excited states of Sm$^{3+}$ ions by using Carnall’s paper [5]. The $^6H_{5/2} \rightarrow ^4F_{3/2}$ and $^6H_{5/2} \rightarrow ^6F_{3/2}$ transitions obey the selection rule $\Delta S = 0$, $|\Delta J| \leq 2$ and $|\Delta L| \leq 2$, so these are hypersensitive transitions of Sm$^{3+}$ ions [4]. The position and intensity of these transitions strongly depend on structural and polarization of ligand. In the UV-Vis regions, the various $2S+1LJ$ energy levels are very close to each other. Therefore, the absorption transitions are overlapped and that creates broad bands. The strongest intensity in this region corresponds to $^6H_{5/2} \rightarrow ^4P_{3/2}$ transition (at the wavelength of 402 nm). This transition is a spin allowed transition which is normally used for fluorescence excitation. The energies of these absorption transitions of Sm$^{3+}$ ion in glass host are also compared with Sm$^{3+}$-diluted acid solution (aquo-ion) system [5] and show in Table 1. From transition energies, the nephelauxetic ratio ($\bar{\beta}$) and Sm$^{3+}$-ligand bonding parameter ($\delta$) have been calculated by using the formulas in references [6,7]. For ABTe:Sm$^{3+}$, the values of $\bar{\beta}$ and $\delta$ are 1.0036 and -0.29, respectively. Thus, the bonding of Sm$^{3+}$ ions with the local host is ionic bond [1-4].
Table 1. Energy transitions ($\nu$), bonding parameters ($\delta$), the experimental ($f_{\text{exp}}$) and calculated ($f_{\text{cal}}$) oscillator strengths for ABTe:Sm$^{3+}$ glass

<table>
<thead>
<tr>
<th>Transition $^6H_{15/2}$ $\rightarrow$</th>
<th>$\nu_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$\nu_{\text{aqua}}$ (cm$^{-1}$)</th>
<th>$f_{\text{exp}} \times 10^{-6}$</th>
<th>$f_{\text{cal}} \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6F_{1/2}$</td>
<td>6.302</td>
<td>6.400</td>
<td>0.36</td>
<td>0.92</td>
</tr>
<tr>
<td>$^6H_{15/2}$</td>
<td>6.534</td>
<td>6.508</td>
<td>1.54</td>
<td>0.03</td>
</tr>
<tr>
<td>$^6F_{5/2}$</td>
<td>6.760</td>
<td>6.630</td>
<td>3.89</td>
<td>3.45</td>
</tr>
<tr>
<td>$^6F_{3/2}$</td>
<td>7.181</td>
<td>7.100</td>
<td>6.05</td>
<td>5.93</td>
</tr>
<tr>
<td>$^6F_{7/2}$</td>
<td>8.143</td>
<td>8.000</td>
<td>6.45</td>
<td>6.46</td>
</tr>
<tr>
<td>$^6F_{9/2}$</td>
<td>9.270</td>
<td>9.200</td>
<td>4.25</td>
<td>4.11</td>
</tr>
<tr>
<td>$^6F_{11/2}$</td>
<td>10.558</td>
<td>10.500</td>
<td>0.72</td>
<td>0.67</td>
</tr>
<tr>
<td>$^4I_{9/2},^4I_{11/2},^4I_{13/2}$</td>
<td>21.262</td>
<td>20.800</td>
<td>3.11</td>
<td>2.89</td>
</tr>
<tr>
<td>$^4I_{15/2}$</td>
<td>22.770</td>
<td>22.700</td>
<td>0.59</td>
<td>0.35</td>
</tr>
<tr>
<td>$^4M_{17/2}$</td>
<td>23.950</td>
<td>24.050</td>
<td>1.53</td>
<td>1.64</td>
</tr>
<tr>
<td>$^6F_{5/2},^6P_{3/2}$</td>
<td>24.743</td>
<td>24.950</td>
<td>12.75</td>
<td>12.71</td>
</tr>
<tr>
<td>$^6F_{7/2}$</td>
<td>26.641</td>
<td>26.750</td>
<td>2.98</td>
<td>2.93</td>
</tr>
<tr>
<td>$^6P_{7/2}$</td>
<td>27.575</td>
<td>27.700</td>
<td>3.64</td>
<td>2.95</td>
</tr>
<tr>
<td>$^4D_{3/2},^4D_{5/2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\beta = 1.0036$, $\delta = -0.29$  
$\text{rms} = 0.59 \times 10^{-6}$

