MICROSTRUCTURAL EFFECTS ON THE LUMINESCENCE INTENSITY OF Pr^{3+}-DOPED $CaTiO_3$

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The microstructural and luminescence characteristics of solid state (SS) and sol-gel (SG) processed $CaTiO_3:Pr^{3+}$ powders have been investigated as a function of the grinding time t, in the case of SS_t samples and of $OH/Ti(OPr)_4$ molar ratios r, in the case of SG_r samples. It is observed that either extended post-synthesis grinding or sol-gel syntheses operated under acid or neutral conditions lead to submicron grained microstructures, $CaTiO_3 + TiO_2$ phase mixing and finally to less efficient phosphors. The observed decrease of luminescence intensity is correlated to the presence of non-luminescent rutile and to the amount of submicron particles.

INTRODUCTION

Pr^{3+}-doped calcium titanate is known for several years as a red emitting phosphor characterized by a single emission peak with chromaticity coordinates positioned at $x = 0.68$, $y = 0.311$, very close to the ones of the "ideal red", as their are defined by the CIE (Commission Internationale de l'Eclairage) [1]. Although this material has been reported in 1994 as an attractive phosphor for low voltage field emission displays [2], no investigation, to our knowlegde, has been further undertaken to improve its brightness. However, in a recent work [3], significant reinforcement of the red luminescence intensity in Pr^{3+}-doped calcium titanate powders has been demonstrated by preparing these phosphors by sol-gel procedure under basic conditions and by adjusting the stoichiometry with appropriate charge compensators. In this study, the influence of the sintering conditions on the optical performance have also been carefully analyzed, since the temperature and the duration of the thermal treatments are known to affect strongly the degree of crystallization and the densification of the powders. Here, we report on an investigation of microstructural effects, including grains size repartition, on the optical performance of Pr^{3+}-doped calcium deficient titanates with nominal formula $Ca_{(1-3x/2)}\#_{x/2}Pr_xTiO_3$ and $x = 0.2$ %. In this material, $x/2$ formula units of Ca vacancies (denoted #) are created per formula units of Pr^{3+} for charge compensation purposes. The materials have been prepared either by solid state reaction or by the sol-gel route, using anhydrous $CaCl_2$, $PrCl_3$ and Ti isopropoxide in isopropanol and aquous NH_4OH as the base (see details of the protocol in [3]). Whatever the synthesis method, the sintering conditions were kept identical at 1200 °C for 4 hours under air. Modulation of the microstructure (especially particle size and its distribution) was operated either mechanically by grinding the solid state processed powders for different times ranging from 5 to 75 minutes or, without grinding, by varying the *pH* of the gel during the sol-gel procedure. In this latter case, the different investigated $OH/Ti(O^iPr)_4$ molar ratios were respectively $r = 0.39$, 0.78, 8.5, 12.7 and 17. The corresponding samples will be denoted SGr in the following, by reference to the values of the molar ratios. For all these syntheses, water was in excess, to ensure appropriate conditions for total hydrolysis of the $Ti(O^iPr)_4$ groups. However, the hydro-lysis-condensation process can be strongly influenced by the $OH/Ti(O^iPr)_4$ molar ratio, as described for example in [4]. Accordingly, when r » 2 (*pH* maintained in a range from 11 to 14), a nucleophilic attack of $Ti(O^iPr)_4$ by OH^- groups can be involved, yielding $Ti(OH)_6^{2-}$ anions following the equation: $Ti(O^iPr)_4 + 4\ H_2O + 2\ OH^- \rightarrow Ti(OH)_6^{2-} + 4$ HOPr. These anions, which contain six-fold coordinated Ti^{4+} ions as in the final perovskite network, are then neutralized by Ca^{2+} cations by internal condensation and release of water, forming appropriate precursors for the $CaTiO_3$ structure.

