**Effects of different TiO2 phases on the luminescence of CaTiO3:Pr3+**

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**Abstract.** CaTiO3 is widely used in the ceramic industry, and when it is doped with Pr3+ it glows with a single red emission at a wavelength of 613 nm. The red emission is attributed to the 1D2 →3H4 radiative transition of Pr3+ upon ultraviolet (UV) or electron beam irradiation. The compound was prepared by using rutile and anatase polymorphs of TiO2 to investigate their effects on the luminescence properties. X-ray diffraction patterns of CaTiO3:Pr3+ 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 TiO2 phases. The unreacted phases resulted in lowered luminescence intensity of the phosphor prepared with the anatase TiO2. The chemical stability of the phosphor was also investigated by exposing it to a prolonged electron beam irradiation.

**Keywords:**CaTiO3: Pr3+ red emission, long afterglow phosphor

1. **Introduction**

The intentervalence charge transfer mechanism is known to be the reason behind the single red emission of Pr3+ doped CaTiO3 at room temperature. The phenomenon is attributed to complete depopulation of the 3P0 level carriers by populating the 1D2 state. However so, the intensity of the single red emission peak from 1D2 → 3H4 transition is highly dependent on energy transfer from the host to the luminescent centers of Pr3+[1,2]. CaTiO3, 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 to tetragonal under different temperature exposure [3,4,5,6]. Solid state reaction is the main route to prepare this compound by directly firing the TiO2 and CaCO3/CaO as initial reagents at temperatures above 1000 oC [6]. The final compound can have different quantities of the different types 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 return affect energy transfer from the host to the luminescent centers of Pr3+ because of many non-radiative centers that may be introduced in the material [7,8,9]. TiO2 that is used as a reagent to fabricate CaTiO3 itself exists in different modifications, such as the rutile, anatase and the brookite polymorphs [10,11]. The three polymorphs have similar crystal structures made of TiO6 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 has an effect of increased distortion and reduced volume to the octahedrons. At higher temperatures the factor of distortion increases the most for anatase and remains unchanged for rutile. This leads to rutile being the most chemically and physically stable polymorph of TiO2 [10]]. The paper presents the effects of preparing CaTiO3:Pr3+ phosphor using rutile and anatase polymorphs of TiO2, to the luminescence intensity at different temperatures. The chemical stability of the phosphor is also investigated by probing its surface with a prolonged electron beam, and the effects to Cathodoluminescence (CL) emission were monitored.

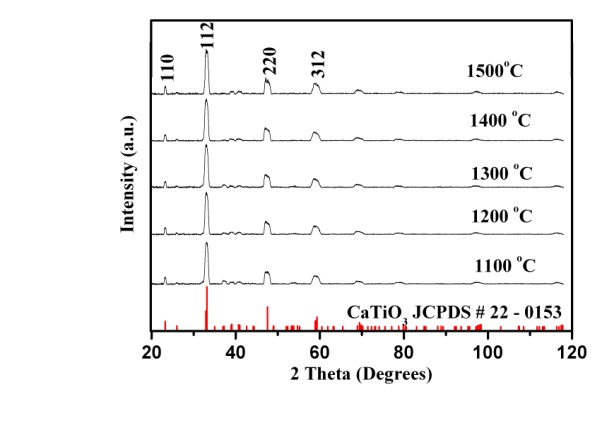
1. **Experimental**

CaTiO3 compound doped with 0.2 mol % of Pr3+ was prepared by stochiometrically reacting CaCO3 with TiO2 rutile and TiO2 anatase in separate experimental setups. PrCl3 was also stochiometrically incorporated into each of the two prepared CaTiO3 products to introduce Pr3+ 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 identity the phases that are present in each compound, and scanning electron microscopy (SEM) (Shimadzu SSX-550, Kyoto, Japan) for 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 CaTiO3:Pr3+ 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.

