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Journal of Alloys and Compounds 323–324 (2001) 768–772

Journal of ALLOYS AND COMPOUNDS

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Pr^{3+} Centers in YSZ single crystals

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Abstract

The low-temperature optical-absorption and fluorescence spectra of Pr^{3+} ions in yttria stabilized zirconia single crystals were extensively investigated. From total site selective spectroscopy and time resolved measurements, at least three different optical centers were identified and associated with Pr^{3+} ions in two different coordinations. In two centers, Pr^{3+} ions are in sevenfold oxygen coordination while in the third one they are in sixfold coordination. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Disordered systems; Point defects; Optical properties; Luminescence and time resolved optical spectroscopies

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1. Introduction

Interest in studying Pr^{3+}-doped solid state materials has been continuously increasing because they exhibit excellent laser capabilities and their emission spectra extend from the blue to the near infrared region. Laser action, including up-conversion lasing under IR excitation, has been reported for Pr^{3+} ions in crystals and in fibers [1–5].

Yttria stabilized zirconia (YSZ) solid solutions have a wide range of technological applications. Most of its properties are related to the presence of a large amount of oxygen vacancies associated with the charge compensation induced when Y_2O_3 is added to ZrO_2 to stabilize the cubic phase. The availability of large YSZ crystals of good optical quality makes this system a good candidate to be used in optical devices. Laser action has been reported in several doped yttria stabilized systems [1,2].

YSZ, or $(ZrO_2)_{1-x}(Y_2O_3)_x$, has the CaF_2 structure for a wide range of x-values. Because of the highly distorted structure, impurities can be located in a large number of sites. The sites of impurity ions and their associated oxygen vacancy redistribution have been analyzed using luminescence as an optical probe. Direct evidence of the presence of several optical centers has been obtained in cubic YSZ doped with relatively small rare-earth ions, such as Er^{3+} and Eu^{3+} [6–8]. In these centers the oxygen coordination around active impurities is not only eightfold (CN8) but also sevenfold (CN7) and sixfold (CN6). However, some impurities such as Nd^{3+} are incorporated only in CN7 configurations [9]. Oxygen vacancies result in slight departures of the local environment from the fluorite-type lattice [7,8]. For impurity ions located at cationic sites the ideal site symmetry is O_h for ions in CN8 sites, C_{3v} symmetry for ions in CN7 and C_{3i}/S_6 or C_{2v} in CN6 sites.

In this work, a systematic research of the low temperature optical spectra (absorption and luminescence) is carried out in order to obtain direct evidence of the presence of several Pr^{3+} centers in YSZ. Because of the highly distorted structure of these crystals, highly inhomogeneous broad optical bands are obtained even at very low temperatures.

2. Experimental details

Single crystals of ZrO_2 stabilized with 16 wt.% Y_2O_3 and doped with 0.05 wt.% Pr_2O_3, were purchased from Ceres Corporation (USA). Excellent optical quality crystals were grown by the skull method. Samples were cut with a diamond saw and polished to optical quality. From X-ray fluorescence analysis, the composition of the sample was determined to be $Y_{0.193}Hf_{0.085}Zr_{0.795}Pr_{0.010}O_{1.901}$ (the praseodymium concentration is 2.2×10^{19} cm^{-3}).

Optical absorption measurements in the UV–Vis–IR were made with a Perkin-Elmer Lambda 19 spectrophotometer. For emission measurements a continuous Spectra Physics Ar^+ laser or a pulsed LSI Dye laser was used as the excitation sources. Emitted light was focused into the entrance slit of a SPEX 1000M monochromator and detected with a Hamamatsu R943-02 cooled photo-

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01082-9

multiplier. The spectra were recorded with a SR400 gated photon counter or a Tektronix TDS-620 digital oscilloscope. A temperature controlled closed-cycle helium cryostat was used for the low temperature measurements. Measurements were made at 15 K.

3. Results and discussion

The optical spectra of rare earth ions in a solid are mostly due to transitions between different states within the $4f^n$ configuration. For Pr^{3+} ions, the $4f^2$ configuration produces a number of *J*-states. Degeneration of these states is partially removed by a symmetric crystal field: any *J* level of the free ion split into a number of Stark levels depending on the *J*-value and the local symmetry of the center (see, for instance, Ref. [1]). In YSZ crystals, the ideal site symmetry for Pr^{3+} ions can be O_h, C_{3v}, C_{3i}/S_6 or C_{2v} depending on the oxygen coordination. The number of Stark sublevels observed in a particular transition provides information about the local symmetry of the center.