EXPERIMENTAL

The solid state processed powders have been crushed in a 50 ml agate mill pot with a total of 10 agate balls of 10-mm diameter, by using a Retsch S100 grinder operated at 500 rpm. The corresponding samples will be denoted respectively SS_t, where the subscript t indicates the grinding time in minutes. In addition, two samples denoted SS_{15} (>5 μm) and SS_{15} (<5 μm) have been obtained by sifting a SS_{15} sample on a 5 μm sieve. The structural properties of the materials, before and after milling, were controlled systematically by X-ray diffraction, using a Siemens D5000 diffractometer equipped with Cu anode operated at 40 kV and 30 mA. The microstructural characteristics were checked either by scanning electron microscopy (SEM) (Cambridge Scan 360) operated at 10 kV or by laser granulometry (Mastersizer, Malvern Instruments). In the case of this latter technique, anionic surfactant and distilled water were used as dispersant and the ultrasonic treatment was fixed at 15 minutes for all samples. The optical measurements of the photoluminescence intensity were carried out at room temperature by using the 345 nm monochromatized radiation supplied by a 250 Watt CW xenon lamp and a computer-controlled Bausch & Lomb double grating monochromator equipped with a EMI 9698 QB photomultiplier, as a detector. The intensity was evaluated by integrating the red emission band in a range from 600 to 650 nm. For comparison purposes, special care was taken to control the beam power of the excitation source and to keep identical the illuminated surface of the sample.

RESULTS AND DISCUSSION

X-ray powder diffraction

Typical X-ray diffraction (XRD) patterns of SS_t and SG_r samples are displayed in figure 1 and 2, respectively. While the pattern of SS_0 is characteristic of single-phased orthorhombic $CaTiO_3$, the patterns of SS_t samples with $t > 0$ clearly show $CaTiO_3 + TiO_2$ phase mixing with increasing amount of rutile TiO_2 as t is increased. The patterns of the two sifted samples SS_{15} (>5 μm) and SS_{15} (<5 μm) confirm the presence of residual rutile in both samples. Concerning SG_r samples, the XRD patterns exhibit also $CaTiO_3 + TiO_2$ phase mixing, but only for the lowest values of r, corresponding to acid or neutral synthesis conditions. The presence of residual CaO is never detected. The samples prepared under basic conditions are single phased.

Laser granulometry

The granulometric characteristics of the solid state titanates SS_t and sol-gel processed titanates SG_r are gathered in table 1. The parameters D(av), D(0.9) and % (D<1 μm) were selected since they provide a global representativity of the microstructure of the powders: D(av) represents the average particle size for particles larger than 1 μm, D(0.9) is the size for which 90 % of the particles have a diameter smaller than the value and % (D<1 μm) represents the volumetric percentage of submicron particules dissociated by the ultrasonic treatment. For all the tested powders, the particle size distribution is either monomodal or bimodal, depending on the t or r values. In the case of SS_t samples, the particles distribution is monomodal only for t = 0 min (unground sample). As the grinding time is increased, the granulometric profiles are shifted to lower particles size values and present a shoulder in the submicrometer region. The volumic proportion of these submicron particles increases gradually as t is increased, while concomitantly, D(av) and D(0.9) decrease in a way such that it leads to a narrowing of the particle size distribution for particules larger than 1 μm. The effect of sifting can be analysed by comparing SS_{15}, SS_{15} (>5 μm) and SS_{15} (<5 μm) samples. As expected, all the submicron particles evidenced in unsifted SS_{15} appear in SS_{15} (<5 μm), which presents therefore a bimodal distribution, while SS_{15} (>5 μm) sample is characterized by a narrow monomodal distribution of particles larger than 1 μm, with an average size of about 20 μm. In SS_{15} (<5 μm), particles as large as 9 μm are detected (see table 1) suggesting a tendency for the smallest particles to re-aggregate. For uncrushed SG_r samples, the granulometric parameters appear to be strongly dependent on the value of r. Under acidic conditions (r = 0.39), the powder is made up of a

