

## OPTICAL SPECTROSCOPIC STUDY OF $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ UNDER HYDROSTATIC PRESSURE

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This work investigates the effect of hydrostatic pressure on the excitation, emission and lifetime of  $\text{Ti}^{3+}$ -doped  $\text{Al}_2\text{O}_3$  in the 0–110 kbar range. The application of pressure induces band shifts that are correlated with the corresponding local structural changes undergone by the  $\text{TiO}_6$  complex. The increase of the Stokes-shift and the reduction of the Jahn–Teller (JT) splittings under pressure are analysed in terms of a simple model based on linear electron–phonon couplings to the  $a_{1g}$  and the JT  $e_g$  vibrational modes.

*Keywords:* Jahn–Teller Effect;  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ ; Hydrostatic pressure; Optical spectroscopy

### 1 INTRODUCTION

The technological application of NIR tunable lasers has motivated the fundamental study of transition metal ions such as  $\text{Ti}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cr}^{4+}$  or  $\text{Mn}^{5+}$ . Among them,  $\text{Ti}^{3+}$  is the ion with the simplest electronic configuration,  $3d^1$ . When this ion is introduced into  $\text{Al}_2\text{O}_3$ , the  $C_{3v}$  crystal field (nearly octahedral) splits the  ${}^2D$  free ion state into  ${}^2E_g$  and  ${}^2T_{2g}$  states. Although  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  has been intensively investigated for its extraordinary laser capabilities, there are fundamental aspects concerning electron–phonon coupling, which deserves clarification. This fact together with the Jahn–Teller (JT) character of  $\text{Ti}^{3+}$  makes it very attractive system as a four-level laser material (Fig. 1). This work investigates the variation of the linear electron–phonon couplings between  ${}^2E_g$  and  ${}^2T_{2g}$  electronic states, and the  $a_{1g}$  and JT  $e_g$  vibrational local modes as a function of the crystal volume (*i.e.*  $\text{Ti}^{3+}-\text{O}^{2-}$  distance). For this purpose, we have carried out excitation, luminescence and lifetime measurements under hydrostatic pressure in the 0–110 kbar range. Previous pressure works on  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  by optical absorption spectroscopy [1] and luminescence at low temperature [2] were not done in purely hydrostatic conditions, what is a serious impediment to achieve this goal.

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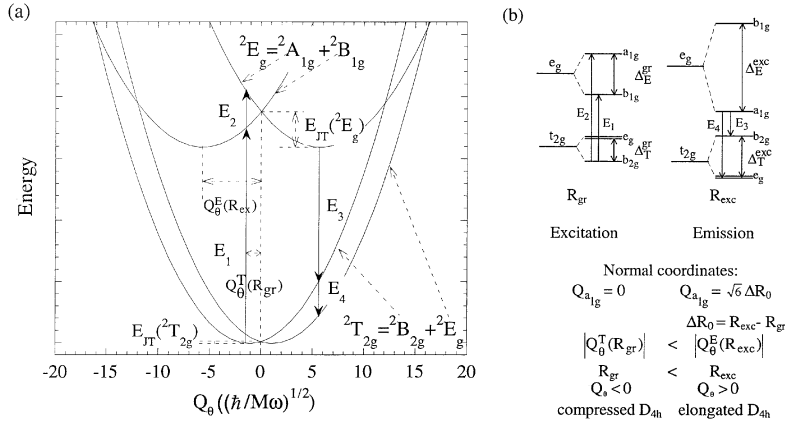


FIGURE 1 (a) Configurational-coordinate potential-energy diagrams of the  ${}^2E_g$  and  ${}^2T_{2g}$  electronic states for the  $TiO_6$  complex.  $E_1$  and  $E_2$  ( $E_3$  and  $E_4$ ) indicate the electronic transitions between the ground-state (excited-state) minimum and the excited (ground) state. (b) One-electron energy level diagrams illustrating the absorption and emission transitions. The splittings correspond to the Jahn–Teller effect in the ground state (left) and in the excited-state (right).

## 2 EXPERIMENT

Microcrystals of  $Al_2O_3$  doped with 0.35 mol%  $Ti^{3+}$  ( $\sim 50 \times 120 \times 70 \mu m^3$ ), grown by the Kyropoulos technique, were studied by hydrostatic pressure experiments using a diamond anvil cell (High Pressure Diamond Optics, Inc.). A mixture of 16:3:1 methanol–ethanol–water was used as pressure transmitter medium. The 530.9 nm line of a  $Kr^{+}$ -ion laser (Coherent CR-500 K) was used to pump the  $Ti^{3+}$  into the  ${}^2E_g$  excited state. We used a Jobin-Yvon U1000 double-monochromator for the emission spectra, while the excitation spectra were obtained by means of a photoluminescence setup specially designed for detecting very weak intensities. For lifetime measurements the excitation beam was modulated with an acousto-optic modulator and the signal processing was accomplished by Tektronix 2430 A digital scope. The pressure was calibrated through the Raman shift of Silicon chips in order to prevent unwanted luminescence signal from Ruby chips (see more details in ref. [3]).

