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Absorption and emission spectra of Tl^{1+} with mixture of oxide and chloride ligands in glasses

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Absorption and emission spectra of Tl^{1+} in a series of $(16\text{-}x)R_2O$, $2x$ RCl, $84B_2O_3$ glasses (where R refers to Na or K, and x varies from 0 to 4 mole) have been studied; and the results compared with those of Tl^{1+} in exclusively oxide and exclusively chloride co-ordinated polyhedra in crystalline phosphors. Both absorption and emission spectra of Tl^{1+} in chloride containing glasses gave strong evidence for complexes of the type: $[\mathrm{Tl(oxide)}_{6-n}(\mathrm{chloride})_n]^{m-}$.

1. Introduction

Tl^{1+} is one of the most well-known phosphor materials for its use as an impurity in many substances like alkali halides, mixed oxides with complex structure, glasses etc. Tl^{1+} introduces a number of strong absorption bands in the ultra-violet region in alkali halides. Seitz [1] named these absorption bands as A, B and C; the location of these bands depends on the host matrix as well as on the concentration of Tl^{1+}. A and C bands introduced near ultra-violet are easily detected; B band is quite weak compared to A and C, and can only be identified under favourable conditions. Some of the peak positions of A and C bands in different alkali halides are given in Tables Ia and b.

TABLE I a Absorption and emission bands of Tl^{1+} in various alkali halides

System	Peak of absorption bands (kK)	Peak of emission bands* (kK)
NaCl:Tl	50.25, 39.37	34.72
KCl:Tl	51.28, 40.49	40.0, 32.78, 21.05
RbCl:Tl	51.28, 40.81	31.75
CsCl:Tl	50.76, 39.52	—
KBr:Tl	47.61, 38.31	31.45, 28.57
KI:Tl	42.37, 34.84	24.10

*Excited with non-monochromatic source.

TABLE I b Absorption bands related to "A" band in different glasses and solutions

Media	Peak position (kK)
Fused silica [18]	46.95
Alumino borate glass [18]	46.30
16 K_2O, 84 B_2O_3 glass	46.51
16 Na_2O, 84 B_2O_3 glass	46.51
14 K_2O, 4 KCl, 84 B_2O_3 glass	46.51, 41.67, 38.46
14 Na_2O, 4 NaCl, 84 B_2O_3 glass	46.51, 41.67, 38.46
H_2O-KCl-TlCl solution [19]	45.45
H_2O-NaCl-TlCl solution [19]	44.44

According to Seitz's model, Tl^{1+} ion replaces an alkali ion in the host crystal, and that Tl^{1+} ions are dispersed at random throughout the lattice. The absorption bands are due to the excitation of the Tl^{1+} ion. The electronic configuration of the ground state of Tl^{1+} ion is $6s^2$ and the electronic state is $^1S_0$; the first excited state of the free ion has the configuration: 6s6p and contains electronic states: $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$. Seitz attributed the C band to the completely allowed $^1S_0 \rightarrow {}^1P_1$ ($^1A_{1g} \rightarrow {}^1T_{1u}$) transition, and the A band to the $^1S_0 \rightarrow {}^3P_1$ ($^1A_{1g} \rightarrow {}^3T_{1u}$) transition. The A band is spin forbidden and thus is expected to be weaker than the C band. In cubic symmetry, other transitions, such as $^1S_0 \rightarrow {}^3P_2$ ($^1A_{1g} \rightarrow {}^3E_u$ or $^3T_{2u}$) and $^1S_0 \rightarrow {}^3P_0$ ($^1A_{1g} \rightarrow {}^3A_{1u}$) are forbidden, but may appear with smaller intensity if the symmetry is lowered, for example, by thermal lattice vibration. The B band was attributed to the $^1S_0 \rightarrow {}^3P_2$ transition. However, it is to be noted that the model of

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Seitz is valid for low concentrations of thallium only.