The optical properties (absorption and luminescence) of Pr^{3+}-doped YSZ crystals have been investigated recently and the fluorescence dynamics has been analyzed under the basic assumption that praseodymium ions were statistically distributed [10]. Assuming a random distribution of oxygen vacancies, the majority (85%) of Pr^{3+} ions must be in the CN7 configuration and trigonally distorted (C_{3v}) cubic symmetry it is expected to be the dominant symmetry of the Pr^{3+} centers. The minority centers are in CN6 configuration, which includes both trigonal (C_{3i}) and orthorhombic (C_{2v}) symmetries. Since only electric-dipole transitions occur [11], luminescence from ions in the C_{3i} symmetry can be neglected because an inversion center is present and very low absorption intensities are induced. Thus, only two types of centers, namely CN6 with C_{2v} ideal symmetry and CN7 with C_{3v} ideal symmetry, are mainly responsible for the optical properties. The Pr^{3+} luminescence is characterized by a weak emission originating from the $^3P_0$ state and a very efficient emission from the metastable $^1D_2$ band (even when the excitation is done in the ^3P_J multiplet). The non-radiative direct relaxation into the $^1D_2$ state via the 4f5d band is the mechanism responsible for this behavior as is shown in Fig. 1. The fluorescence dynamics is satisfactorily explained by the presence of Pr^{3+} ions in CN6 and CN7 centers. The $^3P_0$–4f5d crossover energy gap is very different for each center. Relaxation to the $^1D_2$ state via the 4f5d crossover is more efficient for the CN7 center and hence the CN6 centers are mainly responsible for the $^3P_0$ emission.

3.1. Absorption spectra

The starting point to find direct evidence for different Pr^{3+} centers is the analysis of the low temperature absorption spectra. Low temperature measurements (15 K) permit disregarding the thermalized absorption bands originating from excited Stark sublevels belonging to the $^3H_4$ state. Because of the singlet character of the $^3P_0$ state, the $^3H_4 \to {}^3P_0$ absorption band has already been successfully used to resolve site structures in a crystalline matrix [12].

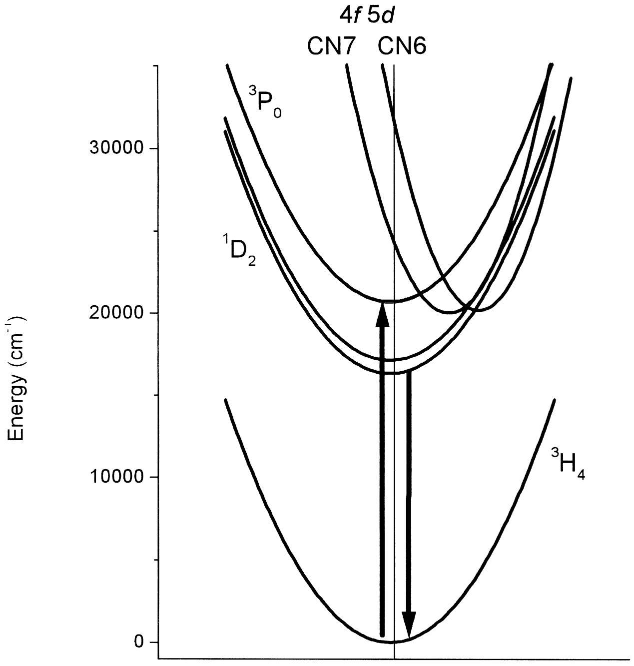

Fig. 1. Schematic representation of luminescence processes in Pr^{3+} ions in YSZ.

Fig. 2 displays the absorption spectra from the $^3H_4$ ground state (hereafter labeled as $^3H_4(0)$ state) to the $^3P_{0,1,2}$ multiplet and to the $^1D_2$ excited state. Three groups of bands are observed in the high energy part of Fig. 2 where the $^3H_4 \to {}^3P_J$ region is depicted. The $^3H_4 \to {}^3P_0$ absorption appears as only one band peaking at 485 nm and slightly asymmetric in shape. The other two groups

