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Improvement of the optical performances of Pr^{3+} in $CaTiO_3$

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Abstract

Trivalent praseodymium-doped calcium titanates are red emitting phosphors upon UV photon excitation in the range 150–300 nm, with a luminescence appearing as a single peak centered at 613 nm. The intensity of this emission is investigated in different samples prepared either by a solid state or a sol–gel method. The study includes analyses of microstructure, sintering temperature, charge compensation and Pr concentration effects.

Keywords: Calcium titanate; Phosphor; Photoluminescence; Praseodymium; Sol–gel

1. Introduction

During the past few years, oxide-based materials doped with trivalent praseodymium have been the object of many investigations for optical imaging or laser purposes. The reason of this renewal of interest is due to the Pr^{3+} energy level scheme which contains several metastable multiplets ($^3P_0$, $^1D_2$, $^1G_4$) from which efficient photoluminescence or laser action have been demonstrated at various wavelengths, ranging from the visible (mainly blue and red) to the infrared [1]. Among the materials devoted to optical applications, the Pr^{3+}-doped perovskite-like calcium titanate is of special interest since this phosphor exhibits red cathodoluminescence with CIE coordinates at $x=0.680$ and $y=0.311$, very close to the coordinates of the 'ideal red' [2].

In a previous work, the optical properties and photoluminescence mechanisms of orthorhombic Pr-doped calcium titanates prepared by solid state reaction have been described [3]. Typical emission and excitation profiles are displayed in Fig. 1. The emission consists of a single narrow band (FWHM=450 cm^{-1} at 300 K) peaking at 613 nm. It is produced either upon 4f→4f ($^3H_4 \rightarrow {}^3P_J$ with $J=0$, 1, 2 and $^3H_4 \rightarrow {}^1D_2$) and 4f→5d excitations or after bandgap excitation, as demonstrated by the excitation profile displayed in Fig. 1. After valence-to-conduction band transition, an energy transfer occurs to the excited 4f or 5d levels of Pr^{3+}, allowing subsequent 4f→4f emission. The peculiar luminescence properties of Pr^{3+} in calcium titanates were explained on the basis of a configuration coordinate diagram, by considering a strong downshift of the 4f5d band by crystal field effect. The position of this band in the energy scale provokes the quenching of the $^3P_0$ emission through non radiative relaxation and makes possible the occurrence of a unique emission from $^1D_2$ level [3]. We report in this work an investigation of the main parameters that affect the optical performances of Pr-doped calcium titanates. The study is focused on the preparation method and the materials compositions, including Pr concentration and charge compensation effects. The influence of sintering temperature is also examined, since this parameter affects strongly the microstructure and the crystallinity of the powders.

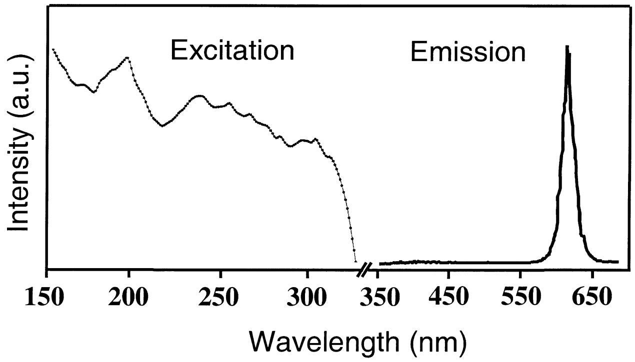

Fig. 1. Typical excitation–emission profiles of Pr-doped calcium titanates at room temperature.

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2. Materials

The phosphors were prepared as polycrystalline powders by a solid state (SS) or a sol–gel (SG) procedure. The nominal compositions of the samples were the following: $Ca_{1-x}Pr_xTiO_3$ for the uncompensated titanate (denoted CTO:Pr in the following), $Ca_{1-2x}Pr_xM_xTiO_3$, where M is a monovalent cation like Na^+ or Ag^+ acting as a charge compensator according to $2Ca^{2+} \rightarrow 1Pr^{3+} + 1M^+$ (the samples will be denoted as Na-CTO:Pr and Ag-CTO:Pr, respectively), $Ca_{1-x}Pr_xTi_{1-x}Al_xO_3$ (Al-CTO:Pr), in which the charge compensation is provided by the substitution of x mol% Ti^{4+} to Al^{3+} and $Ca_{(1-3x/2)\neq x/2}Pr_xTiO_3$ (Ca/CTO:Pr), which is a Ca deficient titanate. In this latter case, charge compensation occurs by $x/2$ formula units of Ca vacancies (denoted $\neq$) per formula units of Pr^{3+}. For all the samples, x varied from 0.1 to 5%.

