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The Studies of Energy Transfer between Sm^{3+} ions in Lead Sodium Telluroborate Glasses Using Inokuti-Hirayama Model

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Abstract: Lead sodium telluroborate (LSTB) glasses doped with different concentrations of Sm^{3+} ions were prepared by melting method. The excitation, emission spectra and lifetimes of LSTB:Sm^{3+} have been investigated. The quenching of luminescence intensity happens after 0.75 mol% concentration of Sm^{3+} ions. The non-exponential decay curves are fitted to the Inokuti and Hirayama model to give the energy transfer parameters between Sm^{3+} ions. The dominant interaction mechanism for energy transfer process is dipole–dipole interaction. The energy transfer probability (W_{DA}) increases whereas lifetime (τ_{exp}) decreases with the increase of Sm^{3+} concentration in glass.

Keywords: Lead sodium telluroborate glass, Inokuti and Hirayama model.

1. Introduction

Luminescence quenching of rare earth (RE) ions in glasses stems from two different mechanisms that are the multiphonon relaxation and energy transfer [1]. The first mechanism is independent of the RE ions concentration. The multiphonon relaxation rate depends on the number of highest energy phonons available in the host that are needed to cover the energy gap between the metastable level and the next lower energy level of Ln ions. In the second mechanisms an excited ion transfers its excitation energy wholly or in part to an unexcited neighbor by multipolar interaction, and next the two interacting ions decay nonradiatively to respective ground states. Importance of this mechanism depends critically on the distance between interacting ions. With increasing Ln concentration in hosts, the distance between Ln ions diminishes and interactions between ions start to increase, leading the increase of the energy transfer rate. A special case of luminescence quenching involving this mechanism is the nonradiative interaction between identical ions, which gives rise to the phenomenon of the self-quenching [2, 3].

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Borate based glasses have been studied extensively due to their special physical properties like excellent heat stability and lower melting temperature compared with other glasses [2, 4]. The borate glasses were added with TeO_2, they can result in significant reduction in the phonon energy [4- 6]. This can increase the fluorescence efficiency of materials.

Trivalent samarium (Sm^{3+}) is widely used in the fields such as undersea communications, in high-density memories, colour displays and solid-state laser [3- 5]. For Sm^{3+} ions the energy gap between the $^4G_{9/2}$ excited level and the next lower energy level ($^6F_{11/2}$) is about 5 times of the highest phonon energy in borate glass [6]. Thus, the multiphonon relaxation rate from $^4G_{9/2}$ level is small and the luminescence quenching is due to the energy transfer process between Sm^{3+} ions [2]. However, to the best of our knowledge, only limited investigations on energy transfer process between Sm^{3+} ions doped the boro-tellurite glass.

In this paper, the energy transfer process between Sm^{3+} ions in lead sodium telluroborate glasses was studied using Inokuti-Hirayama (IH) model [7]. The results have shown that the dominant interaction for energy transfer between Sm^{3+} ions in LSTB glass is dipole-dipole interaction (DD). The energy transfer parameter (Q), interaction parameter (C_{DA}), critical distance (R_0) and energy transfer rate (W_{DA}) have also been determined.

2. Experiments

The LSTB glasses with the composition $(60\text{-}x)B_2O_3+20TeO_2+10Na_2O+10PbO+xSm_2O_3$ (where x = 0.05; 0.10; 0.5; 0.75; 1,0; 1,5 and 2.0 mol%, denoted by LSTB05; LSTB10; LSTB50; LSTB75; LSTB100; LSTB150 and LSTB200, respectively) were 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 LSTB glasses were annealed at 350 °C for 12 h to eliminate mechanical and thermal stress. The excitation and emission spectra were 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. Excitation spectra

The excitation spectrum of the LSTB50 sample monitored at wavelength 600 nm corresponding to the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ fluorescence transition and is shown in Fig. 1. Fourteen excitation bands are observed at the wavelengths of 490, 471, 462, 439, 421, 417, 402, 390, 376, 361, 344, 332, 317 and 306 nm and are assigned to transitions from the ground level $^6H_{5/2}$ to the excited levels $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, ($^4M_{17/2}$, $^4G_{9/2}$, $^4I_{15/2}$), $^4L_{13/2}$, $^6P_{5/2}$, $^6P_{3/2}$, $^4G_{11/2}$, $^4L_{17/2}$, $^4D_{5/2}$, $^4H_{9/2}$, $^4G_{5/2}$, $^4P_{3/2}$ and $^4P_{5/2}$, respectively [8]. The excited transition $^6H_{5/2}\rightarrow{}^6P_{3/2}$ with intense intensity is usually used for measurement of luminescence spectra of Sm^{3+} ions.

