Effects of different TiO_2 phases on the luminescence of $CaTiO_3:Pr^{3+}$

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Abstract. $CaTiO_3$ is widely used in the ceramic industry, and when it is doped with Pr^{3+} it glows with a single red emission at a wavelength of 613 nm. The red emission is attributed to the $^1D_2 \rightarrow {}^3H_4$ radiative transition of Pr^{3+} upon ultraviolet (UV) or electron beam irradiation. The compound was prepared by using rutile and anatase polymorphs of TiO_2 to investigate their effects on the luminescence properties. X-ray diffraction patterns of $CaTiO_3:Pr^{3+}$ phosphor prepared with rutile polymorph show that the phosphor was successfully synthesized without any additional phases, whereas the patterns for the phosphor prepared with anatase polymorph show unreacted TiO_2 phases. The unreacted phases resulted in the reduction of luminescence intensity of the phosphor prepared with the anataseTiO_2. The chemical stability of the phosphor was also investigated by exposing it to a prolonged electron beam irradiation.

Keywords:$CaTiO_3$: Pr^{3+} red emission, long afterglow phosphor

1. Introduction

The intentervalence charge transfer mechanism is known to be the reason behind the single red emission of Pr^{3+} doped $CaTiO_3$ at room temperature. The phenomenon is attributed to complete depopulation of the $^3P_0$ level carriers by populating the $^1D_2$ state. However, the intensity of the single red emission peak from $^1D_2 \rightarrow {}^3H_4$ transition is highly dependent on the energy transfer from the host to the luminescent centers (Pr^{3+})[[1],[2]]. $CaTiO_3$, which is an orthorhombic perovskite, is known to exhibit good dielectric properties. The symmetry of this compound is temperature dependant and it changes from orthorhombic (room temperature to tetragonal (at liquid nitrogen temperature) [[3],[4],[5],[6]]. Solid state reaction is usually used to prepare this compound by directly firing the TiO_2 and $CaCO_3$/CaO as initial reagents at temperatures above 1000 ^oC [[6]]. The final compound can assume different quantities of defects such as line defects, point defects, and vacancies. These are a result of slight changes in the preparation procedures such as heating rate, cooling rate and the rate of the chemical reaction. Different chemical reaction rates may also be introduced by different reagent phases. All these parameters may influence the properties of the final compound, which may in turn affect energy transfer from the host to the luminescent centers of Pr^{3+} because of many luminescence quenching centers that may be introduced in the material, like material defects and unreacted material [[7],[8],[9]]. TiO_2 that is used as a reagent to fabricate $CaTiO_3$, itself exists in different polymorphs, such as rutile, anatase and the brookite [[10],[11]]. The three polymorphs have similar crystal structures made of TiO_6 octahedrons that differ from each other with size and distortion at different temperatures and pressure [[10]]. The octahedrons link to each other through corners and edges, and there are two links for rutile, three links for brookite and four links for anatase [[10]]. The increase in the number of links may cause lattice distortion and reduce the volume of the octahedrons especially in the case of anatase polymorphs at relatively higher temperatures. The rutile phase is usually not affected and this makes it to be the most chemically and physically stable polymorph of TiO_2 [[10]]. This paper presents the effects of preparing $CaTiO_3:Pr^{3+}$ phosphor using rutile and anatase polymorphs of TiO_2, at different temperatures. The chemical stability of the phosphor was also investigated by probing its surface with a prolonged electron beam, and the subsequent effects on the CL emission were monitored.

2. Experimental

$CaTiO_3$ compound doped with 0.2 mol % of Pr^{3+} was prepared by stoichiometrically reacting $CaCO_3$ with TiO_2 rutile and TiO_2 anatase in separate experimental setups. $PrCl_3$ was also stoichiometrically incorporated into each of the two prepared $CaTiO_3$ products to introduce Pr^{3+} ions as activator ions for luminescence. Solid state chemical reaction was used to prepare these materials at different temperatures (1100 to 1500°C). The phosphors were analyzed using X-ray diffraction (XRD) (Bruker Advance D8) to identify the phases that are present in each compound, and the scanning electron microscopy (SEM) (Shimadzu SSX-550, Kyoto, Japan) was used to analyze the surface morphology. Photoluminescence (PL) spectroscopy (Varian – Carry Eclipse fluorescence spectrometer) was used to identify the absorption regions from the excitation spectra and luminescence from the emission spectra of the $CaTiO_3:Pr^{3+}$ phosphor. The electron beam of an AES PHI 549 with 2 keV energy and 10 µA current was used to probe the surface of the phosphor and the cathodoluminescence (CL) spectrometer (Ocean optics inc. PC2000) was used to monitor the CL emission.

