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Luminescence properties of $(La,Pr)_2Ti_2O_7$

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Abstract

The luminescence properties of the pyrotitanates $(La,Pr)_2Ti_2O_7$ are examined as a function of the Pr^{3+} concentration in the range 0.2–15 mol% Pr. Under UV excitation at 337 nm, the compounds exhibit intense luminescence signals due to praseodymium arising mainly in the blue and in the red region of the spectrum. The red emission is due essentially to Pr $^1D_2 \rightarrow ^3H_4$ transitions and appears to be the more intense in the lowest Pr-concentrated compounds. In contrast, the blue luminescence (Pr $^3P_0 \rightarrow ^3H_4$ transitions) is predominant in the highest Pr-activated titanates. This behaviour is explained by considering two distinct categories of sites inside which the Pr^{3+} ions undergo crystal field effects of different strengths. © 1998 Elsevier Science S.A.

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1. Introduction

The investigation of the luminescence properties of the pyrotitanates $(La,Pr)_2Ti_2O_7$ follows the study of the perovskite-like $CaTiO_3$:Pr^{3+} high-gap semi-conductors in which a single bright red photoluminescence due to Pr $^1D_2 \rightarrow ^3H_4$ transitions was observed [1]. This red emission was produced under a blue Pr $^3H_4 \rightarrow ^3P_J$ ($J=1$, 2) excitation and also under UV pumping at 337 nm through either the conduction band states of the calcium titanate host or the Pr 4f5d band states. Similar behaviour was observed in other perovskite-like titanates such as $SrTiO_3$:Pr^{3+} and $BaTiO_3$:Pr^{3+}. In contrast, in the zirconates $CaZrO_3$:Pr^{3+} and in the hafniates $CaHfO_3$:Pr^{3+}, the emission arises predominantly in the blue-green region, which corresponds to Pr $^3P_0 \rightarrow ^3H_4$ transitions [2]. This discrepancy was explained by considering a strong downshift of the Pr 4f5d band by crystal field effects in the titanates, preventing any emission from the $^3P_0$ state to occur, even at low temperature [1].

This paper reports preliminary results regarding the evolution of the luminescence properties of the pyrotitanate $(La,Pr)_2Ti_2O_7$ as a function of the Pr^{3+} concentration.

2. Experimental

The pyrotitanates $(La,Pr)_2Ti_2O_7$ were prepared in the solid state by mixing stoichiometric quantities of titanium oxide, lanthanum oxide and praseodymium chloride in the presence of ethanol. The mixtures were fired under air at 1100°C for 15 h and then annealed at 1200°C for 15 h. For both thermal treatments, cooling was achieved by cutting off the power supply to the furnace. The compounds were checked systematically by X-ray powder diffraction spectroscopy and were all obtained in their monoclinic form. Care was taken to make sure of the absence of any starting product and of any other allotropic form in the patterns. After Ref. [3], the monoclinic structure of $La_2Ti_2O_7$ consists of $(Ti_2O_7)_n^{6n-}$ distorted perovskite-like layers spreading perpendicularly to the *c*-axis. The thickness of these layers corresponds approximately to four corner-linked $(TiO_6)^{8-}$ octahedra, as shown in Fig. 1. The layers contain two kinds of vacancies, both called sites (I) in the following, in which the La^{3+} ions are nine-coordinated. The La–O distances in these sites vary between 2.44 and 2.89 Å. Structural cohesion between the layers is ensured by other La^{3+} ions occupying eight- or seven-coordinated environments, called sites (II) in the following. In these sites, the La–O distances are respectively in the intervals 2.41–2.84 and 2.38–2.57 Å. In this inter-layer region, the La–La separation varies between 3.89 and 4.35 Å. Therefore, the pyrotitanate structure offers four different crystallographic sites for the lanthanide ions, the sites of type (II) certainly presenting a more pronounced covalent character than the sites of type (I).

