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Absorption and emission spectra of thallium activated Na_2O–$NaCl$–B_2O_3 and K_2O–KCl–B_2O_3 glasses

N. L. PATHAK, A. PAUL*, S. C. SEN
Department of Physics, Indian Institute of Technology, Kanpur, India

Absorption and emission spectra of two Na_2O–$NaCl$–B_2O_3 and two K_2O–KCl–B_2O_3 glasses, with large thallium concentrations (about 0.01 mol thallium per litre glass) have been studied. Absorption bands have been observed at 49 000, 44 500 and 40 000 cm^{-1} for the Na_2O–$NaCl$–B_2O_3 glasses, and at 49 000, 43 500 and 38 500 cm^{-1} for the K_2O–KCl–B_2O_3 glasses at 300 K. Emission spectra have been recorded at 83, 308, 445 and 485 K; generally two emission bands have been observed in the ultraviolet region, and the intensity of both bands increased with decreasing temperature. The absorption and emission bands have been assigned to electronic transitions in different centres formed by Tl^+ ions in glass.

1. Introduction

Luminescent glasses are used as dosimeters for measuring high energy radiation, scintillation counters, glass lasers, ophthalmic lenses and in electroluminescence devices etc. The first glass laser was reported by Snitzer [1] in 1961, which contained Nd^{3+} as the lasing ion in barium crown glass. Pearson *et al.* [2] have investigated the laser action in Nd^{3+}-doped borate glasses at 0.918, 1.057 and 1.401 μm. Laser action in glasses has so far mainly been achieved with rare earth ions.

The efficiency of glass laser can be increased considerably by using energy transfer mechanism from the sensitiser ion to the lasing ion. The efficiency of neodymium glass laser can be increased with the use of Mn^{2+} [3] as sensitiser. Nd^{3+} is a weak absorber of energy in the ultraviolet region while Mn^{2+} is a strong absorber. Hence when a xenon flash source, whose energy mainly lies in the ultraviolet and the blue region, is used for pumping, energy transfer from Mn^{2+} to Nd^{3+} is possible, since the emission of Mn^{2+} is in the visible region, where the Nd^{3+} is a reasonably strong absorber. The ultraviolet absorption of some ions having ns^2 electron configuration such as Tl^+, Pb^{2+}, Bi^{3+} etc. is larger by a factor of ~ 10^4 than that of Mn^{2+} [4], and the emission of some of these ions lies in the visible region [5], hence the energy transfer from these ions to Nd^{3+} and other rare earth ions is possible. Botden [6] has reported that the emission from Mn^{2+} in various host lattices is enhanced considerably with the use of Ce^{3+}, Tl^+, Pb^{2+}, Bi^{3+} and Sn^{2+}. Hence an efficient laser by doping the glass with ns^2 ion, Mn^{2+} and rare earth ion seems to be a possibility in future.

The optical absorption and fluorescence spectra of thallium activated alkali halides have received considerable attention both from experimental and theoretical workers [7-16]. Although investigators have been trying to interpret the absorption and emission of Tl^+ in alkali halides for more than 35 years, a complete understanding has still not been reached. In order to explain the complex behaviour of optical spectra and its dependence on temperature and the concentration of thallium, more sophisticated approaches are required. To explain the origin of visible emission bands of thallium-activated alkali halides, many explanations, sometimes contradictory, have been suggested by different investigators [17-23]. Some authors [24-27] have also investigated the optical spectra of aqueous solutions of alkali and ammonium chlorides containing a small amount of TlCl dissolved in it in order to understand the nature of electronic states involved. Tl^+ in aqueous solutions containing halides can form a number of complexes like $[TlX_n(H_2O)_{6-n}]$ where n changes with halide

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*Department of Glass Technology, Sheffield University, England.

activity, pH and temperature of the solvent. Thus effect of temperature on absorption and emission behaviour of Tl^+ with a definite value of *n* can not be studied satisfactorily. On the other hand, some of the halide matrices used for investigating thallium undergo phase transition on heating [30]. Thus the behaviour of thallium-doped phosphors when changed from solid to liquid could not be studied systematically.