Table 1. Granulometric parameters and luminescence intensity of SSt and SGr samples.

	a-SS_0	a-SS_5	a-SS_{15}	a-SS_{35}	a-SS_{75}	a-SS_{15}>5 μm	a-SS_{15}<5 μm	$SG_{0.39}$	$SG_{0.78}$	$SG_{8.5}$	$SG_{12.7}$	SG_{17}
D (av) (μm)	30	10	4	3	2	10	5	200	22	25	30	35
D (0.9) (μm)	47	28	10	4	3	20	9	325	35	40	55	60
% (D < 1 μm)	0	10	16	44	70	0	14	0	19	20	6	0
Luminescence intensity (relative scale)	100	105	120	103	98	124	111	100	92	102	116	150

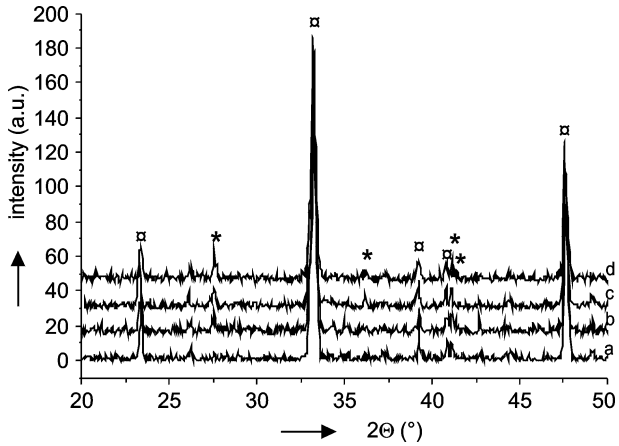


Figure 1. X-ray diffraction patterns of SS_t samples for different grinding times t = 0 min (a), t = 15 min (b), t = 35 min (c) and t = 75 min (d). * indicates TiO_2 (84-1284) and ¤ indicates $CaTiO_3$ (75-2100).

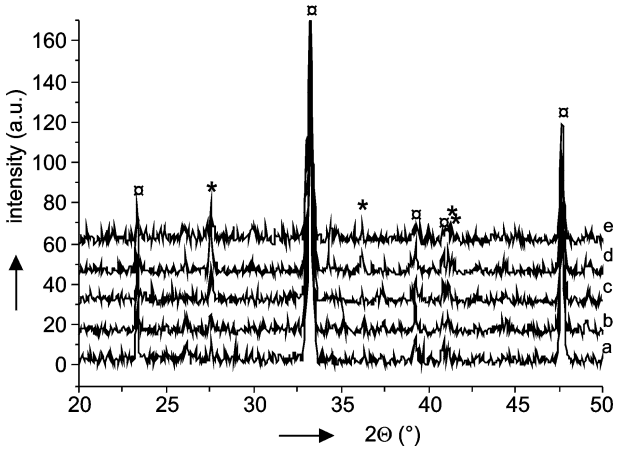


Figure 2. X-ray diffraction patterns of SG_r samples for different values of r : r = 17 (a), r = 12.7 (b), r = 8.5 (c) r = 0.78 (d) and r = 0.39 (e). * indicates TiO_2 (84-1284) and ¤ indicates $CaTiO_3$ (75-2100).