The optical properties of $(La,Pr)_2Ti_2O_7$ were examined at 15 and 300 K for Pr^{3+} molar percentages between 0.2 and 15%. The compounds were excited using either a

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Jobin–Yvon pulsed nitrogen laser or a ND 60 dye laser equipped with mixtures of rhodamines 590+610 or 610+640, pumped by a Continuum Surelite I SL-10 doubled Nd^{3+}:YAG laser (10 ns pulse, 0.1 cm^{-1} bandwidth). A Raman cell filled with 30 atm H_2 was added at the output of the dye laser to pump resonantly into the Pr ^3P_J levels ($J=0$, 1, 2) by using the generated antiStokes beams.

The time-resolved spectra and the luminescence decays were recorded respectively with the help of a EG&G Par Boxcar averager 162/164 and a 9310A Lecroy oscilloscope.

3. Optical results and discussion

The time-resolved emission spectra of $(La,Pr)_2Ti_2O_7$ shown in Fig. 2 were recorded under 337 nm pumping at room temperature. Although this excitation does not coincide with any of the 4f levels of Pr^{3+}, luminescence signals due to praseodymium were observed in the blue and in the red region of the spectrum. These signals are due mainly to Pr $^3P_0 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_4$ transitions, respectively. For short delay times after the laser pulse (i.e. 1 μs), the blue emission is always predominant in the spectra, whatever the composition tested. In contrast, when the delay time is increased to 10 μs, the relative contribution of the red luminescence is strongly enhanced, especially in the lowest Pr-activated pyrotitanates. In the highest Pr-concentrated compound, the emission spectra show no modification with respect to the delay time. The dynamical effects can be rather easily explained by considering the lifetimes of the emitting Pr $^3P_0$ and $^1D_2$ states, which have been estimated respectively at 2 and 50 μs at 15 K. In contrast, it is more difficult to understand why the red Pr $^1D_2 \rightarrow {}^3H_4$ emission is found to be the more intense in the lowest-concentrated pyrotitanates. Usually, the main emitting state of praseodymium in doped systems is $^3P_0$, which results in a blue or a blue-green emission. In oxides, the population of the $^1D_2$ level can be achieved from the $^3P_0$ state, to a certain extent, through non-radiative deexcitation processes involving several phonons coupled to energy transfers between neighbouring ions, as soon as the Pr concentration is high enough. Nevertheless, in such conditions, the red Pr $^1D_2 \rightarrow {}^3H_4$ emission usually remains weaker than the $^3P_0 \rightarrow {}^3H_4$ emission [4].

To clarify this point and to determine which sites in the structure are involved in the luminescence processes, several excitation spectra have been recorded at 15 K in the red domain, i.e. corresponding to $^3H_4 \rightarrow {}^1D_2$ transitions. The Pr concentration dependence of the integrated intensity of the red and blue emission signals has also been analysed through UV excitation. The results are plotted in Figs. 3 and 4, respectively. The spectra shown in Fig. 3a,b are related to the red luminescence in the 0.5 and 5 mol% Pr-activated compounds. Both spectra contain 10 excitation lines which represent in both cases twice the maximum number of Stark components expected for the $^1D_2$ level in a given site. Therefore, for each composition, such features reveal that the Pr ions occupy two sites in the structure. Furthermore, it is obvious that these sites are not equivalent in the two compounds since the excitation lines appear to be globally red-shifted by some 50 cm^{-1} when going from the 0.5 mol% doped sample to the 5 mol% Pr-activated titanate. Accordingly, it seems that the praseodymium ions occupy two sites with a high covalent character in the low Pr-activated materials – such as sites (II) – and two other sites with a lower covalent character (i.e. sites (I)) in the higher Pr-concentrated compounds. In the 5 mol% Pr titanate, the occupation of two distinct sites by the ions is accredited by the observation of two distinct peaks in the time-resolved low temperature excitation spectrum of the green $^3P_0 \rightarrow {}^3H_5$ luminescence (see inset of Fig. 3).