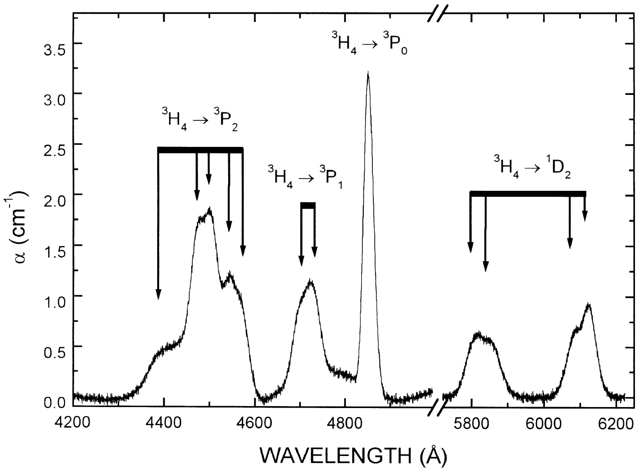

Fig. 2. Absorption spectra at 15 K of Pr^{3+} ions in YSZ. The assigned absorption bands are indicated.

have a more clearly defined structure and are ascribed to the $^3H_4 \rightarrow ^3P_1$ (two peaks) and $^3P_2$ (five peaks) transitions. The $^3H_4 \rightarrow ^1D_2$ absorption spectrum (low energy part of Fig. 2) exhibits two groups of at least two peaks. Since in cubic symmetry only two bands are expected for the $^3H_4 \rightarrow ^1D_2$ absorption transition, the shape of the latter spectrum indicates that oxygen vacancies only induce a slight departure from cubic symmetry, and this is the most important contribution to the splitting of the $^1D_2$ state.

The number of four and five components observed in the $^1D_2$ and the $^3P_2$ absorption bands, respectively, is higher than that predicted by the group theory [1] for the cubic and trigonal symmetries, but could agree for the orthorhombic symmetry. Thus, the observed structure in the absorption spectra cannot be definitely attributed to different centers. The only indication of the existence of different centers is the asymmetric shape of the $^3H_4(0) \rightarrow ^3P_0$ absorption band which could be attributed to the contribution of several components.

3.2. Emission spectra

The $^3P_0 \rightarrow ^3H_4$ fluorescence spectra, obtained at three selected excitation wavelengths (into the $^3P_0$ and $^3P_1$ absorption region), are depicted in Fig. 3a. The only differences among these spectra are the change in the intensities of the $^3H_4$ ground state components, and a slight blue shift in the emission band ending in the $^3H_4(0)$ ground level (peak at ~488 nm). These differences suggest that several Pr^{3+} centers exist. Based on a previous work [10] we assume that this emission is mainly due to CN6 centers, whereas the CN7 centers strongly relax to the $^1D_2$ state. A low intensity emission from CN7 centers (see below) could also explain the observed differences. Thus, no direct evidence of several CN6 centers is obtained from the $^3P_0$ luminescence.

Luminescence from the $^1D_2$ state, induced by excitation in the $^3P_0$ level and relaxation via the 4f5d band, is shown in Fig. 3b. The $^1D_2 \rightarrow ^3H_4$ emission spectra have been recorded for the same three excitation wavelengths as those in Fig. 3a. To avoid the overlapping emission lines from the $^3P_0 \rightarrow ^3H_6$ transitions, the spectra were recorded with a delay of 100 μs from the excitation signal. Next, we will concentrate on the emission ending in the $^3H_4(0)$ ground state, which is enlarged in the inset of Fig. 2b. The $^1D_2 \rightarrow ^3H_4(0)$ emission band is very sensitive to changes in the excitation wavelength, and shows a complex structure that changes with different excitations. Similar results, but with lower resolution, were obtained under selective excitation in the $^1D_2$ absorption band. For the sake of comparison, the $^1D_2 \rightarrow ^3H_4(0)$ emission spectra induced with selected excitations in both the $^3P_0$ and the $^1D_2$ bands are shown in Fig. 3c.