In Tl^{1+} containing phosphors, emission bands are observed when excited in different bands (A, B and C). Increase in the concentration of thallium results in additional absorption and emission bands, these bands have not only created doubts about the simple model of Seitz but also they have made some workers to postulate various types of thallium centres, namely aggregate formation: $x\ Tl^{1+} \rightarrow (Tl^{1+})_x$ [2], appearance of forbidden transitions of Tl^{1+} [3], and complex formation of the type: $[ThCl_n]^{(n-1)-}$ [4]. Hilsch [5], Pringsheim [6] and Makishima *et al* [7] considered that the causes of A, B and C bands are likely to be some kind of electron transfer transitions related to charged complexes because of similarities between the behaviour of the solid phosphor and those of mixed aqueous solutions of the phosphor. However, it may be pointed out that there is no essential difference between the Seitz's substitutional model and Pringsheim's charged complex model if the absorption centre is considered as composed of heavy metal impurity (Tl^{1+} in this case) and six halogen ions surrounding it.

Sensitized luminescence of crystalline inorganic phosphor has been the subject matter of numerous investigations. A number of sensitized systems such as: NaCl-Mn^{2+}-Pb^{2+} [8], $CaCO_3$ (Pb^{2+}-Tl^{1+}-Ce^{3+}) [9], CaF_2(Ce^{3+}-Mn^{2+}) [10] etc. have been studied. Sensitization is also known to occur in glass [11]. Since the discovery of laser action in 1960, there has been widespread interest in the properties of any metal ion which exhibit fluorescence on the absorption of ultra-violet or visible light. Laser action in glass has so far only been achieved with rare earth ions; and the commercially produced neodymium glass laser is the most important. Nevertheless, other fluorescent ions are of interest to laser scientists because of the possibility of increasing the laser efficiency by an energy transfer mechanism, involving both the fluorescing and the lasing ion, in a doubly doped glass or crystal. It has already been noted that the efficiency of a neodymium glass laser can be increased by the presence of Mn^{2+} ion [12]. Nd^{3+}, like all rare earth ions, is a weak absorber of energy in the near-ultra-violet region. The laser emission at 1.06 μm is usually pumped by a xenon flash tube, but the energy of this source is mainly in the near ultra-violet and blue regions, hence the pumping is inefficient. The Mn^{2+} is a stronger absorber in this region, and because the manganese emits in the green or red, energy transfer into Nd^{3+} levels, at this energy, is possible both by radiative and by non-radiative mechanisms. The ultra-violet absorption of some ns^2 ions, e.g. Tl^{1+}, Pb^{2+}, Bi^{3+} etc. is known to be a factor of $\sim 10^4$ times stronger than that of Mn^{2+} [13]. As in certain cases, the emission from these ions extends towards the green and red [14], they also may offer energy transfer possibilities, not only to Nd^{3+}, but to other rare earth ions as well. Thus the use of a triply doped laser glass: ns^2 ion – Mn^{2+} ion – rare earth ion seems to be a technological viability in future.

Tl^{1+} which has been worked out extensively in alkali halides, etc. might prove to be a satisfactory sensitizing agent in glass. On a literature survey, it revealed that all works in crystalline phosphors have been done either with all-oxide co-ordination: $[Tl(\text{oxide}]_n]^{m-}$ or with all-halide co-ordination $[TlX_6]^{5-}$ (where X is a halogen); absorption and emission behaviour of Tl^{1+} in mixed oxide-halide co-ordination: $[Tl(\text{oxide})_{6-n} X_n]^{a-}$ has not been studied. In oxide glass, anionic substitution around different metal ions has recently been reported [15]. Thus in the present investigation we proceeded to study the absorption and emission spectra of Tl^{1+} in Na_2O-B_2O_3, Na_2O-NaCl-B_2O_3, K_2O-B_2O_3, and K_2O-KCl-B_2O_3 glasses. It was expected that in the chloride containing glasses, some Tl^{1+} centres will be formed with a mixture of oxide and chloride ligands, and thus their absorption and emission spectra could be studied. It was also hoped that in favourable cases, emission from some of these mixed complexes may be more suitable for energy transfer to the Nd^{3+} centre in glass.