Owing to this description, an interpretation of the data plotted in Fig. 4 can be given. In the weakly doped compounds, the red luminescence is maximum and is due mainly to the $^1D_2 \rightarrow {}^3H_4$ transitions of Pr ions in sites (II), i.e. in the inter-layer space of the structure. For this concentration range, the contribution of the Pr ions located in sites (I) to the red emission seems very weak. When the Pr concentration increases to 5 mol%, the intensity of the red luminescence starts to decrease rapidly and then shows a kind of horizontal plateau which appears to be correlated with the shape of the blue emission curve. At a Pr composition of 5 mol%, the red luminescence consists essentially of $^1D_2 \rightarrow {}^3H_4$ transitions due to Pr ions located in sites (I), i.e. inside the perovskite-like layers. In this compound, the contribution of the Pr ions located in sites (II) to the red emission is negligible, which means that the luminescence produced by these latter ions is already almost completely quenched. This effect may be due to efficient cross-relaxation energy transfers by means of electric dipole interactions between the Pr ions in the inter-layer space. If the Pr concentration is increased to 10 mol%, the intensity diminishes strongly, but is not quenched. In these concentrated compounds, the evolution of the red and blue signals vs. the Pr concentration remains strictly parallel and shows no modification with respect to the delay time. This suggests that the red emission is due mainly to $^3P_0 \rightarrow {}^3H_6$ relaxations from Pr in sites (I).

Finally, the spectroscopic properties of UV-pumped $(La,Pr)_2Ti_2O_7$ can be interpreted by considering the two energy level diagrams reproduced schematically in Fig. 5. In this matrix, the fundamental absorption edge is around 330 nm and the $^3P_0$ and $^1D_2$ states lie respectively some 9850 and 13 900 cm^{-1} below the conduction band (CB). This makes any direct non-radiative relaxation from this latter band to the Pr $4f^2$ levels unexpected. We assume therefore that the Pr luminescence is produced through pumping into Pr 4f5d or charge transfer band states, which lie below the CB, as was previously observed in perovskite-like calcium titanates [1]. Concerning the ions in sites

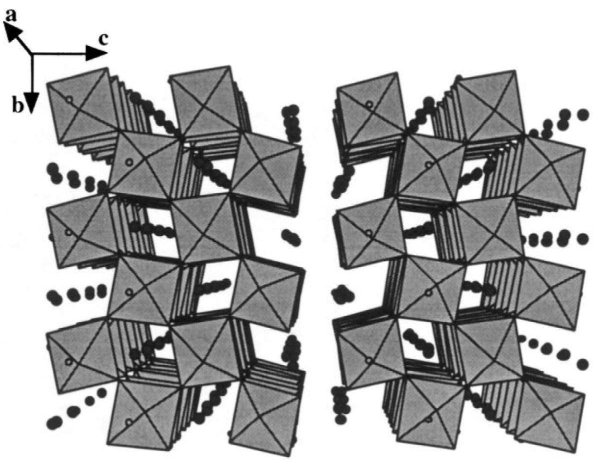

Fig. 1. Three-dimensional view of the structure of $La_2Ti_2O_7$. The $(TiO_6)^{8-}$ octahedra are represented in grey and the La^{3+} ions are in black. Data taken from Ref. [3].

(II), the UV excitation reaches the band and is transferred non-radiatively into the $^1D_2$ state, which emits. In this case, the Pr-related band is strongly downshifted by crystal field effects, so that a radiative relaxation from the $^3P_0$ state is expected only with a very weak probability. The situation concerning the Pr ions in sites (I) is slightly