For solid state reactions, stoichiometric amounts of $CaCO_3$, TiO_2 and $PrCl_3 \cdot 7H_2O$ were mixed together in presence of ethanol and then fired at 1200°C for 4 h under air. When required, the charge compensators were added as Na_2CO_3, $AgNO_3$ or $AlCl_3$. Sol–gel procedures have also been developed under acid or basic conditions. Under acid conditions, stoichiometric amounts of CaO and $PrCl_3 \cdot 7H_2O$ were dissolved in HCl at 60°C before adding titanium isopropoxide in suitable proportions into an equivalent volume of methanol. The pH was around 3. The mixture was then stirred up for 4 h at 60°C under N_2 flow. The protocol was almost the same under basic conditions, with the exception of a starting product ($CaCl_2 \cdot 2H_2O$) and the solvent (isopropanol). A gel formed immediately after addition of NH_4OH, for a pH value at around 10. After drying at 80°C, the powders were fired for a period of 4 h at different temperatures between 750 and 1200°C. Whatever the thermal treatment, the infrared spectra showed no band in the 3000–3600 cm^{-1} range.

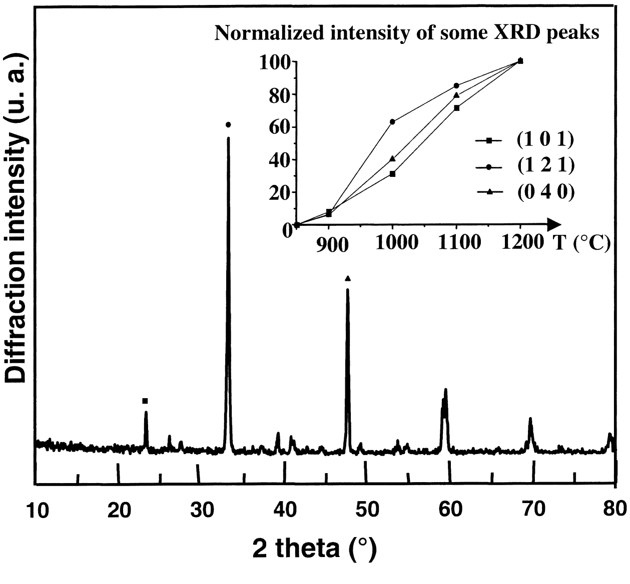


Fig. 2. X-ray diffraction pattern of $CaTiO_3$:0.2% Pr prepared at 750°C by a sol–gel process. The inset shows the variation of the normalized intensity of several diffraction peaks vs. sintering temperature.

3. Experimental details

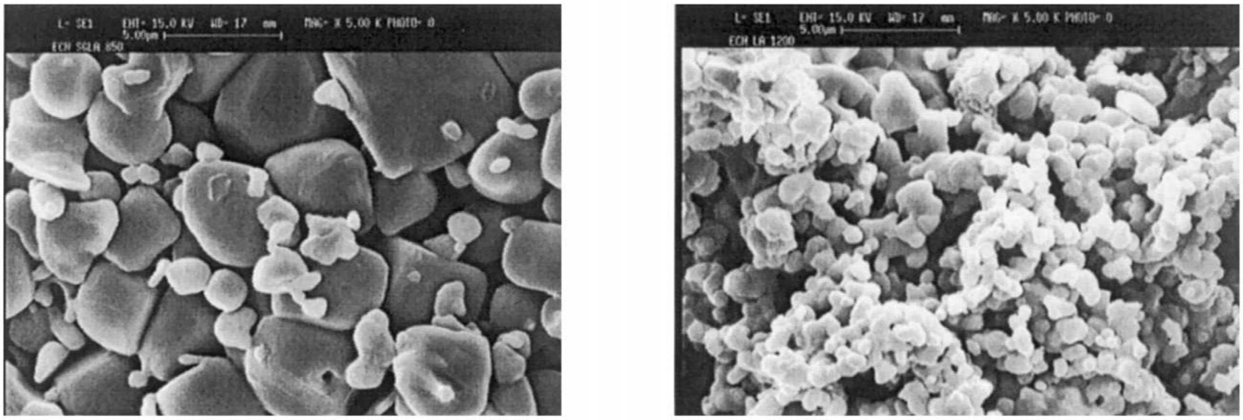
The X-ray diffraction (XRD) patterns were obtained on a Siemens D501 diffractometer with Cu Kα radiation. The SEM micrographs were recorded with the help of a Cambridge Scan 360 microscope operated at 15 kV. The optical measurements were performed by using the 345 nm radiation supplied by a CW xenon lamp. This wavelength corresponds to the value of the energy gap in $CaTiO_3$. For all the measurements, the luminous power of the excitation beam was controlled and the illuminated surface of powder was kept constant. The luminescence was analysed at right angle by using a set-up described elsewhere [3]. The excitation spectrum was recorded at the LURE under synchotron radiation.

