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Photoluminescence of Ti^{3+} in P_2O_5–Na_2O–Al_2O_3 glass

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The optical properties (absorption and luminescence) of Ti^{3+} in a P_2O_5–Na_2O–Al_2O_3 glass have been studied in the temperature range 12 to 300 K. A very broad infrared emission band at 860 nm, has been observed for the first time in an inorganic glass, when excitation is performed in the Ti^{3+} absorption band ($T_{2g} \rightarrow E_g$ transition in cubic field approximation). The spectroscopic characteristics of this system are compared with those of the Ti^{3+} as a dopant in Al_2O_3 single crystals.

1. Introduction

The optical spectroscopy of Ti^{3+} ions in different materials has become an intense research field after the demonstration that $Al_2O_3:Ti^{3+}$ crystals can operate as a tunable solid state laser [1, 2]. In Al_2O_3, Ti^{3+} shows a broad emission band centred at about 750 nm and extending from 650 to 900 nm, corresponding to the transition between the E_g and T_{2g} levels of the $3d^1$ configuration of the ion. This emission provides a wider tuning range and a higher gain cross-section than other transition metal ions used for tunable solid state lasers. This material is considered the first of a class of systems based on Ti^{3+} ions and has renewed the interest in the optical properties of trivalent titanium incorporated in various host materials.

In the case of inorganic glass hosts, information has been published previously concerning site symmetry and levels responsible for the optical absorption of Ti^{3+} (in silicate, borate, phosphate and fluorophosphate glasses) [3–6]. However, the photoluminescence of these materials has not been detected to date, except for the case of titanium-doped fluorophosphate in which an emission band at about 550 nm was observed under excitation in the charge transfer band of Ti^{4+} [5, 6].

The aim of the present work was to study the optical properties of Ti^{3+} in a P_2O_5–Na_2O–Al_2O_3 glass in the spectral region corresponding to the $T_{2g} \rightarrow E_g$ absorption band. An infrared emission band of similar characteristics to that of $Al_2O_3:Ti^{3+}$, but covering the wavelength range from 750 to 1000 nm has been detected and studied in the temperature range 10 to 300 K.

2. Experimental details

A phosphate glass of batch composition $62P_2O_5$–$14Al_2O_3$–$24Na_2O$ was used as matrix host. Titanium was introduced as 0.6 wt % TiO_2. The glass was melted under reducing conditions in a gas furnace at 1400° C for 30 min, resulting in a transparent light-violet glass.

Absorption spectra were taken using a CARY 17 spectrophotometer. For photoluminescence measurements two continuous sources were used: a He–Ne laser (5 mW power, $\lambda = 632.8$ nm) and an argon laser (100 mW power, $\lambda = 514.5$ nm). The emitted light, mechanically chopped at 430 Hz, was focused on a cooled RCA 7102 photomultiplier which has a S1 response extended to the infrared region.

To check the presence in the glass of titanium ions with a valence of +3 EPR measurements were taken on a powdered sample with a Varian E-12, X band spectrometer at 100 kHz field modulation. For g determination, microwave frequency was measured with an HP 5342 A frequency counter and the absolute magnetic field values were measured with a Bruker NMR gaussmeter ER 035 M. The typical asymmetric band of Ti^{3+} (see Fig. 1) in a distorted octahedral field is obtained with a g value of 1.92. It is in good agreement with previous data reported for other phosphate glasses [4], indicating the presence of Ti^{3+} ions.

3. Results and discussion

Fig. 2 shows the optical absorption at liquid nitrogen temperature (LNT) for the doped phosphate glass. It

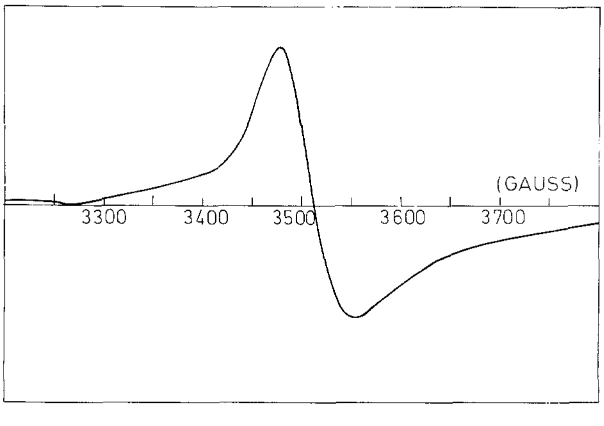

Figure 1 EPR spectrum of Ti^{3+} in phosphate glass at room temperature.