Glasses possess a degree of disorder characteristic of liquids, and at the same time the atoms in glass maintain permanent positions with respect to the location of their neighbours as is characteristic of solids. Thus thallium-activated alkali borate glasses which may be helpful in understanding the optical spectra of thallium doped alkali halides as well as those in solutions, were investigated.

Previously, the absorption and emission spectra of Tl^+ in alkali borate glasses [28] have been reported; the thallium concentration used was of the order of $\sim 10^{-4}$ mol litre^{-1}. It is well known that the optical absorption and emission spectra of thallium-activated alkali halides change considerably as the thallium concentration is increased. In the present investigation we have taken the alkali borate glasses heavily doped with thallium (of the order of $\sim 10^{-2}$ mol litre^{-1}). We have also studied the temperature dependence of optical spectra.

2. Experimental

All the batch materials (alkali carbonates, alkali chlorides, orthoboric acid and thallous chloride) used for making the glass samples were of Analar grade. Thallium was added as thallous chloride solution to the batch. 10 g glass were melted at a time in a Pt + 2% Rh crucible at 950°C in an electric furnace for 4 h. The glasses were cast as rectangular slabs 2.5 cm × 1.0 cm × 0.5 cm and annealed thoroughly. The flat surfaces of glass samples were optically polished to about 0.015 cm thickness. Glasses containing chloride were made by partially substituting alkali halides for alkali carbonates in the batch. These glass melts were stirred with a thick platinum wire to achieve uniform distribution of chloride throughout the melt. The thallium concentration was determined by dissolving 0.2 to 0.4 g glass powder in 50 ml 6N HCl and measuring the absorbance at 40820 cm^{-1} [29]; chloride contents were estimated by the Volhard method. The absorption spectra were recorded on a Cary 14 spectrophotometer at 300 K. The fluorescence spectra were recorded using a double monochromator and AH4 mercury arc lamp whose outer glass envelope was removed in order to get the ultraviolet radiations. The exciting radiations were monochromatized by a Gaertner-234-150 quartz monochromator. The emitted radiations were analysed at right angles to the incident, exciting light by another Gaertner-234-150 quartz monochromator with a 1P28 RCA photomultiplier and a d.c. electrometer. Power to all the units used in fluorescence measurements was regulated by a G.R.C. automatic line voltage regulator in order to avoid fluctuations in supply voltage. The fluorescence at low temperature and at room temperature was measured in a low temperature cell; and at room and above in a high temperature cell. The low temperature cell was fitted with two quartz windows while in the high temperature cells no such windows were used, hence the shape of the individual emission curve at room temperature using two different cells are not perfectly coincident. The slit width was also adjusted in order to obtain sufficient intensity in both. The slit widths of the exciting and the analysing monochromators were kept at 0.15 and 0.25 mm respectively. The emission spectra have been corrected for the spectral distribution of the exciting radiations, relative sensitivity of the photomultiplier and the dispersion of the monochromators. All the absorption and emission envelopes were resolved into a minimum number of gaussian component bands with a Dupont 310 curve resolver; typical resolution is shown in Figs. 1 and 2.

3. Results

The composition of glasses (after chemical analysis) is given in Table I. The absorption spectra of glasses are shown in Fig. 1. One most intense band has been observed at 49 000 cm^{-1} for all four glasses. In addition to this band, less intense bands at 44 500 and 4000 cm^{-1} were observed for glasses SA and SB, and at 43 500 and 38 500 cm^{-1} for glasses PA and PB at 300 K. Typical emission spectra of some glasses at different temperatures are shown in Figs. 2 to 5, and the peak position of resolved fluorescence bands are given in Table II. In all the glasses, emission intensity increased with decreasing temperature, and in certain cases the position of the emission band maxima shifted with temperature. The emission bands of glasses PA and PB are resolved into two distinct bands at 33 000

TABLE I Composition of glasses (after chemical analysis)

Glass	Mol %			Concentration (mol litre^{-1})	
no.	Na_2O	K_2O	B_2O_3	Tl^+	Chloride
SA	14.8		85.2	0.01006	0.2623
SB	15.1		84.9	0.01143	0.3008
PA	–	15.0	85.0	0.01227	0.3008
PB	–	15.1	84.9	0.01213	0.3431