3.2. Emission spectra and the concentration quenching of luminescence

The emission spectra of the LSTB:Sm^{3+} glasses are recorded in the wavelength region 500-850 nm using 402 nm excited wavelength and are shown in Fig. 2. The measurement conditions of all samples are exactly the same. The emission spectra consists of 5 observed emission bands at wavelengths of

560, 600, 645, 710 and 786 nm which correspond to the $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2, 13/2) transitions, respectively. Among of them, the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition have the intense intensity whereas the $^4G_{5/2}\rightarrow{}^6H_{13/2}$ transition is very weak in intensity. Two emission bands $^4G_{5/2}\rightarrow{}^6H_{5/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transitions usually used in high-density optical memory, color display and diagnostics in medicine [4, 9].

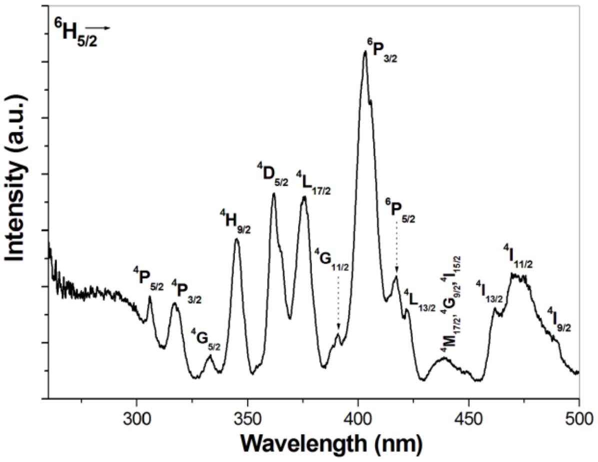

Fig. 1. The excitation spectrum of the LSTB50.

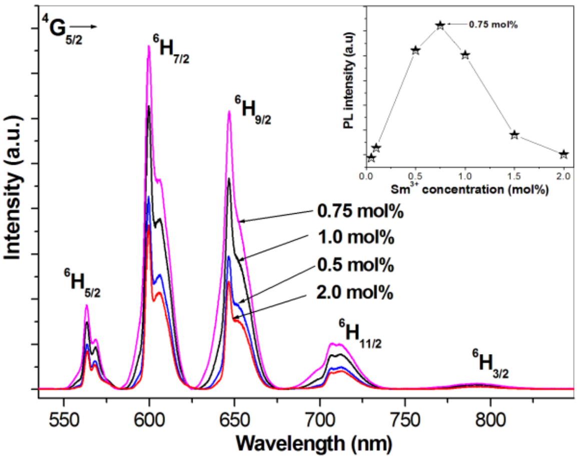

Fig. 2. The emission spectra of the LSTB:Sm^{3+}.

As shown in Fig. 2, the luminescence intensity increases with the increasing of Sm^{3+} concentration and reaches a maximum at 0.75 mol%, then decreases. The change of total luminescence intensity is shown in the inset of Fig. 2. The decrease of luminescence intensity after a certain concentration is called concentration quenching or self-quenching (SQC). The SQC phenomenon is due to the nonradiative processes consisting multiphonon relaxation and energy transfer between the pairs of Sm^{3+} ions [10, 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 $^4G_{5/2}$ and next lower level $^6F_{11/2}$ [1, 2]. In the 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}) [6]. Thus multiphonon relaxation rate is negligible and concentration quenching may be mainly due to energy transfer. 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 [2, 3, 10]. The Inokuti and Hirayama model allows us to find the dominant interaction mechanism between the ions [7].