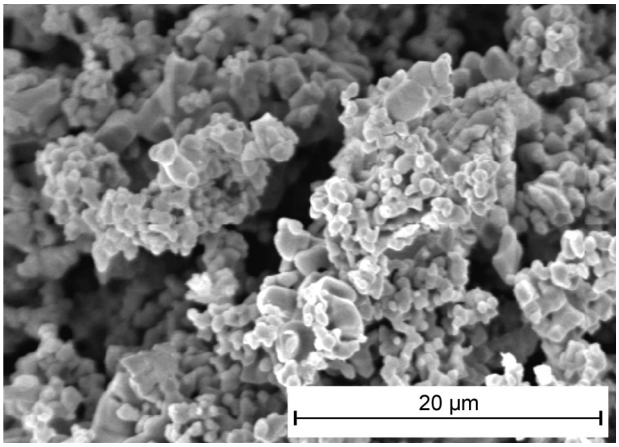
monomodal distribution of particles having an average size of about 200 μm. Under neutral conditions (r = = 0.78), the average particle size is divided by a factor of around 10 and the distribution becomes bimodal with about 20 % of submicron particles. At least, as the basicity is further increased, (r » 2), the average particle size grows slightly and the distribution turns gradually from bimodal to monomodal, suggesting again re-aggregation of the smallest particles.

Scanning electron microscopy

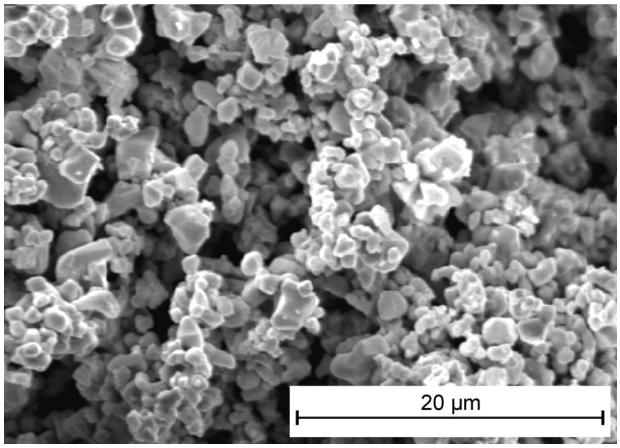
SEM micrographs of SS_t and SG_r samples are shown in figure 3 and 4, respectively. In the case of SS_t powders, the microstructure consists of aggregates of micrometric or submicrometric grains, as can be observed and measured on enlarged views of the micrographs displayed on figure 3 (these views are not shown here). For unground SS_0, the sintering treatment at 1200 °C causes coalescence and aggregation of individual grains in a way such that it gives rise to some porosity. 15 to 35 minutes grinding (samples SS_{15} and SS_{35}) provokes mainly the dissociation of the biggest aggregates, as indicated by a decrease of D(0.9) and D(av) values, thus contributing to release micrometric or submicrometric grains which can partially fill the pores and induce further densification of the microstructure. The comparison between SS_{15} and sifted samples confirms that the microstructure appears less dense when the smallest particles are removed (ie in SS_{15}(>5 μm)) and confirms furthermore that these smallest particles tend to re-aggregate (in SS_{15} (<5 μm)). After 75 minutes grinding, the SEM micrograph shows that most of the grains have been broken, providing a quite narrow grain size distribution centered at around 2 μm, together with a large amount of submicron particles. The SG_r powders consists of rather dense aggregates whose size and microstructure depend strongly on the r value. For r = 0.39, the aggregates are made up of a dense and regular distribution of grains with sizes ranging from 0.7 to 3 μm in average. For r = 0.78, the average aggregates size is about 10 times smaller than for $SG_{0.39}$ powder and the microstructure consits of a dense, almost equisized distribution of submicron grains. For r > 8, the microstructure is very different, since it consists of much larger grains (about 3 to 5 μm large in average) with a geometrical morphology, covered in places by submicron particles.