3.2. Judd-Ofelt parameters

The Judd-Ofelt (JO) theory \cite{8,9} was shown to be useful to characterize radiative transitions for RE-doped solids, as well as RE-doped aqueous solutions. This theory defines a set of three intensity parameters, $\Omega_\lambda$ ($\lambda = 2, 4, 6$), that are sensitive to the environment of the rare-earth ions and can be used to predict a lot of the spectroscopic parameters of the rare earth ions in the host materials. According to the JO theory, the electric dipole oscillator strength of a transition from the ground state to an excited state is given by

$$f_{\text{cal}} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \left( \frac{n^2 + 2}{9n} \right)^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \Psi J \left| U^\dagger \right| \Psi' J' \right\rangle^2$$

(1)

where $n$ is the refractive index of the material, $J$ is the total angular momentum of the ground state, $\Omega_\lambda$ are the JO intensity parameters and $\left\langle U^\dagger \right| \left| \Psi' J' \right\rangle$ are the squared doubly reduced matrix of the unit tensor operator of the rank $\lambda = 2, 4, 6$, which are calculated from intermediate coupling approximation for a transition $|\Psi J\rangle \rightarrow |\Psi' J'\rangle$. These reduced matrix elements are nearly independent of host matrix as noticed from earlier studies \cite{4}.

On the other hand, the experimental oscillator strengths, $f_{\text{exp}}$, of the absorption bands are determined experimentally using the following formula \cite{1-4}

$$f_{\text{exp}} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu$$

(2)

where $\alpha$ is molar extinction coefficient at energy $\nu$ (cm$^{-1}$). The $\alpha(\nu)$ values can be calculated from absorbance $A$ by using Lambert–Beer’s law

$$A = \alpha(\nu) cd$$

(3)

where $c$ is RE$^{3+}$ concentration [dim: L$^{-3}$, units: mol/dm$^3$], $d$ is the optical path length [dim: L; units: cm]
By equating the measured and calculated values of the oscillator strength ($f_{\text{cal}}$ and $f_{\text{exp}}$) and solving the system of equations by the method of least squares, the JO intensities parameters $\Omega_\lambda$ ($\lambda = 2, 4$ and 6) can be evaluated numerically. In the case of ABTe:0.5mol%Sm$^{3+}$ glass, $\Omega_2 = 2.95 \times 10^{-20}$ cm$^2$, $\Omega_4 = 10.99 \times 10^{-20}$ cm$^2$ and $\Omega_6 = 5.26 \times 10^{-20}$ cm$^2$. The $\Omega_2$ is more sensitive to the local environment of the RE$^{3+}$ ions and is often related with the asymmetry of the local crystal field and the valency of RE$^{3+}$–ligand bond. The value of $\Omega_2$ in ABTe:Sm$^{3+}$ glass is smaller than that in TRZNB glass (6.81 \times 10^{-20} \text{cm}^2) [4] but is larger in B4TS glass (0.06 \times 10^{-20} \text{cm}^2) [4], PTBS glass (0.21 \times 10^{-20} \text{cm}^2) [2] and LGT10 glass (0.73 \times 10^{-20} \text{cm}^2) [1]. Thus the asymmetry of crystal field at the Sm$^{3+}$ ions site and covalency of Sm$^{3+}$-ligand bond in ABTe glass is lower than that in the TRZNB glasses but higher in B4TS, PTBS and LGT10 glasses.

3.4. Emission spectrum

The emission spectrum of the ABTe:Sm$^{3+}$ glasses was recorded using 402 nm excited wavelength and is shown in Fig. 2, the spectrum consists of 5 observed emission bands at wavelengths of 560, 600, 645, 710 and 795 nm which correspond to the $^4F_{5/2} \rightarrow ^6H_J$ ($J = 5/2, 7/2, 9/2, 11/2, 13/2$) transitions, respectively. Among emission transitions, the $^4G_{7/2} \rightarrow ^6H_{7/2}$ transition has the most intense intensity whereas the $^4G_{5/2} \rightarrow ^6H_{13/2}$ transition is very weak in intensity. The $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transitions are purely electric dipole transitions, whereas the $^4G_{5/2} \rightarrow ^6H_{5/2}$ and $^4G_{5/2} \rightarrow ^6H_{7/2}$ transitions include both electric and magnetic dipole transitions.