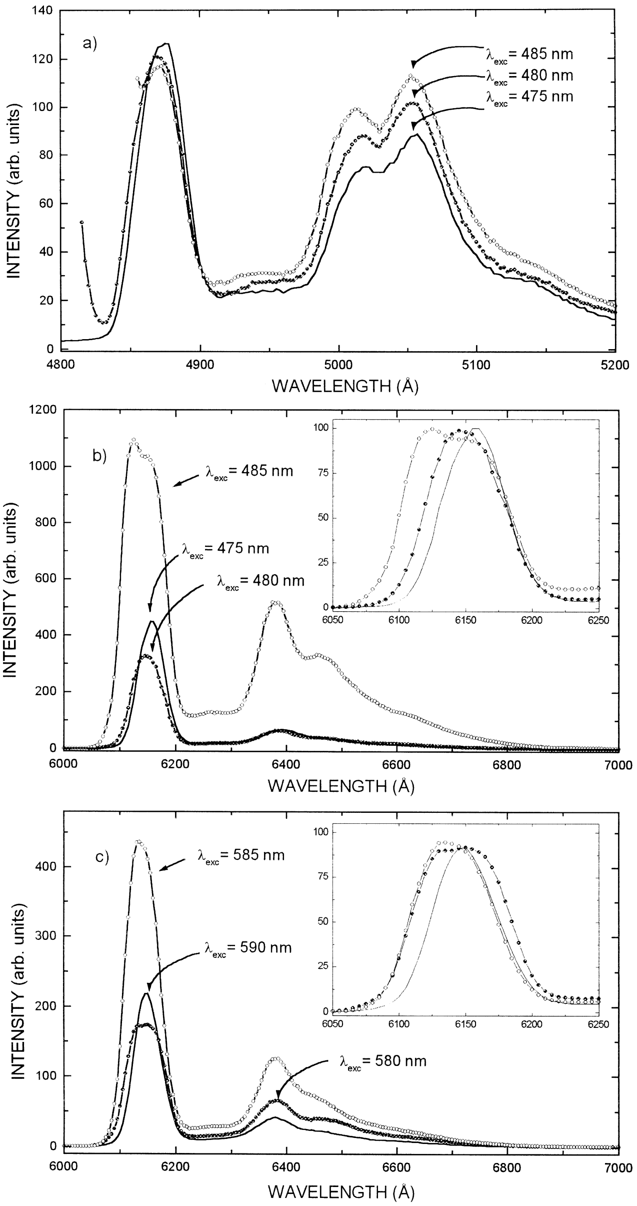

Fig. 3. Emission spectra of Pr^{3+} ions in YSZ recorded at 15 K for selected excitation wavelengths.

Taking advantage of the well-resolved structure of the $^1D_2 \rightarrow ^3H_4$ (0) emission transition, total site selective spectroscopy measurements were made under excitation in the $^3H_4 \rightarrow ^3P_0$ absorption region. Results are depicted in Fig. 4 as a contour plot. At least two maximum positions (sites) can be observed in this figure. The first peaks at about 615.0 nm and appears to be insensitive to excitation changes; the second one, peaks at 612.5 nm, and is strongly excited between 484 and 486 nm.

Assuming that the $^1D_2 \rightarrow ^3H_4$ luminescence is mainly due to the CN7 centers when the excitation is made in the $^3P_0$ absorption region, these results suggest that two CN7 centers exist there in the crystal. The resulting poor resolution of the luminescence when the excitation is done in the $^1D_2$ absorption region is likely related to the excitation of all types of centers. CN6 centers, even being in the minority, may have strong oscillator strength and

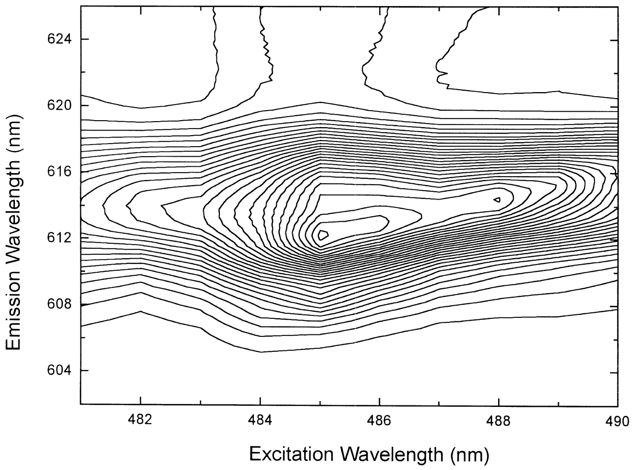

Fig. 4. Total site selective contour plot for the $^1D_2 \rightarrow {}^3H_4(0)$ transition under excitation in the $^3P_0$ absorption band (15 K).

their luminescence masks the emission from other centers yielding a poor resolution.

3.3. Time resolved measurements

In order to obtain additional information about the presence of several centers in YSZ:Pr^{3+} samples, time resolved spectra, taken under excitation in the $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ absorption regions, were made monitoring both the $^3P_0 \rightarrow {}^3H_4$ and the $^1D_2 \rightarrow {}^3H_4$ emissions.