2. Experimental

All the raw materials used were of "Analar" quality. 0.1 to 0.3 wt % (0.01 to 0.03 mol l^{-1}) thallium was added as thallium chloride solution to the batch. 10 g of glass were melted at a time in a Pt + 2% Rh crucible at 950°C in an electric furnace for 4 h. The glass was cast as rectangular slabs: 3 × 1 × 0.02 cm and thoroughly annealed. Two flat surfaces of the glass slab were optically polished and the absorption spectra measured with a Beckman DU-2 spectrophotometer. The emission spectra excited by ultra-violet light in the absorption region of the samples have been measured using Gartner Spectrophotometer along with a RCA 1P28 photomultiplier tube using d.c. electrometer. Glasses containing chloride were melted by partially substituting alkali halides for alkali carbonates in the batch. These glass melts were stirred with a thick platinum wire for uniform distribution of chloride throughout the melt. All the constituents of the glass were estimated chemically [16]. Thallium was estimated by dissolving 0.2 to 0.4 g of glass powder in 50 ml 6N HCl and measuring the absorbence at 245 nm [17]. The results of chemical analysis is given in Table II. In another series of experiments, absorption spectra of Tl^+ in water containing different amounts of HCl was measured.

TABLE II Thallium(I) and chloride content of glasses (after chemical analysis)

Glass no.	Concentration of (mol l^{-1})	
	Thallium(I)	Chloride
SA	3.20×10^{-4}	—
SB	2.97×10^{-4}	80×10^{-4}
SC	2.71×10^{-4}	2200×10^{-4}
PA	2.98×10^{-4}	—
PB	2.81×10^{-4}	272×10^{-4}

All the absorption and emission spectra in aqueous solutions and in glasses were resolved into a minimum number of component Gaussian bands with a Du Pont 310 Curve Resolver; the relative area of the resolved bands and the position of their absorption maxima were determined and some typical band resolution is shown in Figs. 2a and b.

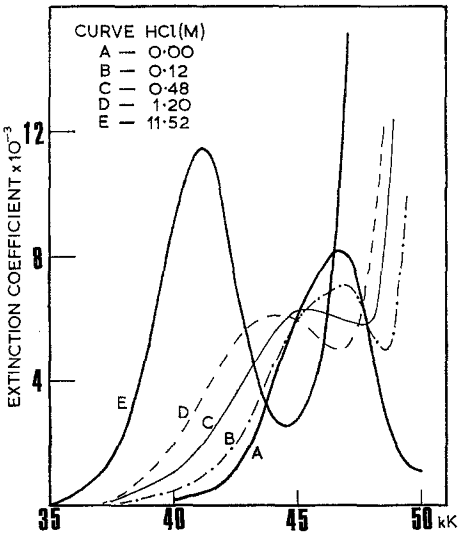

Figure 1 Absorption spectra of Tl^{1+} in H_2O-HCl mixtures.