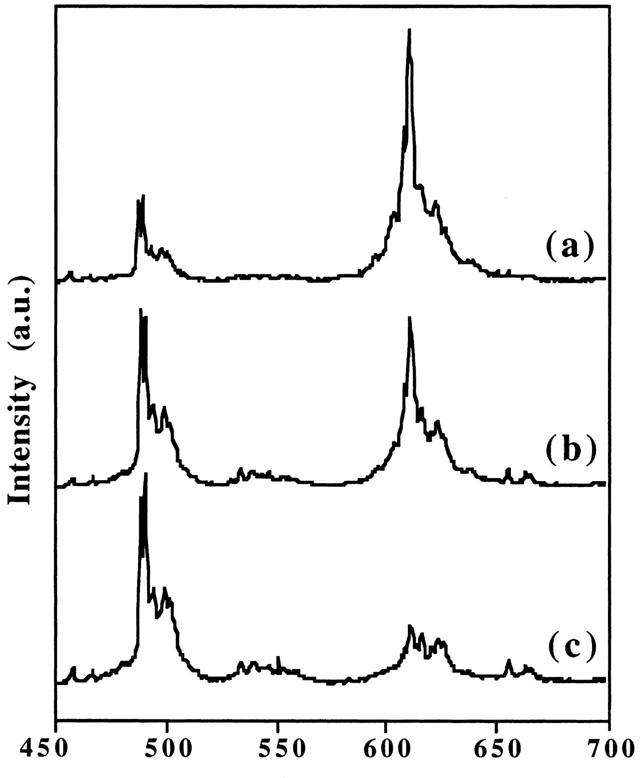

Fig. 2. Time-resolved emission spectra of $(La,Pr)_2Ti_2O_7$ at 300 K under 337 nm excitation for Pr^{3+} molar percentages of (a) 0.5%, (b) 5% and (c) 15%. The delay time after the laser pulse was 10 μs and the gate width was 0.5 μs.

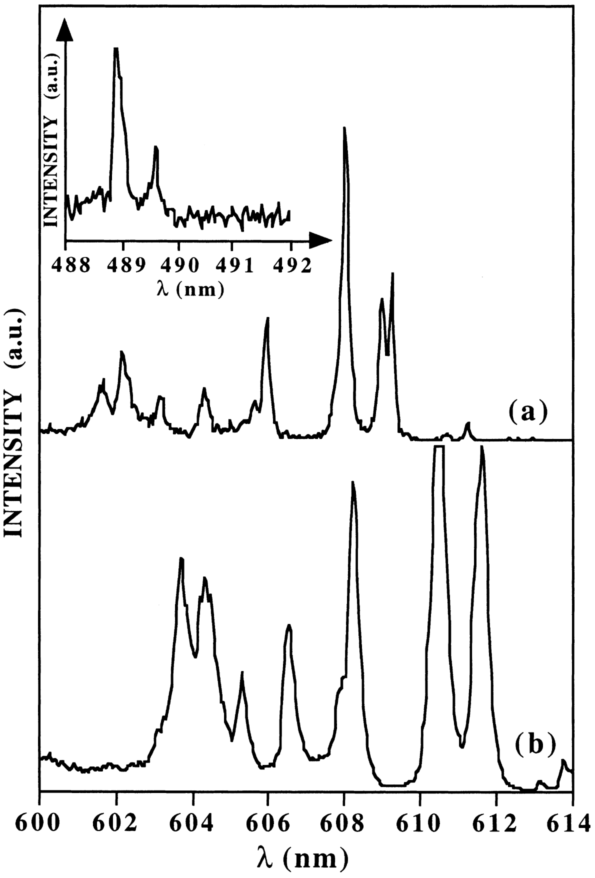

Fig. 3. Time-resolved excitation spectra at 15 K for the red luminescence (λ_{em}=623.5 nm) in a 0.5 mol% Pr (a) and in a 5 mol% Pr-concentrated pyrotitanate (b). The delay time after the laser pulse was 5 μs and the gate width was 0.5 μs. The inset shows the time-resolved excitation spectrum at 15 K for the blue Pr $^3P_0 \rightarrow {}^3H_5$ emission (λ_{em}=545 nm) in the 5 mol% Pr compound (delay time 0.5 μs, gate width 50 ns).

