

LUMINESCENCE QUENCHING OF Sm^{3+} IONS IN ALKALI BOROTELLURITE GLASSES

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Abstract. *The dependence of luminescence intensity on Sm^{3+} ions concentration in alkali borotellurite (ABTe) glasses has been studied. The quenching of luminescence intensity happens around 0.75 mol% concentration of Sm^{3+} ions and it can relate the energy transfer process through cross-relaxation (CR), the CR channels in ABTe: Sm^{3+} have been shown. The method of Van Uitert was used to find the dominant interaction mechanism for energy transfer process.*

Keywords: alkali borotellurite glass; luminescence quenching.

Classification numbers: 78.20.

I. INTRODUCTION

Borate glasses doped with trivalent rare earth (RE^{3+}) have been extensively investigated due to intriguing properties such as good transparency in the IR, low melting point and high solubility of rare earth [1–3]. Disadvantages of these glasses are high phonon energy with strong occurrence of multi-phonon and reduced luminescence efficiency of the material. The tellurite glass exhibits some outstanding features as low melting points, slow crystallization rates, good thermal and chemical stability, low cut off phonon energy in the order of $600\text{--}800\text{ cm}^{-1}$ and high refractive index, which favors the high spontaneous transition rates [4]. The presence of an amount of TeO_2 in the alkali borate glass can reduce the cut-off phonon energy of glass, which minimizes multi-phonon decay processes between energy levels which are very close to those of the lanthanide ions, and therefore the quantum efficiency of fluorescent processes increases [4, 5].

Among the RE^{3+} ions, Sm^{3+} ion is widely used in the fields such as undersea communications, high-density memories, colour displays and solid-state laser [1–5]. Recently there have been many investigations on optical properties of Sm^{3+} and the energy transfer process between Sm^{3+}

ions in $\text{B}_2\text{O}_3\text{-TeO}_2$ glasses [4–7]. Authors used Inokuti-Hirayama (IH) model to study the energy transfer process between Sm^{3+} ions in telluroborate [5–7]. However, this model only considers the cross-relaxation and ignores the energy migration, leading to a discrepancy between theory and experiment. In this work, we have studied the energy transfer process between Sm^{3+} ions through the generalization Yokota–Tanimoto (YT) model [8]. This model which takes into account both the energy migration and cross-relaxation so it is close to the practice and proved to be better than IH model [8, 9].

II. EXPERIMENTS

Alkali-borotellurite glass (ABTe) with the composition of $(45-x)\text{TeO}_2+30\text{B}_2\text{O}_3+5\text{Al}_2\text{O}_3+10\text{Na}_2\text{O}+10\text{CaO}+x\text{Sm}_2\text{O}_3$, where $x = 0.05; 0.1; 0.5; 0.75; 1.0; 1.5, 2.0$ and 3.0 mol% was prepared by conventional melt quenching. All the above weighed chemicals were well-mixed and heated for 120 min in a platinum crucible at 1300°C in an electric furnace, then cooled quickly to room temperature. The ABTe glasses were annealed at 350°C for 12 h to eliminate mechanical and thermal stress. The photoluminescence and excitation spectra were recorded by Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer.

III. RESULTS AND DISCUSSION

III.1. Emission spectra

The emission spectra of the ABTe: Sm^{3+} glass with different contents of Sm^{3+} (0.5, 0.75, 1.0 mol.%) are measured and showed in Fig. 1.