Luminescence

The luminescence intensity of the red emission of praseodymium in all the Pr^{3+}-doped titanate powders SS_t and SG_r has been carefully analysed. The luminescence intensity of SS_0 and $SG_{0.39}$ samples has been assigned arbitrarly to 100, making the comparison of emission intensities accurate only within the serials SS_t (as a function of t) and SG_r (as a function of r), respectively. For SS_t samples, the luminescence intensity increases up to t = 15 min and then decreases as t is further increased. This behaviour can be discussed by considering mainly structural and microstructural arguments. Accordingly, from SS_0 to SS_{15}, the improvement of the luminescence intensity can be accredited mainly to the enhancement of powder densification due to grinding, which contributes to increase the luminescence emitted



a)



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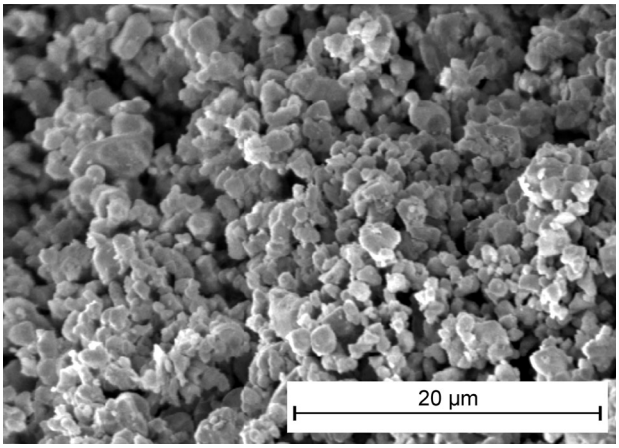

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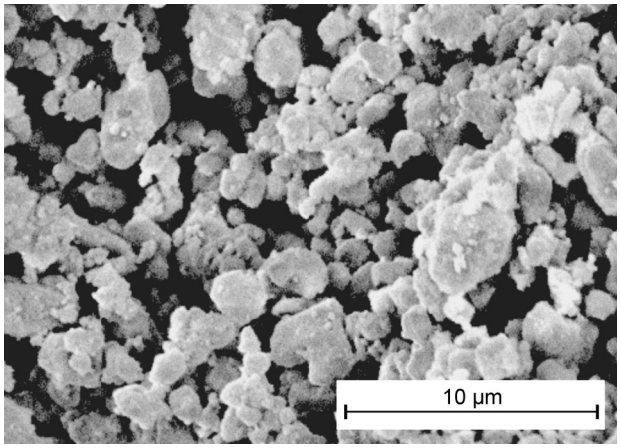
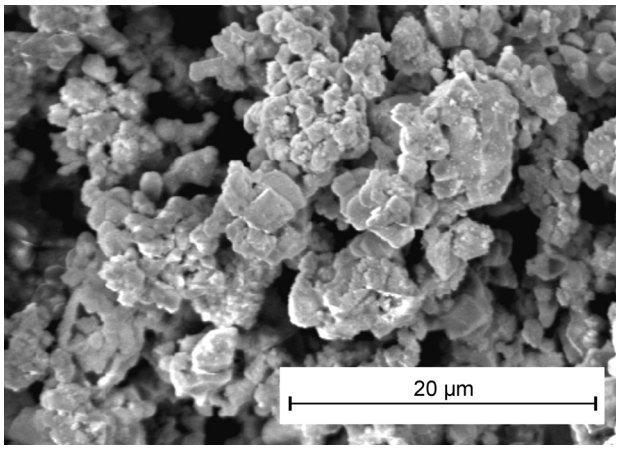
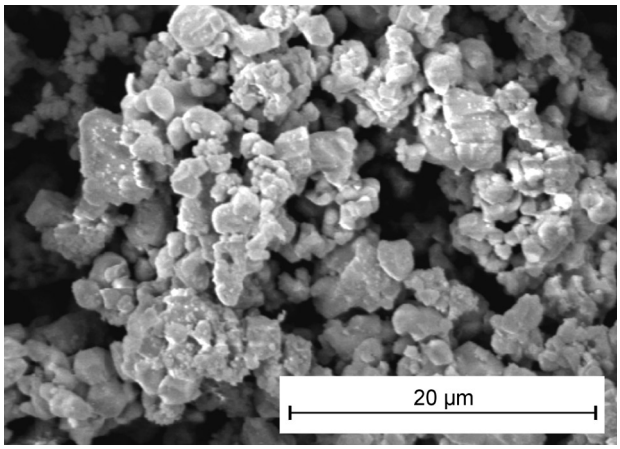


d)