TABLE II The peak positions of the fluorescence bands at liquid nitrogen temperature (L.N.T. = 83 K), room temperature (R.T. = 308 K) and at high temperatures

Glass	Excitation energy (cm^{-1})	Temperature	Positions of fluorescence bands (cm^{-1})	
P_A	41 670	L.N.T.	29 500	–
		R.T.	29 000	–
P_A	38 910	L.N.T.	27 000	–
		R.T.	27 200	–
		445 K	30 000	26 500
		485 K	33 000	26 500
P_B	41 670	L.N.T.	28 500	–
		R.T.	28 300	–
		445 K	32 700	27 000
	38 910	L.N.T.	25 200	–
		R.T.	26 300	–
		445 K	33 000	26 000
		485 K	33 000	26 000
S_A	41 670	L.N.T.	30 300	–
		R.T.	30 700	–
		445 K	31 700	–
		485 K	32 200	27 700
	38 910	L.N.T.	29 500	–
		R.T.	30 000	–
S_B	41 670	L.N.T.	29 500	–
		R.T.	29 700	–
		445 K	32 000	26 500
	38 910	L.N.T.	28 500	26 000
		R.T.	28 300	25 500

and 27 000 cm^{-1} at 445 and 485 K (Fig. 4b) when excited at 40 320 and 38 910 cm^{-1}. Klement [30] has reported considerable changes in the emission spectra of NH_4Cl:Tl phosphor at ~ 200°C; but NH_4 Cl changes from CsCl-type to NaCl type structure around 185°C. Thus it is not clear whether the changes in emission that he reported are due to Tl impurity or due to changes in the host lattice.

4. Discussion

As is known, three absorption bands, A, B and C, of impurity ions with ns^2 electron configuration (such as Tl^+, Pb^2, In^+ etc.) in alkali halides are associated to the changes from $(S)^2$ ground state to (S)(P) excited electronic states. The C band is attributed to the allowed transition: $^1S_0 \rightarrow {}^1P_1$ ($^1A_{1g} \rightarrow {}^1T_{1u}$) and B band to the $^1S_0 \rightarrow {}^3P_2$ ($^1A_{1g} \rightarrow {}^3E_u$ or $^3T_{2u}$) allowed in the case of lower symmetry caused by lattice vibrations etc. and A band to the spin forbidden $^1S_0 \rightarrow {}^3P_1$ ($^1A_{1g} \rightarrow {}^3T_{1u}$) transition. The A, B and C bands for KCl:Tl occur at 40 300, 48 500 and 51 000 cm^{-1}, and that for NaCl:Tl occur at

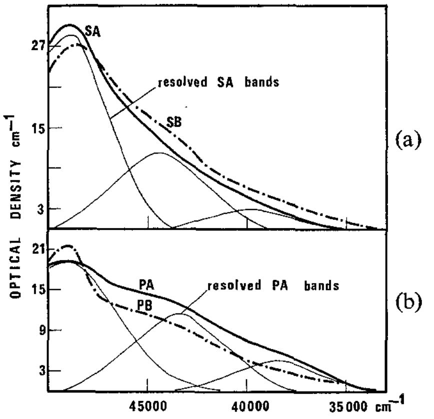

Figure 1 Absorption spectra of Tl^+ in (a) Na_2O–NaCl–B_2O_3 glasses and (b) K_2O–KCl–B_2O_3 glasses.