3.3. Decay curve analysis of Sm^{3+} ion in LSTB glasses by IH model

3.3.1. Inokuti and Hirayama model

The IH model was shown to be useful to study transfer process between ions [2, 3, 10, 11]. 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. However when the concentration is larger than a certain value, interaction between the ions become strong enough to give rise to the energy transfer process from an excited RE^{3+} ion (donor) to a nonexcited RE^{3+} ion (acceptor). This leads to decay curves to become nonexponential. There are two important mechanisms to explain the energy transfer process: the first mechanism is cross–relaxation between the pairs of Sm^{3+} ions, the second one is the migration of the excitation energy to the structural defects acting as quenching traps. When the migration process is negligible, decay curves can be expressed as [2, 3]:

$$I = I_0 \exp\left\{ -\frac{t}{\tau_0} - Q\left(\frac{t}{\tau_0}\right)^{3/S} \right\} \tag{1}$$

where t is the time after excitation, τ_0 is the intrinsic decay time of donor in absence of acceptor. The value of S (= 6, 8, 10) depends on whether the dominant mechanism of interaction is dipole–dipole (DD), dipole–quadrupole (DQ) or quadrupole–quadrupole (QQ), respectively. The energy transfer parameter (Q) is found in the fitting process and is calculated by:

$$Q = \frac{4\pi}{3}\Gamma\left(1 - \frac{3}{S}\right) N R_0^3 \tag{2}$$

$\Gamma(x)$ is the gamma function, its value is equal to 1.77, 1.43 and 1.30 for DD, DQ and QQ interaction, respectively; N is the concentration of Sm^{3+} ions; R_0 is the critical distance defined as donor–acceptor separation for which the rate of energy transfer to the acceptors is equal to the rate of intrinsic decay of the donor. The microinteraction parameter (C_{DA}) at distance R and are calculated by [10, 11]:

$$C_{DA} = R_0^s \tau_0^{-1} \tag{3}$$

With the multipolar interaction and the energy migration is not considered, the energy transfer probability is found by the formula:

$$W_{DA}(R) = C_{DA} R^{-S} \tag{4}$$

where R is the mean distance between donor and acceptor, and calculated according to the Ref [2]:

$$R = \left(\frac{3}{4\pi N}\right)^{1/3} \tag{5}$$

3.3.2. Decay curve analysis of Sm^{3+} ion in LSTB glasses

The fluorescence decay curves for the $^4G_{5/2}$ level of Sm^{3+} ions for different concentrations in LSTB glass were represented in Fig.3. The measured lifetimes ($\tau_{\exp}$) of samples have been determined by the formula [3, 4]:

$$\tau_{\exp} = \frac{\int tI(t)dt}{\int I(t)dt} \tag{6}$$

The lifetime of all concentrations was determined and presented in Table 1. For the LSTB:Sm^{3+} glasses, the lifetime decreases from 1.725 ms to 0.262 ms when the Sm^{3+} concentration increases from 0.05 mol% to 2.0 mol%. The quenching of lifetime is due to SQC, which can happen through cross-relaxation process: 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 $^6F_{n/2}$ states located in the middle from $^6H_{5/2}$ to $^4G_{5/2}$ level. Finally these ions relax to the $^6H_{5/2}$ ground level by multiphonon or infrared emission. The cross–relaxation channels in Sm^{3+} ions may be: the resonant channel (RET ($^4G_{5/2}\rightarrow{}^6H_{5/2}$) → ($^6H_{5/2}\rightarrow{}^4G_{5/2}$)) and nearly resonant channels (CR1: ($^4G_{5/2}\rightarrow{}^6F_{5/2}$) → ($^6H_{5/2}\rightarrow{}^6F_{11/2}$)), (CR2: ($^4G_{5/2}\rightarrow{}^6F_{9/2}$) → ($^6H_{5/2}\rightarrow{}^6F_{7/2}$)), (CR3: ($^4G_{5/2}\rightarrow{}^6F_{9/2}$) → ($^6H_{5/2}\rightarrow{}^6F_{7/2}$)) and (CR4: ($^4G_{5/2}\rightarrow{}^6F_{11/2}$) → ($^6H_{5/2}\rightarrow{}^6F_{5/2}$)) as the energy difference between these transitions is negligible. The CR channels are shown in Fig.4.