4. X-ray powder diffraction

The crystallochemical purity of the materials was checked systematically by XRD. Whatever the preparation method, the patterns were characteristic of the orthorhombic form of calcium titanate. In the case of SG-processed samples, this latter structure was observed after sintering at 750°C for 4 h under air, as shown in Fig. 2. The inset in Fig. 2 shows that the intensity of three of the main diffraction peaks increases strongly with the sintering temperature, demonstrating a significant improvement of the powders' crystallinity.

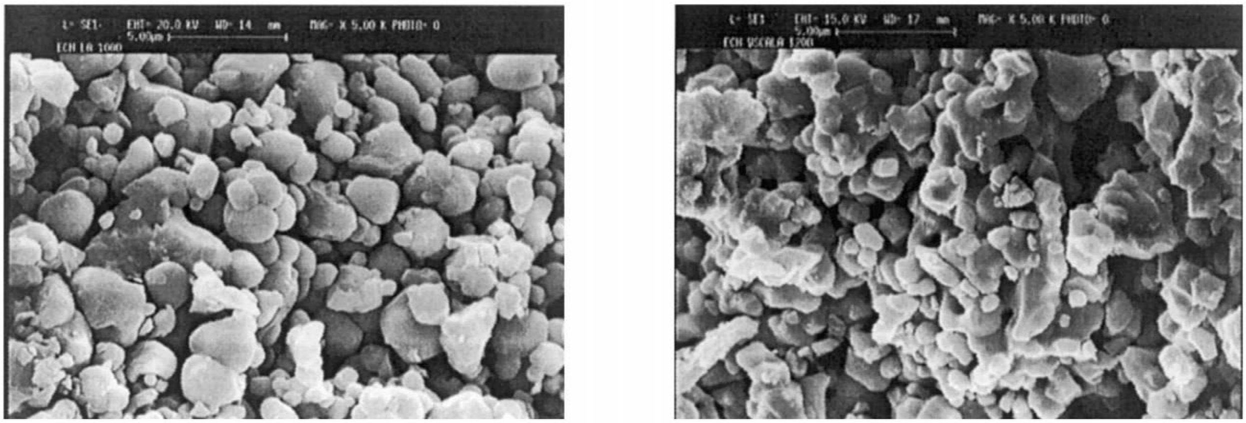
5. Microstructure

Series of SEM micrographs were realized to characterize the microstructure of several 0.2 mol% Pr-doped titanates prepared by SS or SG procedures. The investigated materials were Al-CTO:Pr and Ca/CTO:Pr. We observe from Fig. 3 a decrease of the particles' size in Al-CTO:Pr powders as the sintering temperature is increased, leading to a homogeneous fine-grained and almost equi-sized microstructure after sintering at 1200°C. In the case of Ca/CTO:Pr samples, a similar thermal treatment induced the coalescence of the submicronic grains and led to a better densification of the powders with no observable porosity. In contrast, the microstructure of the Al-CTO:Pr samples prepared at 1200°C by solid state reaction consists of aggregates of 10–15 μm in diameter with observable porosity.