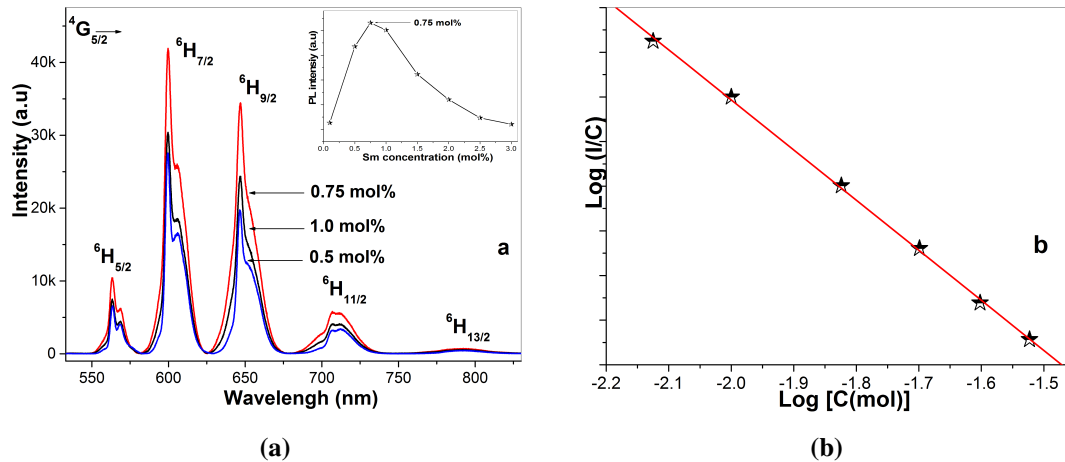


Fig. 1. a) Emission spectra of ABTe: Sm^{3+} glasses with several different values (C) of Sm^{3+} content (0.5, 0.75 and 1.0 mol.%); b) Plot of $\log(I/C)$ versus $\log(C)$ of ABTe: Sm^{3+} glasses.

There are five emission bands in the emission spectra of Sm^{3+} ions at peak wavelengths of 560, 600, 645, 710 and 795 nm which correspond to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2, 13/2$) transitions, respectively [10]. The ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ transition band has the most intense intensity whereas the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{13/2}$ transition is very weak intensity. The ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$ and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{13/2}$ transitions are purely electric dipole (ED) transitions, whereas the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ transitions include both electric and magnetic dipole (MD) transitions but the magnetic dipole is dominant mechanism in ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ transitions [6]. Thus, the intensity of the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transition band (red) strongly depends on the nature of ligand such as asymmetry and covalency of RE^{3+} -ligand bond whereas the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ transition band (orange) is less dependent on those. Therefore, the intensity ratio O/R (orange/red) can be used to evaluate the characteristics of the local environment around the RE^{3+} ions [5, 6]. The O/R ratios increase slightly from 1.04 to 1.12 in the ABTe:Sm samples when the concentration of Sm^{3+} increases from 0.05 to 3.0 mol%. The small change of these ratios indicates that the asymmetry of ligand and covalency of RE^{3+} -ligand bond nearly does not depend on the Sm^{3+} concentration. However, the values of the O/R ratios in ABTe:Sm glass are lower than those of the zinc potassium fluorophosphate (PKAMZF) [11], boro-tellurite (BTS) glasses [5] and telluroborate (TB) glass [6]. This indicates the asymmetry of crystal field at the RE^{3+} ions site and the covalency of RE^{3+} -ligand bond for ABTe glass is higher than those in the PKAMZ, BTS and TB glasses.

III.2. Concentration quenching mechanism of Sm^{3+} ions in ABTe glass

As shown in Fig. 1a, the luminescence intensity increases with the increasing of Sm^{3+} concentration and reaches a maximum about 0.75 mol %, then decreases. The change of total luminescence intensity is shown in the inset of Fig. 1a. The decrease of luminescence intensity over a certain concentration is called concentration quenching or self-quenching (SQC). The SQC phenomenon is due to the non-radiative processes consisting multiphonon relaxation and energy transfer between the pairs of Sm^{3+} ions [6, 11]. The multiphonon relaxation rate can be estimated by “energy gap law” that relates to the number of phonons needed to bridge the energy difference between fluorescent level ${}^4\text{G}_{5/2}$ and next lower level ${}^6\text{F}_{11/2}$. In the case of Sm^{3+} ions, this energy gap is around 7300 cm^{-1} which is 5 times higher than the highest phonon energy in borate glass (about 1400 cm^{-1}) [2, 6, 7]. Thus multiphonon relaxation rate is negligible and concentration quenching may be mainly due to energy transfer through cross-relaxation. This process can follow the path: an excited Sm^{3+} ion transfers energy by electric multipolar interaction to a neighboring Sm^{3+} ion in ground state. Both ions then enter into a ${}^6\text{F}_{n/2}$ state located in the middle from ${}^6\text{H}_{5/2}$ to ${}^4\text{G}_{5/2}$ level. Finally these ions relax to the ${}^6\text{H}_{5/2}$ ground level by multiphonon or infrared emission. The cross-relaxation (CR) channels in ABTe:Sm³⁺ glass may be: the resonant channel (RET (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$) \rightarrow (${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{5/2}$)) and nearly resonant channels (CR1: (${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{5/2}$) \rightarrow (${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{11/2}$)), (CR2: (${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{9/2}$) \rightarrow (${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{7/2}$)), (CR3: (${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{9/2}$) \rightarrow (${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{7/2}$)) and (CR4: (${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{11/2}$) \rightarrow (${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}$)) as the energy difference between these transitions is negligible [6–8]. The CR channels are shown in the energy level scheme of Sm^{3+} ion (Fig. 2), which has been determined from absorption, excitation (Fig. 3) and emission spectra of Sm^{3+} ion in ABTe glass.