All emissions ending in the $^3H_4(0)$ ground state show a complex behavior that involves several components. As an example, Fig. 5 shows the temporal evolution of the $^1D_2 \rightarrow {}^3H_4(0)$ emission after excitation at 485 nm ($^3P_0$ absorption band). The spectra in the inset are normalized to aid comparison. In the first 10 μs after the excitation pulse, the $^3P_0 \rightarrow {}^3H_6$ emission is almost lost. The three remaining bands, corresponding to the $^1D_2 \rightarrow {}^3H_4$ emission, show a similar evolution with time, but it is clear that the shoulders at 615 and 608 nm decrease more rapidly than the central band peaking at 612 nm. Luminescence decays are well fitted by three exponential decays with lifetimes of 90, 200 and 310 μs, and occasionally, some short lived components from the $^3P_0 \rightarrow {}^3H_6$ emission. In addition, the emission starting in the $^3P_0$ level appears to involve two single exponential components, but the decomposition is very difficult because the short component has a very low intensity. Lifetimes ranging from 8 to 10 μs for the long-lived component and about 2 μs for the short-lived component are determined.

4. Conclusions

Our results show that at least three centers are present in Pr^{3+}-doped YSZ crystals. Based on a previous work [10], these centers are associated with two types of CN7 centers and a CN6 center, respectively. Their absorption lines strongly overlap, confirming previous findings [7,8] that the presence of oxygen vacancies induces only a slight departure from the main cubic symmetry. Total site selective spectroscopy and time resolved measurements support the hypothesis that the $^3P_0$ emission is mainly due

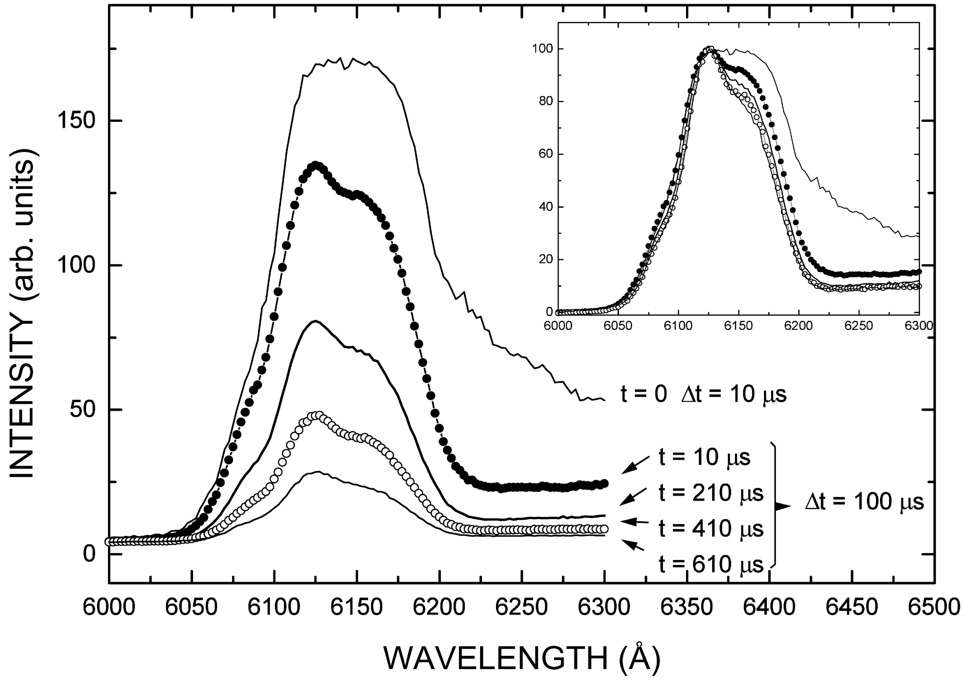

Fig. 5. Temporal evolution of the $^1D_2 \rightarrow {}^3H_4(0)$ transition, $\lambda_{exc}=485$ nm, $T=15$ K.

to the CN6 center with a lifetime of 10 μs. Due to the strong relaxation of the CN7 centers to the $^1D_2$ state (via the 4f5d crossover), only a very small contribution of these latter centers to the $^3P_0$ emission is observed. As a result, the luminescence lifetime of these centers has a short lifetime of ~2 μs. The $^1D_2$ emission shows that at least two types of CN7 centers are involved, which are better resolved when the excitation is carried out in the $^3P_0$ absorption region. This emission is properly described by three single exponential decays with lifetimes of 90, 200 and 310 μs related to the CN6 center and the two CN7 centers, respectively.

Acknowledgements

This work has been supported by the DGyCYT of the Spanish government under project PB97-087.

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