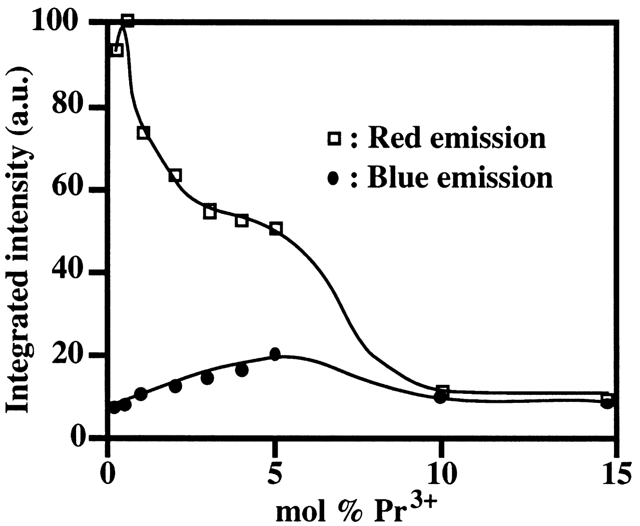

Fig. 4. Evolution of the integrated intensity of the blue (●) and red (□) luminescence signals versus Pr concentration at 300 K under 337 nm pumping. Delay time 100 μs, gate width 5 μs.

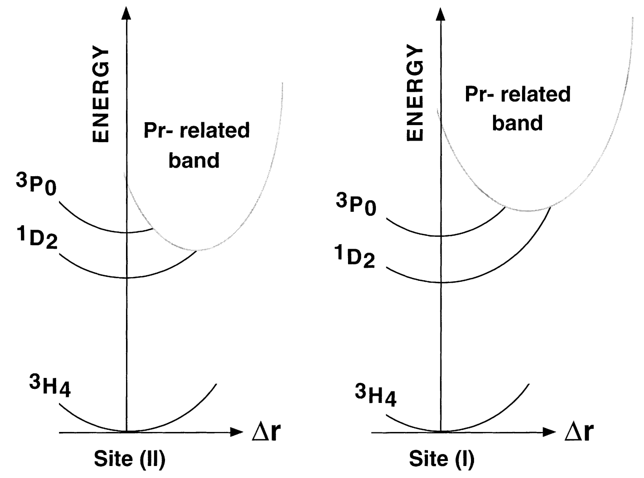

Fig. 5. Schematic one-coordinate energy level schemes proposed for Pr^{3+} ions occupying sites (I) and sites (II) in $(La,Pr)_2Ti_2O_7$.

different since these ions undergo a less pronounced crystal field effect. Therefore, one expects in this case a less important lowering of the band coupled with a larger Δr offset, as shown schematically in Fig. 5. Accordingly, UV pumping into this band is followed by a non-radiative de-excitation in the $^3P_0$ and $^1D_2$ states, which can both emit. Luminescence decay measurements are now in progress to clarify this observation and to improve our knowledge of the dynamical processes involved.

4. Conclusion

The luminescence properties of $(La,Pr)_2Ti_2O_7$ are explained by considering two categories of sites inside which praseodymium undergoes crystal field effects of variable strengths. The Pr^{3+} ions accommodated in the inter-layer space exhibit a single red $^1D_2 \rightarrow ^3H_4$ luminescence, for example as in $CaTiO_3:Pr^{3+}$, whereas the Pr^{3+} ions distributed inside the distorted perovskite-like layers emit mainly in the blue-green region ($^3P_0 \rightarrow ^3H_4$) and to a certain extent in the red region ($^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_6$), for example as in Ca-modified $ZrO_2:Pr^{3+}$ [1,5]. These results suggest that the observation of a bright red luminescence from the Pr $^1D_2$ level may be a typical feature for Pr^{3+}-activated titanate-based compounds. Other systems are now under investigation to confirm this general behaviour.

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