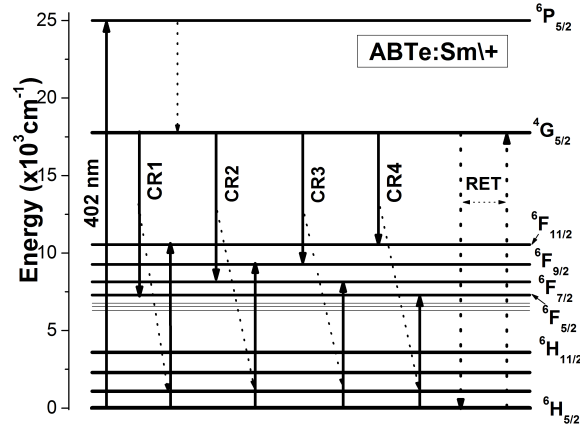


Fig. 2. Energy level diagram and cross-relaxation channels for Sm^{3+} ions in ABTe glass.

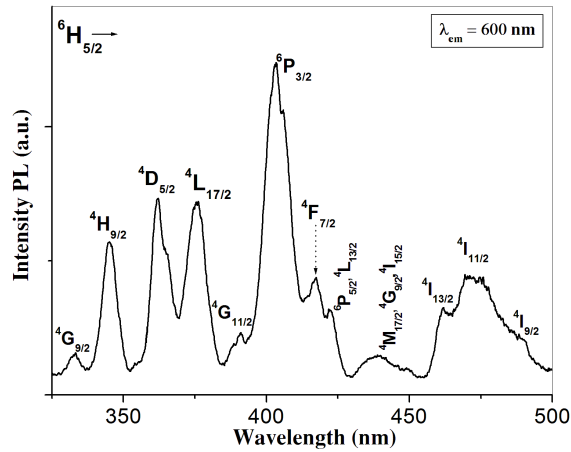


Fig. 3. Excitation emission spectrum of ABTe glass doped with 1.0 mol% of Sm^{3+} ions.

III.3. Interaction mechanism between the ions in energy transfer process

The main interaction mechanism between the ions is usually dipole-dipole (DD). However, it can happen by the interaction of higher order such as dipole-quadrupole (DQ), quadrupole-quadrupole (QQ) when the selected rule is not satisfied. Van Uitert has proposed the method to determine the main interaction mechanism through fluorescence spectra [12]. He showed when the doping contents are higher than quenching concentration, the dependence of total emission intensity on doping content obeys the equation [13]:

$$\log \frac{I}{C} = A - \frac{S}{3} \log C \quad (1)$$

where I is total emission intensity; C is the activator concentration; $S = 6, 8, 10$ for dipole-dipole (DD), dipole-quadrupole (DQ), quadrupole-quadrupole (QQ) interactions, respectively; A

is constant with the same excitation conditions for a given host. For ABTe:Sm³⁺ glass, the plot of $\log(I/C)$ versus $\log C$ is shown in Fig. 1b. The graph is a linear and the its slope is - 2.14. Therefore, the value of S is calculated to be 6.42, which is close to 6. This indicates that the DD interaction is the main interaction mechanism of energy transfer process between Sm³⁺ ions in ABTe:Sm³⁺ glass. The dominant interaction between Sm³⁺ ions seems to depend on the host. The DD interaction was found in zinc potassium fluorophosphate [11], KMgAl phosphate [14], PbKAlNa phosphate [15], lead fluoroborate [16], zinc fluorophosphate [17], telluroborate [6] and fluoride containing phosphate glasses [18]. In fluoroborate glass the dominant interaction is QQ interaction [8], whereas all mechanisms (DD, DQ, QQ) are probable in K₅Li₂LaF₁₀ crystal [19].