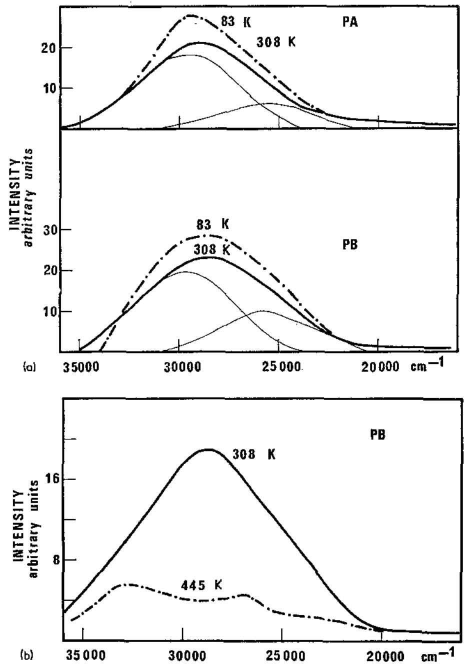

Figure 2 (a) Emission spectra of Tl^+ in K_2O–KCl–B_2O_3 glasses and (b) excited at 41 670 cm^{-1} at different temperatures.

39 400, 45 900 and 49 800 cm^{-1} [7, 11, 13]. Patterson [31] has observed additional absorption bands with large thallium concentration in KCl; two bands in the A band region at 39 700 and 38 200 cm^{-1}, one band in the B band region at 45 900 cm^{-1}, and one band in the C band region at 49 800 cm^{-1}. He has attributed the additional bands to different types of thallium centres such as Tl^+ in a local CsCl-type environment, pairs and aggregates.

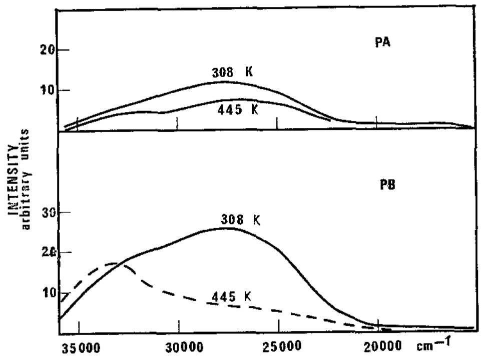

Figure 3 Emission spectra of Tl^+ in K_2O–KCl–B_2O_3 glasses excited at 40 320 cm^{-1} at different temperatures.

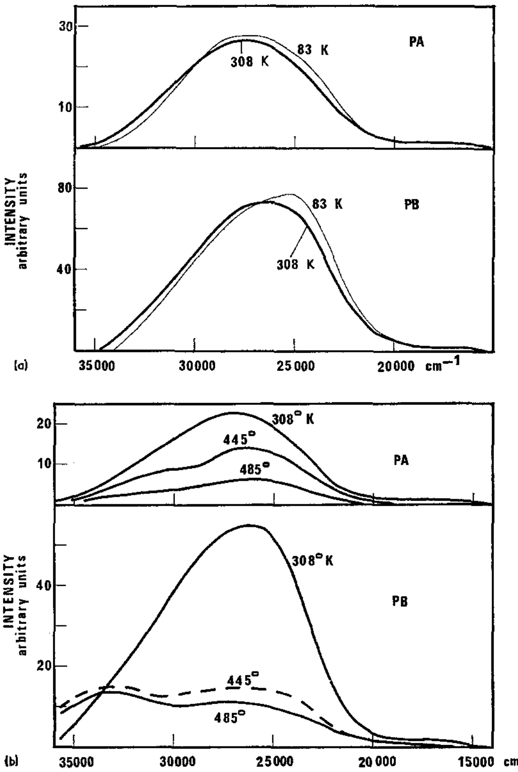

Figure 4 (a) Emission spectra of Tl^+ in K_2O–KCl–B_2O_3 glasses and (b) excited at 38 910 cm^{-1} at different temperatures.

Burstein *et al.* [32] and Cook and Dryden [33] have studied the aggregation of divalent cationic impurities in alkali halides. For NaCl:Tl, Dryden and Harvey [34] have reported four

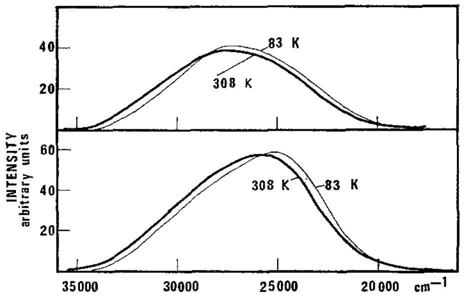

Figure 5 Emission spectra of Tl^+ in K_2O–KCl–B_2O_3 glasses excited at 37 740 cm^{-1} at different temperatures.

emission bands when excited at 36 630 cm^{-1}, and attributed these to different types of thallium centres such as dimers, trimers and heptamers and other centres formed by more Tl^+. Hutten and Pringsheim [9] have observed emission bands at 33 300, 26 000, 21 900 and 18 600 cm^{-1} for KCl:Tl under A band excitation. At low concentration of thallium the emission band at 33 300 cm^{-1} was most intense while other bands appeared at higher thallium concentrations. Abdusadykov [35] has also observed the similar effects of concentration on emission spectra in KBr:Tl.