![Fig. 2. The emission spectrum of the ABTe:Sm$^{3+}$ glass.](image)

3.4. Radiative parameters

From the JO parameters and emission spectrum, the radiative properties of Sm$^{3+}$ ion such as: transition probabilities ($A_i$), radiative lifetime ($\tau_\text{R}$), branching ratios ($\beta_{\text{cal}}$ and $\beta_{\text{exp}}$), effective line width ($\Delta \lambda_{\text{eff}}$), stimulated emission cross-section ($\sigma(\lambda_P)$) and integrated emission cross section ($\Sigma_{ij}$) have been calculated for $^4G_{5/2} \rightarrow ^4H_J$ radiative transitions. The detail formulas for these parameters have been given in previous reports [6,7]. The results are displayed in Table 2.
Table 2. Radiative parameters of $^4G_{5/2} \rightarrow ^6H_J$ transition for Sm$^{3+}$ ions in ABTe:Sm$^{3+}$ glass

<table>
<thead>
<tr>
<th>$^4G_{5/2}$</th>
<th>$^6H_J$</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\beta_{\text{cal}}$ (%)</th>
<th>$\beta_{\text{exp}}$ (%)</th>
<th>$\Delta \lambda$ (nm)</th>
<th>$\Sigma_{ij} \times 10^{-18}$ cm</th>
<th>$\sigma \times 10^{-22}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6H_{5/2}$</td>
<td>17,746</td>
<td>5.20</td>
<td>6.50</td>
<td>9.33</td>
<td>0.52</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>16,674</td>
<td>49.90</td>
<td>45.60</td>
<td>12.85</td>
<td>5.48</td>
<td>14.82</td>
<td></td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>15,457</td>
<td>23.70</td>
<td>34.94</td>
<td>14.94</td>
<td>3.02</td>
<td>8.49</td>
<td></td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>14,158</td>
<td>14.24</td>
<td>10.86</td>
<td>24.12</td>
<td>2.18</td>
<td>4.46</td>
<td></td>
</tr>
<tr>
<td>$^6H_{13/2}$</td>
<td>12,623</td>
<td>1.72</td>
<td>2.10</td>
<td>36.68</td>
<td>0.32</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

It is noted that there is a good agreement between experimental ($\beta_{\text{exp}}$) and calculated ($\beta_{\text{cal}}$) branching ratios. The stimulated emission cross-section, integrated emission cross section and branching ratio are important parameters affecting the potential laser performance. These parameters of $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition gets a maximum value and they are larger than those of some other glasses [1-4]. Thus, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition of Sm$^{3+}$ ions in ABTe glass is found to be suitable for developing the visible laser and fiber optic amplifier.

Fig. 3. Luminescence decay profiles of the $^4G_{5/2}$ of Sm$^{3+}$ ions in ABTe glass

The emission decay profile of the $^4G_{5/2}$ excited state of Sm$^{3+}$ ions in ABTe glass was obtained by exciting the sample at 402 nm and was shown in Fig. 3. The measured lifetimes ($\tau_{\text{exp}}$) of samples have been determined by the formula:

$$\tau_{\text{exp}} = \frac{\int I(t)dt}{\int I(t)dt}$$ (4)

The measured lifetime of $^4G_{5/2}$ level is $\tau_{\text{exp}} = 1.31$ ms whereas the calculated lifetime is $\tau_{\text{cal}} = 1.79$ ms, respectively. The discrepancy between the measured and calculated lifetime may be due to the nonradiative transitions. The quantum efficiency of the fluorescent level is defined as: $\eta = \tau_{\text{exp}}/\tau_{\text{cal}}$ [7]. In this case, the luminescence quantum efficiency is 73.2 %. This relatively high value indicates that the nonradiative processes are not too strong at low-doping level of Sm$^{3+}$ ions in ABTe glass.
4. Conclusions

The optical properties of Sm$^{3+}$-doped alkali borotellurite glass have been investigated. Negative value for the bonding parameter indicates the ionic nature of Sm$^{3+}$-ligand bond in ABTe glass. Moreover, the small value of $\Omega_2$ shows that the coordination structure surrounding the Sm$^{3+}$ ions has high symmetry. By using JO theory, the radiative properties such as branching ratios, the stimulated emission cross-section and integrated emission cross section have been predicted. The results show that the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition of Sm$^{3+}$ ions in ABTe glass is acceptable for one of parameters of laser material emission and fiber optic amplifier.

References