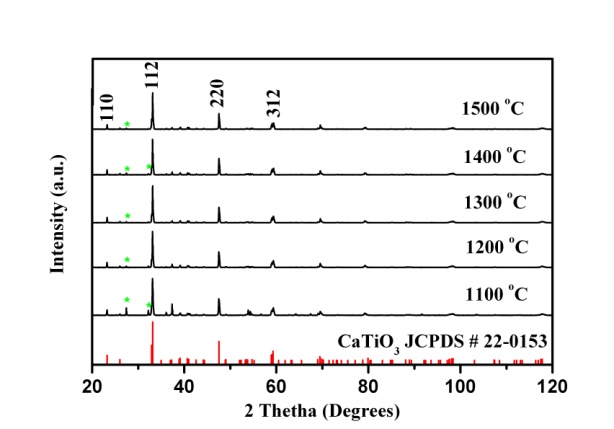
1. **Results**

CaTiO3:Pr3+ XRD patterns are presented for compounds prepared by using rutile (figure 1(a)) and anatase (figure 1(b)) TiO2polymorphs, which were sintered at different temperatures as indicated. TheXRD pattern of CaTiO3 prepared with the rutile TiO2 shows single phase formation when compared to the standard (JCPDS card no. 22-0153). On the contrary the XRD pattern of CaTiO3 prepared with the anatase TiO2 shows additional phases (marked by \*) when compared to the standard (JCPDS card no. 22-0153), which match with those of TiO2. The presence of the additional phases is attributed to the unreacted TiO2. 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 size effect. The effect may be attributed to particles of the phosphor of the sample prepared by the earlier polymorph being smaller than the latter polymorph of TiO2[12]. The existence of TiO2 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 Ti3+ and Ti4+ point defects, oxygen vacancies, line defects, different electronic structures, and different chemical and physical stability [8,13,14,16].Anatase TiO2 has a greater quantity of point defects and oxygen vacancies compared to the rutile TiO2 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 CaTiO3 prepared using a rutile TiO2 exists as a single phase as opposed to that prepared using anatase TiO2, which has additional phases (figure 1(b)).

The surface morphology of the two CaTiO3 phases prepared at 1300 oC using rutile TiO2 phase (figure 2(a)) and anatase TiO2 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 oC) involved for the preparation of CaTiO3 compounds.

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(a)

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(b)

**Figure 1**: The XRD patterns of CaTiO3 compounds prepared using different TiO2 phases; rutile (a) and anatase (b) phases.

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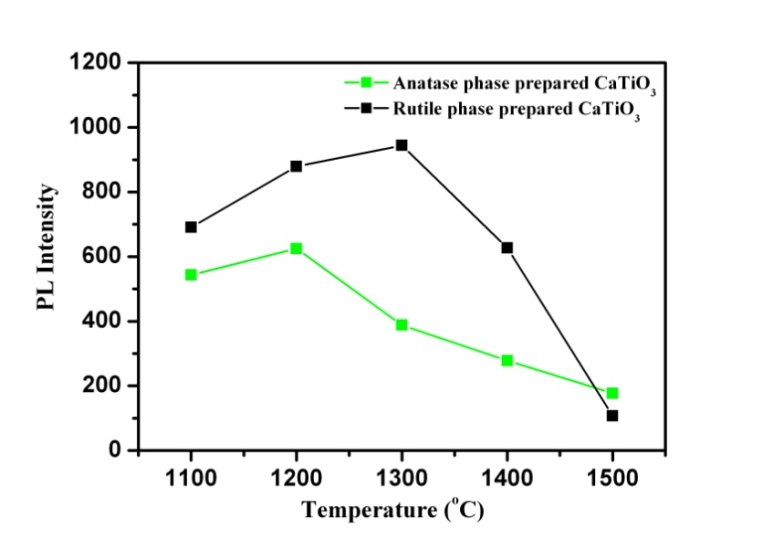
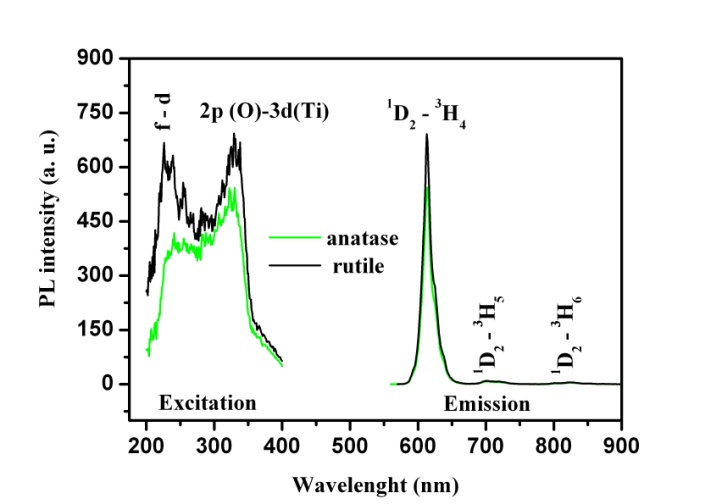
(b)

(a)