3. Results

$CaTiO_3:Pr^{3+}$ XRD patterns are presented for compounds prepared by using rutile (figure 1(a)) and anatase (figure 1(b)) TiO_2 polymorphs, which were sintered at different temperatures as indicated. The XRD pattern of $CaTiO_3$ prepared with the rutile TiO_2 shows single phase formation when compared to the standard (JCPDS card no. 22-0153). On the contrary the XRD pattern of $CaTiO_3$ prepared with the anatase TiO_2 shows additional phases (marked by *) when compared to the standard (JCPDS card no. 22-0153), which match with those of TiO_2. The presence of the additional phases is attributed to the unreacted TiO_2. The peaks of the phosphor prepared using rutile polymorph are broader than those of the phosphor prepared using anatase polymorph, and this is correlated with the particle size effect. The effect may be attributed with particles of the phosphor of the sample prepared by the earlier polymorph being smaller than the latter polymorph of TiO_2[12].

The existence of TiO_2 in different polymorphs, rutile, anatase and brookite, gives it the unique ability to react with a particular material to fabricate a product with different properties. The properties referred to are; different quantities of Ti^{3+} and Ti^{4+} point defects, oxygen vacancies, line defects, different electronic structures, and different chemical and physical stability [[8],[13],[14],[16]]. Anatase TiO_2 has a greater quantity of point defects and oxygen vacancies compared to the rutile TiO_2 due to its much more distorted nature, and this leads to it forming products that have much more point defects [[10],[14],[16]]. The greater chemical stability of the rutile polymorph allows it to react more effectively than the anatase, and form products with a greater chemical stability [[14],[15]]. Hence $CaTiO_3$ prepared using a rutile TiO_2 exists as a single phase as opposed to that prepared using anatase TiO_2, which has additional phases (figure 1(b)).

The surface morphology of the two $CaTiO_3$ phases prepared at 1300 °C using rutile TiO_2 phase (figure 2(a)) and anatase TiO_2 phase (figure 2(b)) showed approximately the same crystal shapes. They both had particles of different sizes and shapes. The particles for both SEM images are agglomerated because the high temperature (1300 ^{o}C) involved for the preparation of $CaTiO_3$ compounds.

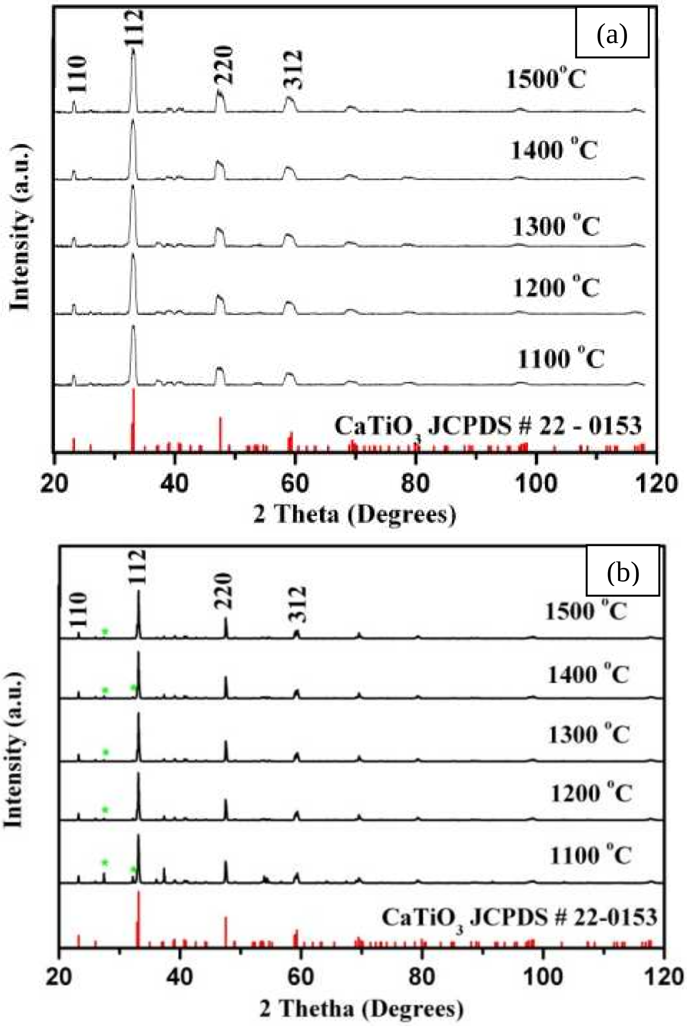

Figure 1: The XRD patterns of $CaTiO_3$:Pr^{3+} compounds prepared using different TiO_2 phases; rutile (a) and anatase (b) phases.