## 3 RESULTS

Figure 2(a) shows the luminescence and corresponding excitation spectra of  $Al_2O_3:0.35 \text{ mol\% } Ti^{3+}$  at ambient conditions. Both spectra consist of a broad band exhibiting a double-humped structure, which is mainly associated with the JT effect. The variation of the transition energy upon pressure is plotted in Fig. 2(b). The splittings related to the JT effect and the trigonal crystal-field components for excitation and emission are respectively given by

$$\begin{aligned} \Delta E_E^{gr}(P) &= E_2 - E_1 = 2900 - 1.66 P \\ \Delta E_T^{exc}(P) &= E_4 - E_3 = 1220 - 0.53 P \end{aligned}$$

The  $\Delta E_E^{gr}(P)$  and  $\Delta E_T^{exc}(P)$  splittings correspond to an average  $Ti^{3+}-O^{2-}$  distance  $R_{gr}$  for the ground state and  $R_{exc}$  for the excited state. The splittings decrease both upon increasing

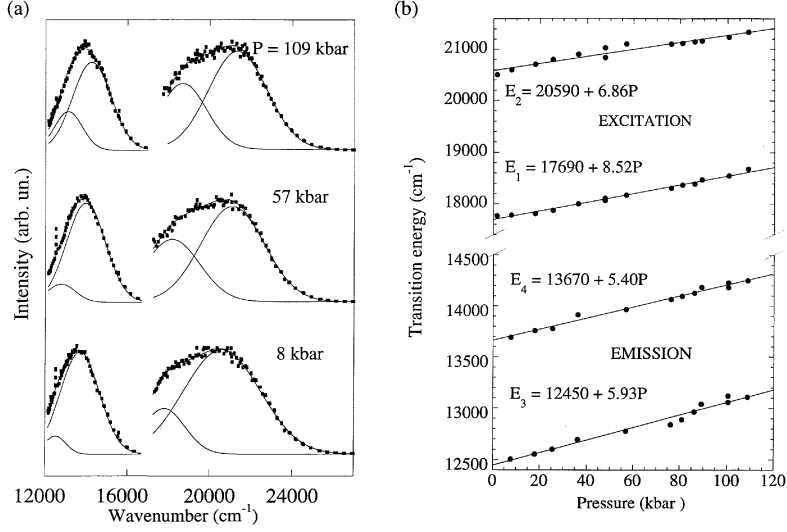


FIGURE 2 (a) Variation of the emission and excitation spectra with hydrostatic pressure at  $T = 293$  K. All the spectra have been fitted to the sum of two gaussians. Solid lines represent the gaussians and the corresponding sums, together with the experimental data (dots). (b) Emission and excitation shifts corresponding to the peak energy of the two components of the luminescence and excitation spectra. Straight lines are linear fits of the data.

the pressure. On the other hand, the variation of the centroid of the bands, directly related to  $10Dq$ , increases by  $7.7 \text{ cm}^{-1}/\text{kbar}$  with the pressure, as it is expected for a reduction of the  $\text{Ti}^{3+}-\text{O}^{2-}$  distance.

#### 4 DISCUSSION

The emission and excitation spectra at ambient pressure and room temperature of  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ , can be explained on the basis of simple octahedral  $\text{TiO}_6$  complex, through linear electron–phonon couplings between the  ${}^2T_{2g}$  electronic ground state (for excitation) and the  ${}^2E_g$  electronic excited-state (for emission) with the totally symmetric  $a_{1g}$  and the JT  $e_g$  ( $Q_\theta$ ,  $Q_\epsilon$ ) vibrational local modes [4]. Within this scheme two transitions are possible for excitation ( $E_1$  and  $E_2$ ) and also for emission ( $E_3$  and  $E_4$ ) (Fig. 1). The corresponding splitting shown in Fig. 1(b) gives directly the JT distortion of the complex in their respective  ${}^2E_g$  and  ${}^2T_{2g}$  electronic states ( $\Delta_E^{\text{gr}}(R_{\text{gr}}) = 2740 \text{ cm}^{-1}$  for excitation, and  $\Delta_T^{\text{exc}}(R_{\text{exc}}) = 1540 \text{ cm}^{-1}$  for emission). It is noteworthy that these splittings are similar although the electron–phonon coupling of the  ${}^2E_g$  octahedral state for the same value of the configuration coordinate,  $Q_\theta$ , is about four times higher than for  ${}^2T_{2g}$  [5, 2]. Within a linear electron–phonon coupling to  $e_g$  vibration, the JT splittings can be expressed as [3]

$$\Delta_T^{\text{exc}}(R_{\text{exc}}) = |A_1^T Q_\theta^E| = \frac{A_1^T A_1^E}{K_{\text{exc}}} \quad \text{and} \quad \Delta_E^{\text{gr}}(R_{\text{gr}}) = |A_1^E Q_\theta^T| = \frac{A_1^E A_1^T}{K_{\text{gr}}}$$