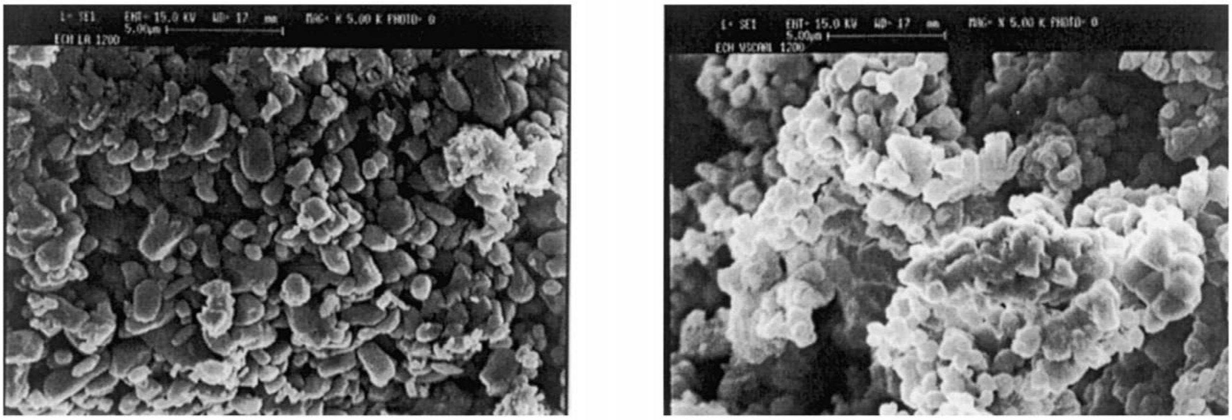
a - Al-CTO:Pr Basic SG - 850°C

d - Ca/CTO:Pr Basic SG - 1200°C



b - Al-CTO:Pr Basic SG - 1000°C

e - Ca/CTO:Pr Solid state - 1200°C



c - Al-CTO:Pr Basic SG - 1200°C

f- Al-CTO:Pr Solid state - 1200°C

Fig. 3. SEM micrographs of different Pr-doped titanates. The scale is kept the same for all the pictures.

6. Luminescence properties

The intensity of the red luminescence shown in Fig. 1 was measured at room temperature in all the materials under the same experimental conditions. The intensity was estimated by integration of the emission band. In the case of SG-processed samples, the influence of the sintering temperature on the emission intensity is illustrated in Fig. 4. An increase of more than 200% of this intensity is observed when the temperature increases from 850 to

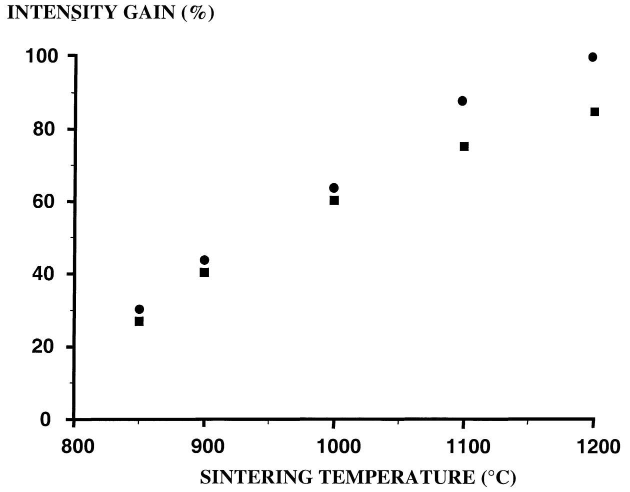


Fig. 4. Evolution of the red emission intensity vs. sintering temperature for Al-CTO:Pr (■) and Ca/CTO:Pr (●). The intensity gains are expressed in % with respect of the emission intensity of samples sintered at 800°C.

1200°C. The emission intensity depends also strongly on the Pr concentration. The luminescence is systematically maximum for a Pr molar percentage of 0.2 and is quenched in 5 mol%-doped titanates, probably after energy migration through the material due to Pr–Pr interactions. Fig. 5 shows the variation of the red emission intensity in 0.2 mol% Pr-doped titanates prepared by using different methods but all fired at 1200°C for 4 h. The intensity gains in % plotted on the vertical scale are evaluated with respect to the emission intensity of the uncompensated titanate prepared by SS reaction, for which the optical performances were found to be the poorest. Charge compensated Al-CTO:Pr and Ca/CTO:Pr phosphors prepared under SG basic conditions appeared to be the most performant, with intensity gains estimated, respectively, at around 200 and 260%.