III.4. Decay curve analysis of Sm³⁺ ion in TAB glass by YT model

To determine the interaction mechanism and micro-parameters in energy transfer process, some authors used Inokuti-Hirayama (IH) model [5–8, 17–19]. This model only considers the cross-relaxation and ignores the energy migration. In practice, the energy migration can not ignore. This process may happen through RET channel, for which a Sm³⁺ ion in ⁴G_{5/2} excited level can relax to ⁶H_{5/2} ground state by transferring energy to a neighboring ion in ⁶H_{5/2} level, the second ion will transfer to ⁴G_{5/2} excited level. The excitation energy can migrate through a large number of ions before being emitted. However, there is always a certain concentration of defects in materials that can act as acceptors, so that the excitation energy can be transferred finally to them. These centers can relax to their ground state by multiphonon or infrared emission [20].

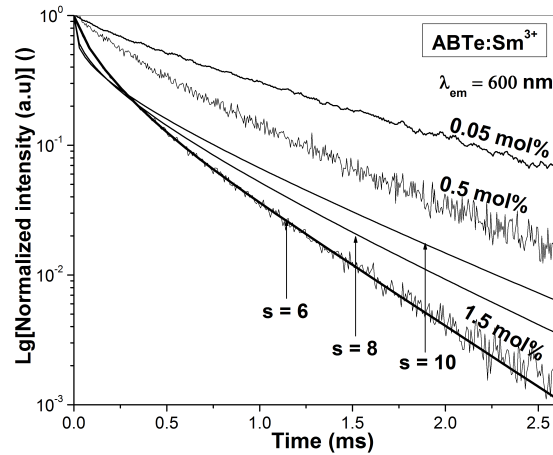


Fig. 4. Luminescence decays were fitted to the Yokota -Tanimoto diffusion model.

Fig. 4 shows the fluorescence decay curves for the ⁴G_{5/2} level of Sm³⁺ ions for different concentrations in ABTe glass. The measured lifetime (τ_{exp}) have been determined by the formula [5, 7]:

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)dt} \quad (2)$$

For our samples, the lifetimes decrease from 1.746 ms to 0.312 ms when the Sm^{3+} concentration increases from 0.05 to 3.0 mol%. The quenching of lifetime is due to energy transfer process between Sm^{3+} ions.

The generalization Yokota–Tanimoto (YT) model was used to determine micro-parameters in energy transfer process. According to this model, the interaction between RE^{3+} ions is negligible at very low concentrations of ions dopant. Therefore, the fluorescence decay curves are nearly single exponential. When the concentration is larger than a certain value, interaction between the ions becomes strong enough to give rise to the energy transfer process from an excited RE^{3+} ion (donor) to a non-excited RE^{3+} ion (acceptor). This leads to decay curves to become non-exponential. When both the cross-relaxation and migration processes are taken into account, decay curves can be expressed as [8, 9]:

$$I = I_0 \exp \left\{ -\frac{t}{\tau_0} - Qt^{3/S} \left(\frac{1 + a_1 X + a_2 X^2}{1 + b_1 X} \right)^{(S-3)/(S-2)} \right\}, \quad (3)$$

where $X = DC_{DA}^{-2/S} t^{1-2/S}$; a_1 , a_2 and b_1 are the Padé approximant coefficients that depend on the multipolar character of the interaction and taken from Refs. [8, 19]; D is the diffusion coefficient that characterizes the energy migration; Q is energy transfer parameter, this parameter is found in fitting process; C_{DA} is microinteraction parameter that characterizes the cross-relaxation.

By using the YT model, the decay curves of the ABTe:Sm samples is best fitted with $S = 6$, where $\tau = 1.746$ ms is lifetime of the sample doped with 0.05 mol% of Sm^{3+} ions. This result is consistent with that found by the Van Uitert method [12]. The C_{DA} and D parameters are found from curves fitting. The results are showed in Table 1.

Table 1. Microinteraction parameter (C_{DA}) and the diffusion coefficient ABTe:Sm glass.