Here,  $K_i = \mu \cdot \omega_i^2$  is the force constant for the  $e_g$  vibration and  $\omega_i$  is the corresponding angular frequency with  $i = \text{gr}$  and  $\text{exc}$  for the parent octahedral  ${}^2E_g$  and  ${}^2T_{2g}$  electronic

states, respectively. The total contributions to the Stokes-shift including both JT  $e_g$  and  $a_{1g}$  couplings are:  $E_{SS}^{JT} \equiv \frac{1}{2} [|A_1^E Q_\theta^E| + \frac{4}{3} |A_1^T Q_\theta^T|]$  and  $E_{SS}(a_{1g}) = |A_{a_{1g}} Q_{a_{1g}}|$ , where  $A_{a_{1g}} = (\partial_{10} Dq / \partial Q_{a_{1g}})_{Q_{a_{1g}}=0}$ . These values can be measured independently as a function of the crystal volume by optical spectroscopy under pressure. Figure 2 shows that the JT splittings decrease under pressure, while the Stokes-shift contribution for  $a_{1g}$  increases.

Assuming variations of the linear electron–phonon coupling with volume (or  $R$ ) as  $A_{a_{1g}} \propto R^{-(n+1)}$  with  $n = 5$  for oxides [1] and  $\omega_{a_{1g}} \propto R^{-3\gamma}$ , then  $Q_{a_{1g}} \propto R_{gr}^{-6(1-\gamma)}$ , thus  $E_{SS}(a_{1g}) \propto R^{-6(2-\gamma)}$ . Taking  $\gamma \approx 1.31$  [6], we can justify why Stokes-shift increases upon increasing the pressure. On the assumption that  $A_1^T \propto R_{gr}^{-(n_T+1)}$  and  $A_1^E \propto R_{exc}^{-(n_E+1)}$ , we obtain, analogously, the JT splitting as a function of the ground- and the excited-state equilibrium geometries,  $R_{gr}$  and  $R_{exc}$ , are given by:

$$\Delta_E^{gr}(R_{gr}) \propto \frac{R_{gr}^{-(n_E+1)} R_{gr}^{-(n_T+1)}}{\omega_{gr}^2} \quad \text{and} \quad \Delta_T^{exc}(R_{exc}) \propto \frac{R_{exc}^{-(n_T+1)} R_{exc}^{-(n_E+1)}}{\omega_{exc}^2}$$

where  $R_{exc} = R_{gr} + \Delta R$  and  $n_E < n_T$ . Taking  $10 Dq = 19130 \text{ cm}^{-1}$ ,  $\hbar\omega_{a_{1g}} = 515.3 \text{ cm}^{-1}$  [7] and  $R_{gr} = 1.9 \text{ \AA}$ , then we estimate  $R_{exc} = 2.06 \text{ \AA}$  at  $P = 0$ . Vibrational energies for  $\text{TiO}_6$  in  $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$  are:  $\hbar\omega_T = 239 \text{ cm}^{-1}$  and  $\hbar\omega_E \approx 200 \text{ cm}^{-1}$  [4]. Using  $n_T = n_E = 4$ , we find a relationship between their corresponding JT splittings as

$$\frac{\Delta_E^{gr}(R_{gr})}{\Delta_T^{exc}(R_{exc})} \equiv \left( \frac{R_{gr}}{R_{exc}} \right)^{-(n_E+n_T+2)} \left( \frac{\omega_{exc}}{\omega_{gr}} \right)^2 = 1.57,$$

which is very similar to the observed value of  $(\Delta_E^{gr}(R_{gr})/\Delta_T^{exc}(R_{exc})) = 2740/1530 \sim 1.8$ .

However, the situation is rather different for the pressure dependence of the JT splitting, which decreases with the pressure (Fig. 2(b)). Considering  $\Delta_E^{gr}(R_{gr}) \propto A_1^E A_1^T \omega_{gr}^{-2} \propto R_{gr}^{-(10-6\gamma)}$ , a decrease of the JT splitting induced by pressure can be explained through this model provided that  $\gamma > 1.7$ , for the  $e_g$  local mode.

In conclusion, the opposite pressure behaviour exhibited by the Stokes-shift and the JT splittings associated with the  ${}^2E_g$  and  ${}^2T_{2g}$  electronic states, can be explained in terms of a simple  $\text{TiO}_6$  octahedral model, considering linear electron–phonon coupling to the local  $a_{1g}$  and the JT  $e_g$  vibrational modes. The distinct pressure behaviour is mainly associated with a different Grüneisen parameter for each mode:  $\gamma_{a_{1g}} < 1.7$  and  $\gamma_{e_g} > 1.7$ .

A complete analysis of the present results is given elsewhere [3].

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