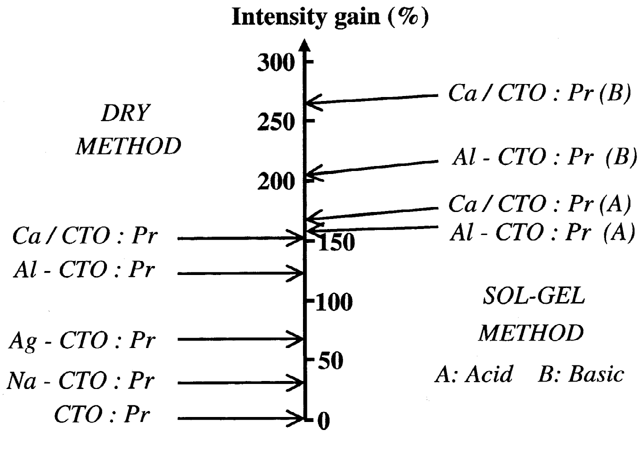


Fig. 5. Variation of the red emission intensity in several Pr-doped calcium titanates prepared either by SS reaction or SG method, under acid or basic conditions. The intensity gains are expressed with respect to the emission intensity of SS-processed CTO:Pr.

7. Discussion

The intensity of the red luminescence of Pr^{3+} in calcium titanates depends severely on the preparation method and on the material composition. For all the samples, a high sintering temperature improves the intensity of the red luminescence because it favours densification of the submicrometer-size powders and contributes, to some extent, to remove some residual hydroxyl groups from the structure. In opposition to the dry method, SG methods facilitate quantitative reactions because the SG processes improve the homogeneity of the atomic repartition and thus facilitate intergranular migrations of Ca and Ti atoms, even at lower temperatures than in the solid state. As a consequence, SG-processed powders are characterized by a better crystallinity and a denser microstructure than powders prepared in the solid state. These two characteristics account for the observation of high luminescence intensities, as argued for example in Ref. [4] and also confirmed in the present work.

The fact that basic SG conditions lead to more efficient phosphors than acid conditions can be understood by considering the condensation process [5]. Under acid conditions, the condensation extents over several h, during which a 1D polymeric gel forms progressively. This process leads to incomplete condensation, leaving Ti-OH like endings randomly dispersed in the framework. As these defects possess high phonons frequencies, their presence inside the structure contribute to lower the luminescence intensity of the Pr ions via radiationless de-excitations. In opposition, basic conditions allow fast condensation through a nucleophilic attack of $Ti(OPr)_4$ groups by OH^- ions, in presence of water, yielding $Ti(OH)_6^{2-}$ anions which are neutralized by Ca^{2+} ions by internal condensation and release of water [6]. From this process, a 3D polymerization is expected with a lower concentration of Ti-OH-like defects than in samples prepared under acid conditions, which therefore favours the probability of radiative 4f→4f de-excitation.

Furthermore, it is shown that the optical performances of Pr-doped calcium titanates depend critically on charge compensation. In air-fired donor perovskites like CTO:Pr, the charge compensation occurs by the formation of intrinsic defects such as negatively charged Ca vacancies, positively charged oxygen vacancies and/or by reduction of Ti^{4+} to Ti^{3+} [7–9]. Associations of Ti^{3+} defects and oxygen vacancies can also be anticipated, leading to neutral or singly ionized centers. Several of these defects are undesirable because their presence in the phosphors, even at low concentration, can contribute to quench the Pr luminescence. Firstly, a part of the red emission can be reabsorbed in the broad d→d absorption band of Ti^{3+}. Secondly, it can be expected that the positively charged defects act as traps for electrons promoted in the conduction band after bandgap excitation. This electron capture constitutes an alternative radiationless de-excitation channel that competes with the energy transfer to the excited levels of Pr^{3+} and contributes to decrease the intensity of the 4f→4f emission. In this scheme, the role of charge compensation is to limit the concentration of these undesirable defects in the phosphors, leading consequently to the reinforcement of the optical performances.

8. Conclusion

Significant reinforcement of the red luminescence intensity has been demonstrated in 0.2 mol% Pr-doped orthorhombic CTO powders prepared with a basic SG procedure. The best optical performances are observed in Ca/CTO:Pr and Al-CTO:Pr samples which are both characterized by a dense microstructure and a good crystallinity. Experiments will now be undertaken to increase further the intensity of the red luminescence in the SG-processed titanates by studying the influence of mechanical pressure effects combined with thermal treatments for longer periods at temperatures greater than 1200°C.

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