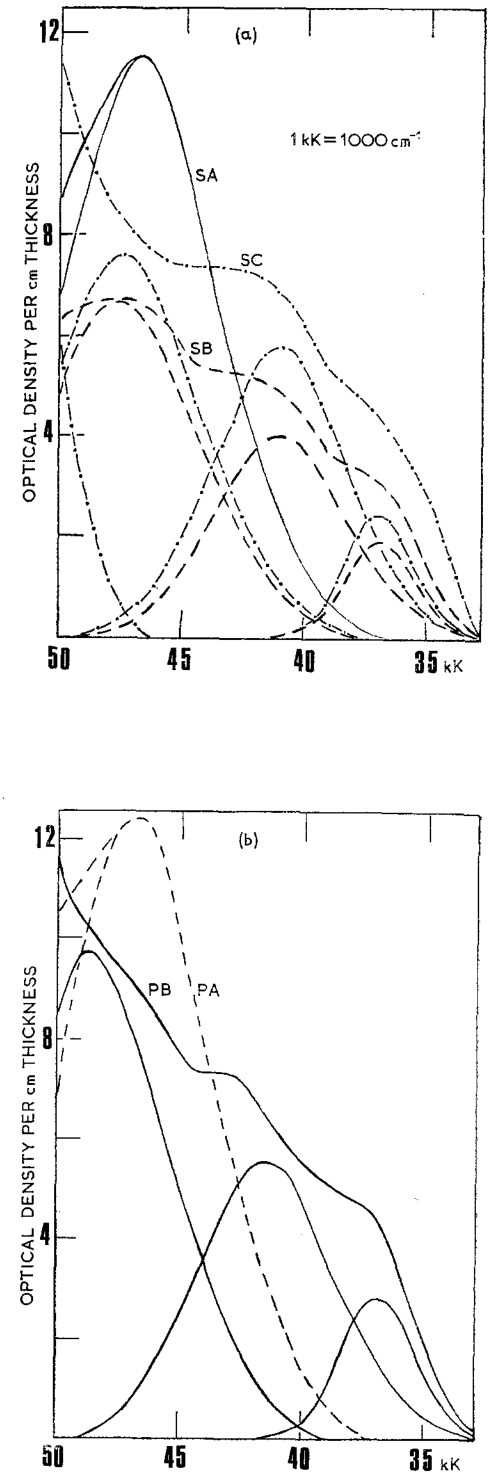

Figure 2 (a) Absorption spectra of Tl^{1+} in Na_2O-NaCl-B_2O_3 glasses. (b) Absorption spectra of Tl^{1+} in K_2O-KCl-B_2O_3 glasses.

3. Results

The absorption spectra of Tl^{1+} in H_2O-HCl mixtures are shown in Fig. 1. In the absence of HCl, Tl^{1+} shows one absorption band at 46.70 kK with an extinction coefficient, $\epsilon \sim 8000$ mol^{-1} cm^{-1}. On addition of a very small amount of HCl the height of this band decreases and another band develops around 45.00 kK indicating the formation of a chlorocomplex species such as: [TlCl] [20]. On adding further amounts of HCl, extra bands are developed on the low energy side of the spectrum and the band around 45.00 kK increases at the expense of that at 46.70 kK. The change of absorption spectrum of Tl^{1+} in water with HCl indicates the formation of a number of complexes such as:

[TlCl], $[TlCl_2]^{1-}$, and $[TlCl_4]^{3-}$ [21].

The absorption spectra of Tl^{1+} in different glasses are shown in Figs. 2a and b. In chloride free glasses, a strong band ($\epsilon \sim 8000$ mol^{-1} cm^{-1}) with absorption maximum at 46.51 kK is obtained. Influence of chloride on the absorption spectra of Tl^{1+} in both the system of glasses are very similar to that in aqueous solutions containing chloride (compare Fig. 1 with Fig. 2a). On adding chloride the intensity of the band at 46.51 kK decreases and two more bands with absorption maxima at 41.67 and 37.10 kK are developed. It may be noted from Figs. 2a and b that although the position of these new bands are the same in both the system of glasses, their relative intensity differs.

The emission spectra of Tl^{1+} in different glasses are shown in Fig. 3. For samples containing NaCl an emission band with maximum at 34.48 kK along with a shoulder at 30.30 kK is obtained. In the case of K_2O-KCl-B_2O_3 glasses the emission bands are obtained at 30.30 and 26.32 kK. The position of emission bands when excited at different energies in various glasses are given in Table III.

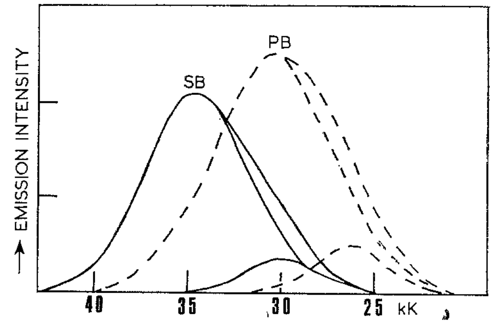

Figure 3 Typical emission spectra of Tl^{1+} in some R_2O-RCl-B_2O_3 glasses.