Previously, we have reported [28] absorption and emission spectra of thallium activated R_2O–RCl–B_2O_3 (R refers to Na or K) glasses with thallium concentration $\sim 10^{-4}$ mol $litre^{-1}$; in the present investigation the thallium concentration has been increased to $\sim$ 10^{-2} mol $litre^{-1}$, the chloride concentration has also correspondingly been increased. With low concentration of thallium we observed two emission bands at 30 300 and 26 320 cm^{-1} for the K_2O–KCl–B_2O_3 glass and at 34 480, 30 300 cm^{-1} for the Na_2O–NaCl–B_2O_3 glass; the intensity of the low energy emission band in both the glasses was much poorer than the high energy band. In the present study also we observed two emission bands, for example in glass PA, emission bands were obtained at 29 500 and 25 500 cm^{-1} when excited at 41 670 or 38 910 cm^{-1} at room temperature, but the intensity of the 25 500 cm^{-1} band was more than that of the 29 500 cm^{-1} band. This concentration dependence of emission bands may be due to some "aggregate" of Tl^+ as has been suggested in KBr:Tl system. However, from our studies the exact nature of this polymer, if present, can not be deduced.

In glass PB the emission band gets clearly resolved at 445 K (Fig. 3) into two bands with maxima at 32 700 and 27 000 cm^{-1}, which are the approximate positions of ultraviolet emission bands of KCl:Tl phosphor. Hence the emission band at 32 700 cm^{-1} can be attributed to the $^3P_1 \rightarrow {}^1S_0$ ($^3T_{1u} \rightarrow {}^1A_{1g}$) electronic transition in Tl^+ and the corresponding absorption band at $\sim$ 44 000 cm^{-1} to the $^1S_0 \rightarrow {}^3P_1$ ($^1A_{1g} \rightarrow {}^3T_{1u}$) transition. The emission band at 27 000 cm^{-1} can be tentatively attributed to the same electronic transition in other centres formed by more than one Tl^+ ion, with a corresponding absorption band at $\sim$ 40 000 cm^{-1}. In all our glasses the absorption band at 49 000 cm^{-1} is the most intense, so it can be attributed to the fully allowed $^1S_0 \rightarrow {}^1P_1$ ($^1A_{1g} \rightarrow {}^1T_{1u}$) electronic transition in a single Tl^+ centre ligated with six chlorides in a cubic symmetry as in the case of thallium-activated alkali halides. It should be pointed out at this point that although our glasses contain 0.2 to 0.3 mol chloride per litre glass, the activity of chloride in these melts is very high, and existence of such all chloride complexes in glass has been found for many other transition and non-transition metal ions [36].

The decrease of emission intensity with increasing temperature is due to conversion of excitation into vibrational energy which can be explained as follows: let the probability of luminescence be P_{lum} and that of dissipation process be P_{diss}. Then the efficiency, η of the fluorescence process is given by:

$$\eta = \frac{P_{\text{lum}}}{P_{\text{lum}} + P_{\text{diss}}} = \frac{1}{1 + (P_{\text{diss}}/P_{\text{lum}})} \; .$$

Since P_{lum} is independent of temperature, so p_{diss} must mainly be responsible for the temperature dependence of the efficiency such as has been observed.

None of our glasses showed emission bands at energies lower than 21 000 cm^{-1}; this gives the evidence that visible emission bands around 18 500 and 17 000 cm^{-1} obtained in thallium activated alkali halides at high thallium concentrations are due to other centres which were not formed in our glasses.

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