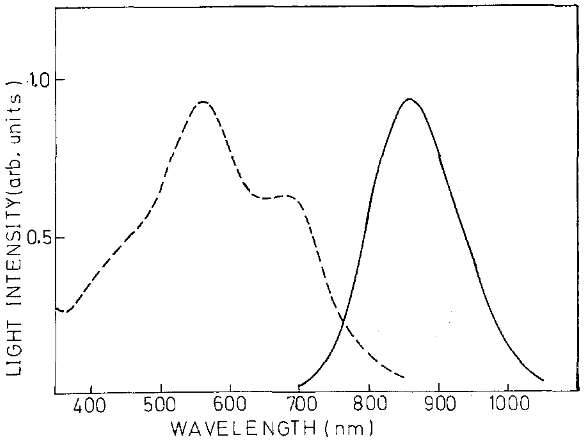

Figure 2 (– – –) Absorption spectrum of titanium-doped phosphate glass at LNT; (——) fluorescence spectrum of Ti^{3+} in phosphate glass at LNT under excitation at 632.8 nm.

consists of a band with two components peaking at 560 and 697 nm. This spectrum is analogous to that previously reported for Ti^{3+} in phosphate glasses [4]. The absorption spectrum at room temperature (RT) is also very similar to the corresponding RT absorption spectrum reported for $Al_2O_3:Ti^{3+}$ [1], although broader and slightly shifted to lower energies (see Table I). The increase in the width of the absorption band is obviously due to inhomogeneous broadening. This absorption band is due to transitions between sublevels of the $3d^1$ configuration of trivalent titanium, which in an octahedral cubic field splits into two levels, T_{2g} ground state and E_{2g} excited state. From the middle position of the absorption spectrum it is possible to calculate a 10 Dq value of 16130 cm^{-1}. This indicates that the cubic crystal field acting on the site in which Ti^{3+} is located is lower than that corresponding to Al_2O_3, for which 10 Dq = 19120 cm^{-1}.

The two peaks present in the absorption spectrum have been interpreted as a dynamical Jahn–Teller splitting in the E_g excited state [4, 5], although this level is also split by taking into account tetragonal field distortion and spin-orbit interaction. From the maxima positions of these bands an experimental value of the splitting can be obtained: 3510 cm^{-1} at RT. This result is in agreement with that previously reported for other Ti^{3+}-doped phosphate glasses [4], and greater than that obtained from the absorption spectrum reported for sapphire (Al_2O_3) at the same temperature ($\sim$2500 cm^{-1}) [7].

The temperature dependence of the absorption spectrum has also been investigated in the range 77 to 300 K. Only small changes in the band intensity have been observed.

TABLE I Comparison between the optical spectroscopic parameters of Ti^{3+} in Al_2O_3 and in phosphate glass

	$Ti^{3+}:Al_2O_3$	Ti^{3+} : glass
Abs. peaks (nm)	500–569	560–697
Emission peak (nm)	746	860
Stokes shift (cm^{-1})	5710	4840
Abs. width (cm^{-1})	4600	7820
10 Dq (cm^{-1})	19120	16130
Splitting in absorption (cm^{-1})	2500	3510
Emission width at LNT (cm^{-1})	2340	2020

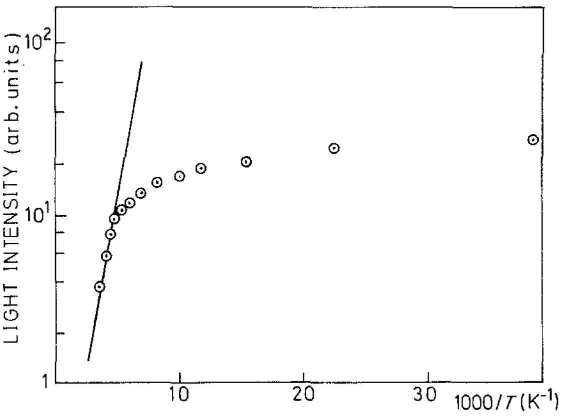

Figure 3 Temperature dependence of the intensity of the emission band.

Photoluminescence measurements were taken under excitation in the two regions of the absorption band (λ = 514.5 and 623.8 nm) leading to a similar emission spectrum. As an example, Fig. 2 includes the LNT emission spectrum obtained under excitation with the He–Ne laser line (632.8 nm). A broad and structureless band (full width at half maximum 2020 cm^{-1}) centred at 860 nm is observed, and it can be associated with the transition between the lowest Jahn–Teller component of the E_g excited state and the split components of the groundstate manifold T_{2g}.

Measurements of the variation of emission intensity with temperature have also been carried out in the range 10 to 300 K. As the temperature rose a decrease in the intensity was observed (see Fig. 3). This decrease is attributed to a thermal depopulation of the excited level in a similar way to the $Al_2O_3:Ti^{3+}$ system [7, 8]. The activation energy for this process has been calculated as 730 cm^{-1}.

Table I shows, for the sake of comparison, the most relevant spectroscopic parameters of Ti^{3+} for the two matrices: Al_2O_3 crystal and phosphate glass. In summary, the similarities between the optical properties of Ti^{3+} in both matrix hosts should be noted and it is important to point out that the different emission ranges covered by the glass could allow another possible spectral range for tunability.

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