**Figure 2**: SEM images showing the surface morphology of CaTiO3 prepared using rutile (a) and anatase (b) TiO2 phases.

Perovskite materials are reported to be stable at temperatures above 1000 oC, and solid state reaction has so far been the famous route to prepare these materials [6]. However, recent reports have also shown chemical routes for their preparation [4,16]. The spectra in figure 3(a) show the PL excitation and emission of the CaTiO3:Pr3+(0.2 mol %) prepared by anatase and rutile TiO2 polymorphs at 1200 oC. According to the excitation spectra, the two compounds can best be excited using a 330 nm wavelength source to excite electrons from the valence band to the conduction band, or excite them from the 4f level to the 4f5d level. The intensity of the 1D2 – 3H4 emission of CaTiO3 prepared using rutile TiO2 is more intense than that of the one prepared using the anatase TiO2 phase. This outcome is attributed to the difference in phase purity of the two CaTiO3 compounds, as evidenced in their XRD patterns (figure 1). The additional phases present in the CaTiO3:Pr3+ phosphor prepared with anatase TiO2 introduce luminescent quenching centers that promote non-radiative relaxation to the excited carriers [17]. Figure 3(b) presents the comparison of the PL intensity of CaTiO3:Pr3+(0.2 mol %) phosphor at different preparation temperatures. PL intensity increases as a result of improved crystallinity of the material and it is at its maximum for the sample prepared at 1200 oC for the anatase prepared phosphor and 1300 oC for the rutile prepared phosphor. The decrement is attributed to increased point defects that act a 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, the CL emission of the CaTiO3:Pr3+ phosphor prepared using the rutile TiO2 phase is stable compared to that prepared using the anatase phase. The CL emission of the anatase TiO2 phase dropped with 60 %, until 2000 C.cm-2 electron doses, before it stabilized.

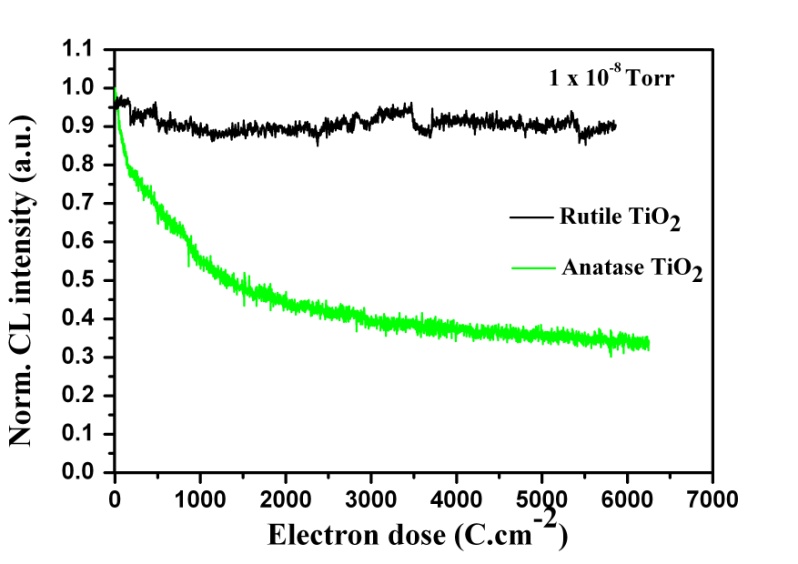
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(b)

(a)

**Figure 3**: The excitation and PL emission spectra of CaTiO3 at 1200 oC and the maximum PL intensity at different temperatures (b).

Oxide phosphors are known to be chemically stable materials, and are good candidates for fabricating television screens. This is because of their CL intensity that resists degradation under prolonged electron beam irradiation [21,22]. According to the ESSCR mechanism, CL degradation is a result of surface chemical changes which occur to non-chemically stable surfaces [23]. The CL intensity of CaTiO3:Pr3+ (0.2 mol %) prepared using the rutile TiO2 shows stability against prolonged electron beam, as opposed to that prepared by the anatase phase. This may be attributed to the CaTiO3 prepared using the rutile TiO2 being more chemically stable compared to that prepared using the anatase TiO2 [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 separated 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 CaOx as well as TiO2/Ti2O3 non-luminescent species on the surface of (anatase phase) CaTiO3:Pr3+.

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**Figure 4**: Cathodoluminescence of CaTiO3:Pr3+ under prolonged electron exposure.

1. **Conclusion**

CaTiO3:Pr3+ (0.2 mol %) was prepared using two different polymorphs of TiO2, 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 1D2 →3H4 radiative transition at room temperature, due to complete quenching of the blue emission by the intervalence charge transfer. The rutile TiO2 was effective in preparing phase pure CaTiO3:Pr3+ (0.2 mol %) phosphor at different temperatures as evidenced from the XRD. 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 TiO2 was discovered to be more stable against prolonged electron beam irradiation.

**Acknowledgement**

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