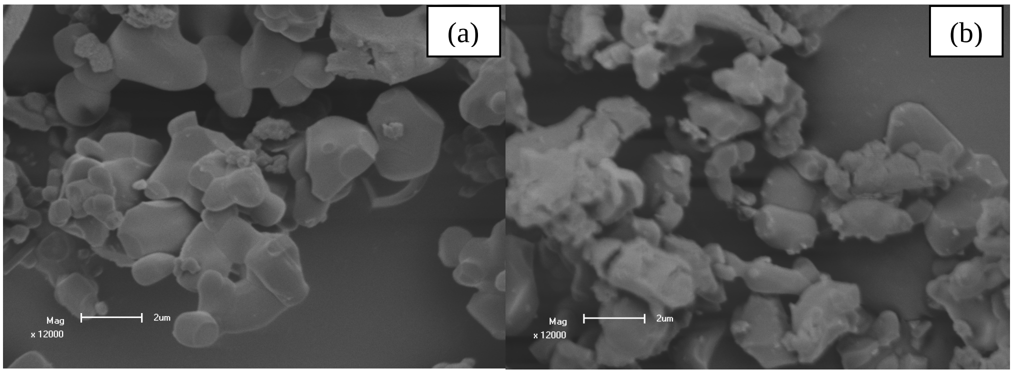

Figure 2: SEM images showing the surface morphology of $CaTiO_3:Pr^{3+}$ prepared using rutile (a) and anatase (b) TiO_2 phases.

Perovskite materials are reported to be stable at temperatures above 1000 °C, and solid state reaction has so far been the common route used to prepare these materials [[6]]. However, other preparation methods have been reported recently [[4],[16]]. The spectra in figure 3(a) show the PL excitation and emission of the $CaTiO_3:Pr^{3+}$(0.2 mol %) prepared by anatase and rutile TiO_2 polymorphs at 1200 °C. According to the excitation spectra, the two compounds can best be excited using a 330 nm wavelength. The intensity of the $^1D_2 – ^3H_4$ emission of $CaTiO_3$ prepared using rutile TiO_2 is more intense than that of the one prepared using the anatase TiO_2 phase. This outcome is attributed to the difference in phase purity of the two $CaTiO_3$ compounds, as evidenced in their XRD patterns (figure 1). The additional phases present in the $CaTiO_3:Pr^{3+}$ phosphor prepared with anatase TiO_2 have probably introduced luminescent quenching centers that promote non-radiative relaxation to the excited carriers [[17]]. Figure 3(b) presents the comparison of the PL intensity of $CaTiO_3:Pr^{3+}$(0.2 mol %) phosphor as a function of preparation temperatures. The PL intensity increases as a result of improved crystallinity of the material and it is at its maximum for the sample prepared at 1200 °C for the anatase prepared phosphor and 1300 °C for the rutile prepared phosphor. The decrease is attributed to increased point defects that act as quenching centers with an increase in temperature[[17],[18],[19]]. The energy required to produce defects in the material, is proportional to the temperature as modeled using the Arrhenius equation. This leads to the concentration of the defects to increase exponentially as temperature is increased [20].

The chemical stability of the compounds was investigated by probing the surface of the phosphor with a prolonged electron beam of 2 keV energy and 10 µA current *in-situ*. From the spectra (figure 4), the CL emission of the $CaTiO_3:Pr^{3+}$ phosphor prepared using the rutile TiO_2 phase is stable compared to that prepared using the anatase phase. The CL emission of the anatase TiO_2 phase dropped rapidly almost by 60 %, until at 2000 $C.cm^{-2}$ electron doses, where the rate of degradation began to decrease.