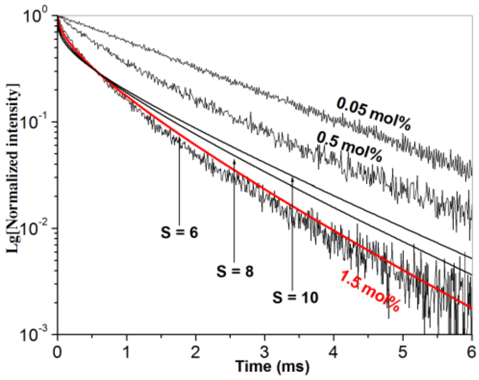

Fig. 3. Decay profiles of $^4G_{5/2}$ level of Sm^{3+} ions doped LSTB glass.

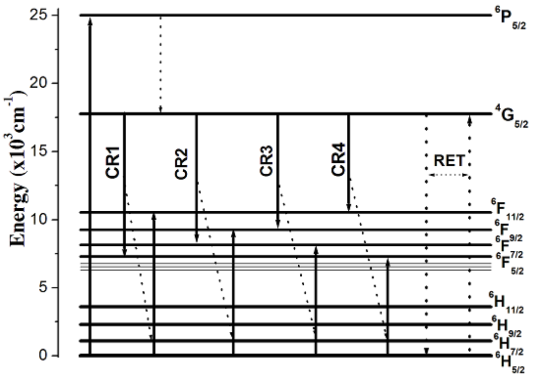

Fig. 4. Energy level diagram and cross-relaxation (CR) channels for Sm^{3+} ions in LSTB glass.

Fig. 3 shows that the decay curve is the single exponential with concentration of 0.05 and becomes nonexponential with the residual concentrations. By using the IH model, the decay curves of the LSTB:Sm^{3+} samples is best fitted with S = 6, where τ_0 = 1.725 is lifetime of LSTB glass doped with 0.05 mol% Sm^{3+} because at this concentration the energy transfer process is negligible. With S = 6, it is noted that the dominant interaction for energy transfer process is of dipole–dipole interaction [1, 2, 3]. The dominant interaction between Sm^{3+} ions seems to depend on the host. The DD interaction was found in zinc potassium fluorophosphate [10], KMgAl phosphate [9], PbKAlNa phosphate [12], fluoride containing phosphate glasses [11], and lead fluoroborate [13]. In fluoroborate glass the dominant mechanism is the QQ interaction [14]. The DQ interaction is found in K_2GdF_5 crystals [3] whereas all mechanisms (DD, DQ, QQ) are probable in $K_5Li_2LaF_{10}$ crystal [15]. The energy transfer parameter (Q) also was found in fitting decay curves. From value of Q, the critical transfer distance (R_0) was calculated by Eq (2). The value of R_0 increases from 7.59 Å to 7.77 Å when the Sm^{3+} concentration increases from 0.5 to 2.0 mol%. The obtained results are in a good agreement with similar in some other glasses [9-12]. The critical transfer distance and measured lifetime of the 0.05 mol% concentration (τ_0) were used to calculate the donor–acceptor microinteraction parameter C_{DA} and the energy transfer probability W_{DA} by using Eqs.(3) and (4), respectively. The results are shown in Table 1.

Table 1. The energy transfer parameters of LSTB:Sm^{3+} glass

C (mol%)	τ_{exp} (ms)	η (%)	Q	C_{DA} cm^6s^{-1}	R (Å)	R_0 (Å)	W_{DA} (s^{-1})	W_{ET} (s^{-1})
0.05	1.725	-	-	-	21.72	-	-	-
0.10	1.707	98.9	-	-	17.24	-	-	6.1
0.50	1.301	75.4	0.74	1.12×10^{-40}	10.20	7.59	102.4	188.9
0.75	1.128	65.4	1.12	1.20×10^{-40}	9.23	7.68	194.5	311.5
1.00	0.789	39.9	1.72	1.22×10^{-40}	8.06	7.91	443.5	687.7
1.50	0.502	29.1	2.73	1.26×10^{-40}	6.79	7.74	1283	1412
2.00	0.319	18.5	3.17	1.29×10^{-40}	6.42	7.77	1879	2555

The energy transfer probabilities is very small at low concentrations (0.05 mol%) and becomes very large at the high concentrations. Fig.5 shows the dependence of the parameters R, Q, W_{DA} and τ_{exp} on Sm^{3+} doping concentration. The change in Q and W_{DA} with concentration is opposite to that of the R and τ. These results can be explained as follows: when the impurity concentration increases, the average distance between RE^{3+} ions decrease, leading to the interaction between the ions increases, this increases the energy transfer probability and as a corollary the lifetime decreases.