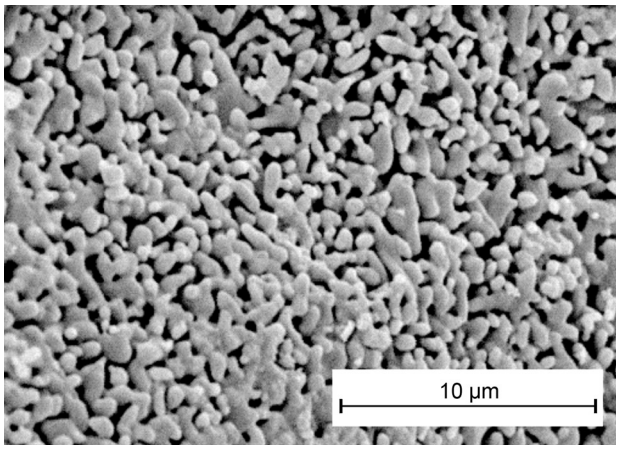


e)

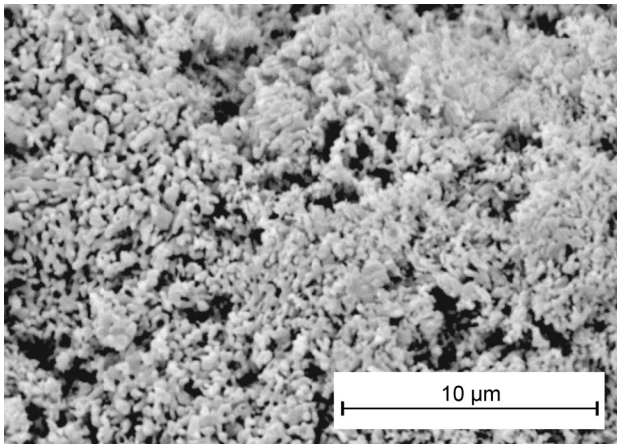


f)

Figure 3. SEM micrographs of SS_0 (*a*), SS_{15} (*b*), SS_{35} (*c*), SS_{75} (*d*), SS_{15} (>5 µm) (*e*) and SS_{15} (<5 µm) (*f*).



a)



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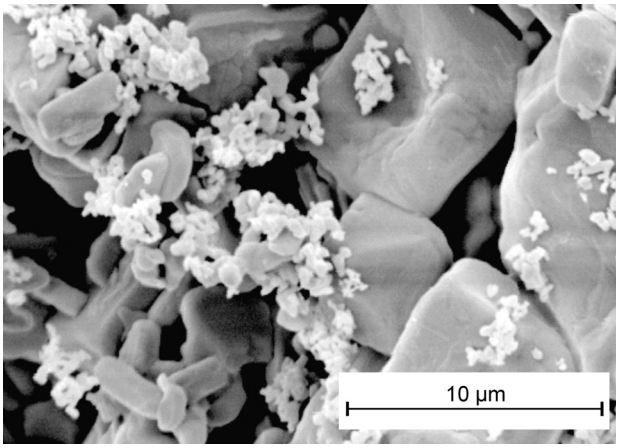

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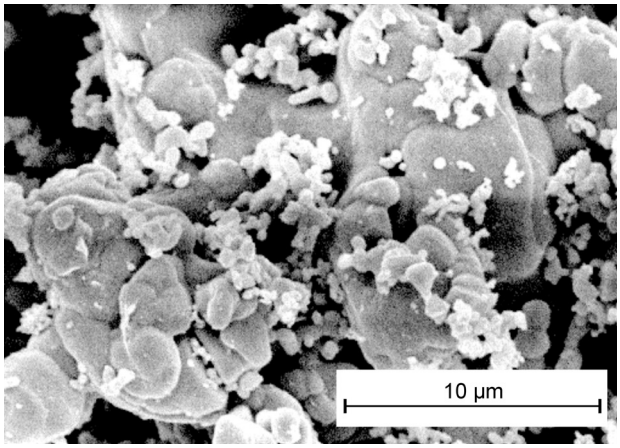

d)