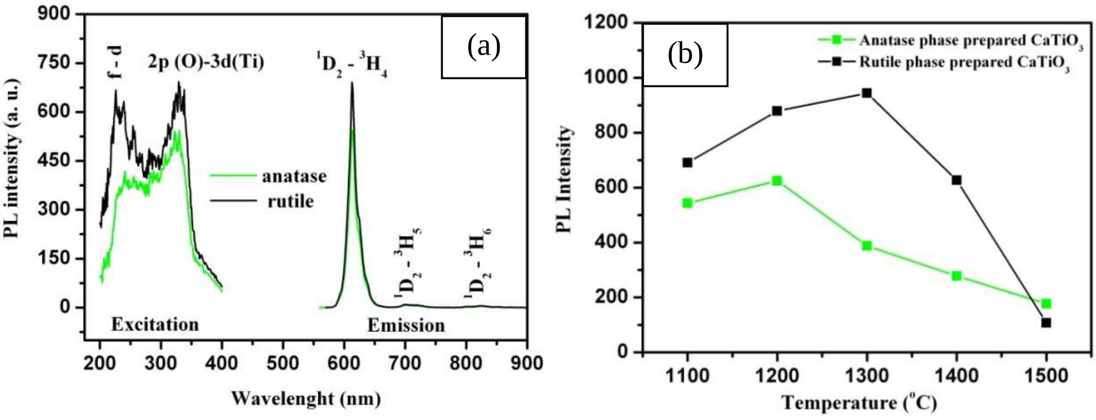

Figure 3: The excitation and PL emission spectra of $CaTiO_3:Pr^{3+}$ at 1200 °C and the maximum PL intensity at different temperatures (b).

Oxide phosphors are known to be chemically stable materials, and are good candidates for application in colour television screens. This is because of their chemical stability under prolonged electron beam irradiation [[21],[22]]. According to the electron stimulated surface chemical reaction (ESSCR) mechanism, CL degradation is a result of surface chemical changes due to the electron beam, and the phenomenon is common on less chemically stable surfaces [[23]]. The CL intensity of $CaTiO_3:Pr^{3+}$ (0.2 mol %) prepared using the rutile TiO_2 shows to be stable against prolonged electron beam exposure, as opposed to that prepared by the anatase phase. This may be attributed to the $CaTiO_3$ prepared using the rutile TiO_2 being more chemically stable compared to that prepared using the anatase TiO_2 [[11]]. The surface of the compound with a higher chemical stability tends to resist dissociation by an electron beam more than the compound with a lesser chemical stability [22]. The surface dissociation follows the ESSCR mechanism proposed by Swart et al [23]. A 4 eV shift in the AES spectra (not shown) was, however, measured during the degradation of the anatase phase leading to band bending in which the excited electrons and holes are swept apart before recombination leading to a lower CL intensity. Similar surface charging occurs during electron bombardment of aged ZnS:Ag,Cl phosphor due to the formation of a non-conductive ZnO surface layer [24]. Noto et al. [25] also measured the formation of CaO and CaO_x as well as TiO_2/Ti_2O_3 non-luminescent species on the surface of (anatase phase) $CaTiO_3:Pr^{3+}$.

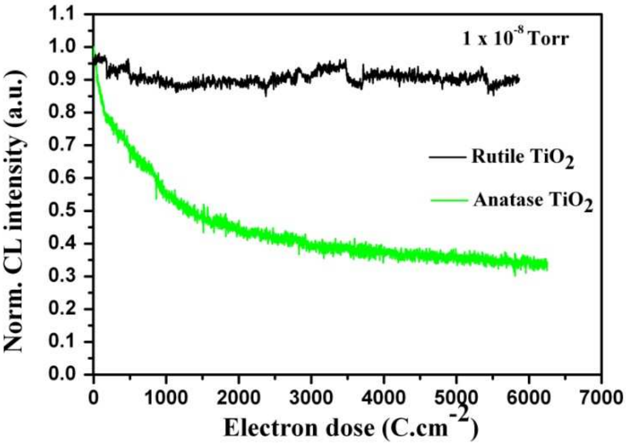

Figure 4: Cathodoluminescence of $CaTiO_3:Pr^{3+}$ under prolonged electron exposure.

4. Conclusion

$CaTiO_3:Pr^{3+}$ (0.2 mol %) was prepared using two different polymorphs of TiO_2, the anatase and the rutile that is more chemically and physically stable. The phosphor glowed with a single red emission of 613 nm wavelength from the $^1D_2 \rightarrow {}^3H_4$ radiative transition at room temperature, due to complete quenching of the blue emission by the intervalence charge transfer. Pure $CaTiO_3$ phase was obtained when using the rutile TiO_2 at different temperatures as evidenced from the XRD data. This effect led to samples prepared with rutile at different temperatures to have higher luminescence intensity. The surface of the phosphor prepared with the rutile TiO_2 was discovered to be more stable against prolonged electron beam irradiation.

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