4. Discussion

In chloride free glasses a single absorption band was obtained at 46.51 kK. In silicate, phosphate and alumino-borate glasses, Ghosh [18] has observed a similar band around 46.95 to 46.30 kK, and ascribed this to $^1S_0 \rightarrow {}^3P_1$ transition. In glasses containing chloride, in addition to the band at 46.51 kK, two other bands are developed at 41.67 and 37.10 kK; the intensity of these two new extra bands increases with increasing chloride content of the glass (Fig. 2a). The band at 41.67 kK has been observed as a composite band in H_2O-KCl-TlCl, H_2O-NaCl-TlCl, and H_2O-NH_4Cl-TlCl solutions by various workers [19] and has been assigned to some mixed aqueo-chloride complexes of Tl^{1+}. In the case of crystalline KCl:TlCl and NaCl:TlCl phosphors where Tl^{1+} is surrounded by six chloride ligands (all-chloride complex), only one absorption band is obtained at 40.49 and 39.37 kK respectively. It is clear that the absorption bands at 41.67 and 37.10 kK are quite different from the absorption band in all-oxide complex (46.51 kK in SA and PA) and all-chloride complex (40.49 to 39.47 kK in alkali halides). Similar to aqueous solutions the origin of these bands are new complexes of

TABLE III Position of the emission maxima when excited with monochromatic sources

System	Excitation energy (kK)	Position of emission maxima (kK)
Fused silica [18]	43.86	35.21
Alumino borate glass [18]	43.86	32.47
K_2O-KCl-B_2O_3 glass	42.55	30.30, 26.32
	40.32	30.30, 26.32
Na_2O-NaCl-B_2O_3 glass	42.55	34.48, 30.30
	40.32	34.48, 30.30
KCl – crystalline	39.44	32.74, 26.32, 21.74, 18.52, 17.24
NaCl – crystalline	39.44	34.48 26.32, 21.74, 18.52, 17.24

Tl^{1+} with a mixture of oxide and chloride ligands. Similar complexes of Pb^{2+} with mixture of oxide and chloride ligands have been reported in glass [13].

With large concentrations of Tl^{1+} Ghosh observed an additional band at 38.46 kK and explained this as due to aggregate formation of Tl^{1+}. However, as can be seen from our results that unless one is particularly cautious about chloride contamination, this band may also arise due to Tl^{1+}-oxide-chloride complex formation.

Exciting the KCl:TlCl crystalline phosphor at 40.49 kK gives rise to emission band at 32.79 kK; when NaCl:TlCl crystalline phosphor is excited at 39.37 kK the emission band is obtained at 34.72 kK. Whereas when the glass K_2O-KCl-B_2O_3 containing Tl^{1+} is excited at 41.67 kK the emission band occurs at 30.30 kK, and that for NaCl-Na_2O-B_2O_3 glass containing Tl^{1+} occurs at 34.48 kK on excitation at 41.67 kK. On excitation at 37.10 kK absorption band in the chloride containing glasses, emission spectra were obtained which resemble very closely the emission spectra from corresponding glasses when excited at 41.67 kK.

On comparing the position and nature of the emission bands of Tl^{1+} in glasses containing chloride with those of chloride-free glasses, it is clear that the absorption band at 41.67 kK in chloride containing glasses is not the Seitz's A band which occurs around 46.5 to 47.0 kK in oxide co-ordination and around 40.81 to 39.37 kK in chloride co-ordination. The most probable origin of the 41.67 kK band seems to be a mixed Tl^{1+}-oxide-chloride complex which Pringsheim has described as: $TlCl_n^{(n-1)-}$ centre.

The origin of the 37.10 kK absorption band cannot be deduced satisfactorily from the present studies; this band may be due to a higher chloride complex of Tl^{1+} or may be due to a transition to another excited level of Tl^{1+} which became allowed through lowering of site symmetry due to partial chloride association.

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