Figure 4. SEM micrographs of $SG_{0.39}$ (*a*), $SG_{0.78}$ (*b*), $SG_{8.5}$ (*c*) and $SG_{12.7}$ (*d*).

by surface unit of powder. This effect of densification is strong enough to compensate for the appearence of a small amount of non-luminescent rutile, as detected in the XRD pattern of SS_{15}. In contrast, the brightness of SS_{35} is more than 14 % lower than SS_{15} despite a microstructure as dense as the SS_{15} one, a lower average grain size and a similar amount of rutile (see figure 1). Accordingly, it is assumed that the decrease of luminescence intensity in SS_{35} can be induced by the increasing amount of submicron particles (see table 1) for which stronger light scattering processes can compete with absorption / emission processes. Such an assumption is corroborated by the comparison of SS_{15} and corresponding sifted samples, since it is observed an improvement of the luminescence intensity in the sample SS_{15} (> 5µm) containing no submicron particles and a decrease of the brightness in SS_{15} (<5 µm). Similarly, the sample SS_{75} exhibits the weakest luminescence intensity of the whole SS_t series, in spite of a narrow grain size distribution and a dense microstructure, which can again be interpreted as a consequence of an important proportion of submicron particles, together with a slight increase of the amount of non-luminescent rutile. Concerning SG_r samples, it is observed, as in the case of SS_r samples, that the luminescence intensity decreases in samples $SG_{0.39}$ and $SG_{0.78}$, which present $CaTiO_3$ + TiO_2 phase mixing and for which the microstructure contains a large amount of submicron particles.

CONCLUSION

The microstructural and luminescence characteristics of solid state (SS) and sol-gel (SG) processed $CaTiO_3:Pr^{3+}$ powders have been investigated as a function of the grinding time *t*, in the case of SS_t samples and of the $OH/Ti(OPr)_4$ molar ratios *r*, in the case of SG_r samples. It is observed that either a post-synthesis grinding time longer than 35 minutes or sol-gel syntheses operated under acidic or neutral conditions (without any grinding before or after firing at 1200 °C) lead to submicron microstructures, $CaTiO_3$ + TiO_2 phase mixing and to less efficient phosphors. The observed decrease of the luminescence intensity in both series of samples is then attributed to the presence of non-luminescent rutile and to the amount of submicrometric particles, for which stronger light scattering processes can compete with absorption / emission processes.

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VLIV MIKROSTRUKTURY NA INTENZITU LUMINISCENCE $CaTiO_3$ DOPOVANÉHO IONTY Pr^{3+}

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U vzorkù práškù $CaTiO_3$ dopovaných ionty Pr^{3+} byla sledována závislost doby mletí (u vzorkù pøipravených mechanickou cestou), resp. molárního pomìru $OH/Ti(O^iPr)_4$ (u vzorkù pøipravených metodou sol-gel) na jejich mikrostrukturní a luminescenèní charakteristiky. Bylo pozorováno, že jak pøíliš dlouhé mletí vzorku po syntéze, tak syntézy sol-gel provedené v kyselém nebo neutrálním prostøedí, vedou k tvorbì submikronové mikrostruktury, k tvorbì smìsné fáze $CaTiO_3$ + TiO_2 a v dùsledku toho k ménì úèinným luminoforùm. Pozorované sní□ení intenzity luminiscence je v souladu s pøítomností rutilu ve vzorcích, který nemá luminiscenèní vlastnosti, a s mno□stvím submikronových èástic ve vzorcích.