ABTe:Sm ³⁺ (mol%)	$C_{DA}(YT)$ (cm ⁶ /s)	D (cm ² /s)
0.05	–	–
0.50	0.19×10^{-40}	0.04×10^{-13}
0.75	0.25×10^{-40}	0.11×10^{-13}
1.00	0.32×10^{-40}	0.16×10^{-13}
1.50	0.45×10^{-40}	0.28×10^{-13}
2.00	0.72×10^{-40}	0.43×10^{-13}
3.00	0.89×10^{-40}	0.52×10^{-13}

The values of C_{DA} and D parameters increase i.e the energy transfer rate through cross-relaxation and energy migration increases with the increasing of Sm^{3+} concentrations. These results are well agreement with other authors [8, 9, 18] and can be explained as follows: when the impurity concentration increases, the average distance between RE^{3+} ions decreases, leading to the interaction between the ions increases, this increases the energy transfer probability and as a corollary the lifetime of ${}^4\text{G}_{5/2}$ level decreases

IV. CONCLUSION

The emission spectra of Sm^{3+} -doped alkali borotellurite glass with different concentrations have been investigated. The small values of intensity ratio O/R (orange/red) in emission spectra of ABTe:Sm^{3+} glasses showed the low asymmetry of crystal field at the Sm^{3+} ions site. The concentration quenching of luminescence occurs at concentrations greater than 0.75 mol%. The phenomenon is due to the energy transfer process between Sm^{3+} ions through cross-relaxation. The main interaction mechanism between Sm^{3+} ions is dipole-dipole interaction.

REFERENCES

- [1] Y. Ratnakaram, D. T. Naidu, A. V. Kumar and N. O. Gopal, *Physica B: Cond. Matt.* **358** (2005) 296.
- [2] Y. C. Ratnakaram, A. Balakrishna, D. Rajesh and M. Seshadri, *J. Mol. Struct.* **1028** (2012) 141.
- [3] Y. S. M. Alajerami, S. Hashim, W. M. S. W. Hassan, A. T. Ramli and A. Kasim, *Physica B: Cond. Matt.* **407** (2012) 2398.
- [4] O. Ravi, C. M. Reddy, L. Manoj and B. D. P. Raju, *J. Mol. Struct.* **1029** (2012) 53.
- [5] K. Maheshvaran, K. Linganna and K. Marimuthu, *J. Lumin.* **131** (2011) 2746.
- [6] P. Van Do, V. P. Tuyen, V. X. Quang, L. X. Hung, L. D. Thanh, T. Ngoc, N. Van Tam and B. T. Huy, *Opt. Mater.* **55** (2016) 62.
- [7] B. Jamalaiah, M. V. Kumar and K. R. Gopal, *Opt. Mater.* **33** (2011) 1643.
- [8] V. Lavin, I. Martin, C. Jayasankar and T. Tröster, *Phys. Rev. B* **66** (2002) 064207.
- [9] C. Basavapoornima and C. K. Jayasankar, *J. Lumin.* **153** (2014) 233.
- [10] W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.* **49** (1968) 4424.
- [11] S. Thomas, R. George, S. N. Rasool, M. Rathaiah, V. Venkatramu, C. Joseph and N. Unnikrishnan, *Opt. Mater.* **36** (2013) 242.
- [12] L. G. Van Uitert, *J. Electrochem. Soc.* **114** (1967) 1048.
- [13] Y. Song, Q. Liu, X. Zhang, X. Fang and T. Cui, *Mater. Res. Bull.* **48** (2013) 3687.
- [14] C. S. Rao and C. K. Jayasankar, *Opt. Commun.* **286** (2013) 204.
- [15] C. Basavapoornima and C. K. Jayasankar, *J. Lumin.* **153** (2014) 233.
- [16] S. Arunkumar and K. Marimuthu, *J. Alloys Compd.* **565** (2013) 104.
- [17] K.-S. Lim, N. Vijaya, C. R. Kesavulu and C. K. Jayasankar, *Opt. Mater.* **35** (2013) 1557.
- [18] T. Suhasini, J. S. Kumar, T. Sasikala, K. Jang, H. S. Lee, M. Jayasimhadri, J. H. Jeong, S. S. Yi and L. R. Moorthy, *Opt. Mater.* **31** (2009) 1167.
- [19] P. Solarz and W. Ryba-Romanowski, *Phys. Rev. B* **72** (2005) 075105.
- [20] J. Solé, L. Bausa and D. Jaque, *An introduction to the optical spectroscopy of inorganic solids*, John Wiley & Sons, 2005.