The quantum efficiency η and nonradiative relaxation rate W_{NR} is given as [1]:

$$\eta(\%) = \frac{\tau}{\tau_r} \times 100 \tag{7}$$

$$W_{NR} = \frac{1}{\tau_r} - \frac{1}{\tau} = W_{ET} + W_{MP} \tag{8}$$

where τ_r called the radiative lifetime, would be the luminescence decay time measured for a purely radiative process, τ is the lifetime of a certain sample, it is important to stress that this lifetime value gives the total decay rate (radiative plus energy transfer rates), W_{MP} is the multiphonon relaxation rate. Since the W_{MP} is ignored, the equation (8) is rewritten as:

$$W_{ET} = \frac{1}{\tau_r} - \frac{1}{\tau} \tag{9}$$

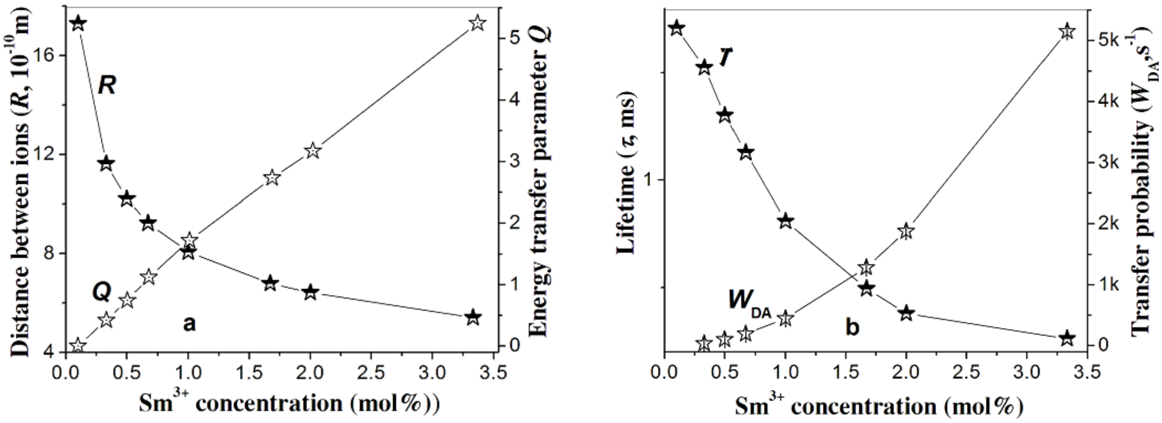

Fig.5. The dependence of the parameters R, Q (a) and W_{DA}, τ (b) on the doping content.

In this study, the results show that when the Sm^{3+} concentrations are lower than 0.1 mol%, the energy transfer rate is so small that the radiative lifetime τ_r can take approximately τ_0 (lifetime of sample doped with 0.05 mol% Sm^{3+}). Therefore, the values of W_{ET} and η have been calculated and shown in Table 1. The quantum efficiency decreases, whereas energy transfer probability increases with increasing of Sm^{3+} concentration in glass. The calculated results show that the value of W_{DA} is smaller than W_{ET}, this may be related to the energy migration. This process may happen through RET channel [14]: a Sm^{3+} 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 finally be transferred to them. These centers can relax to their ground state by multiphonon or infrared emission [1, 2] and the luminescence is quenched. The energy transfer process between Sm^{3+} ions and intrinsic defects leads the deviation between the theoretical and experimental decay curves because the IH model ignores this process [16].

4. Conclusions

The optical spectra of Sm^{3+} -doped lead sodium telluroborate glasses have been investigated. The luminescence shows the self-quenching happening after concentration of about 0.75 mol%. This phenomenon is due to the energy transfer process between the pairs of Sm^{3+} ions. This process leads to the reduction of the lifetime. The non-exponential decay curves are well fitted to the IH model and it is found that the energy transfer between Sm^{3+} ions is of dipole–dipole nature. The energy transfer parameters have been calculated for samples. When energy migration process is ignored, the energy transfer probabilities decrease. Therefore, the fluorescence quenching also involves the energy migration process.

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