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# Thermoluminescence of calcium phosphate co-doped with gadolinium and praseodymium

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## HIGHLIGHTS

- The kinetic analysis of collocated glow-peaks in $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ is reported.
- At least 10 closely collocated components were recovered using digital-mustering.
- Analysis of the first three prominent peaks I, II, III was done by glow-curve deconvolution.
- Corresponding activation energies found were 0.78 ± 0.01 eV; 0.95 ± 0.01 eV; 1.07 ± 0.01 eV.
- Features of the most prominent component, peak I, best mirrors that of the unresolved main peak.

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## ABSTRACT

The thermoluminescence of beta-irradiated $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ is reported. A glow-curve measured at 5 °C $s^{-1}$ after beta irradiation to 12 Gy revealed an apparently single wide peak at 88 °C. The natural thermoluminescence also showed a single peak with an expanse of over 400 °C. Analysis of the glow-peak after laboratory irradiation using the partial heating procedure $T_m$–$T_{stop}$ and its dependence on irradiation was suggestive of the peak being made up of an overlap of closely spaced ones. At least 10 closely collocated components were experimentally recovered using a combination of partial heating and digital mustering. Kinetic analysis of the first three prominent peaks I, II, III using glow-curve deconvolution showed their activation energies to be 0.78 ± 0.01 eV, 0.95 ± 0.01 eV and 1.07 ± 0.01 eV, respectively, and the corresponding frequency factor to be of the order of $10^{10}$, $10^{12}$ and $10^{13}$ $s^{-1}$ in that order. Complementary analysis using the initial-rise and variable heating rate methods gave similar values for the trap depth. The dose-dependence of the main unresolved peak over the range 6–185 Gy was determined as supralinear using the superlinearity and supralinearity indices.



## 1. Introduction

The study of thermoluminescence of hydroxyapatite has a long genesis e.g. (Lapraz et al., 1979) because of its particular features which have been exploited in a wide range of applications. The many reports on the application of hydroxyapatite including its use in radiation therapy and related fields (Manjunatha and Rudraswamy, 2012; Ikeya, 1993; Madhukumar et al., 2007; Hung et al., 2012) and attempts to alter the features of its TL peaks by doping as reported in ref. (Fukuda et al., 1993) attest to its utility. As a biomaterial, hydroxyapatite has many excellent properties such as being nontoxic, biocompatible, osteoconductive and inflammable and these mostly account for its reported versatility (Vallim de Alencar, 2009).

One of the notable applications of hydroxyapatite, relevant in this report, is as a phosphor. To achieve this, hydroxyapatite is used as a host for rare earth ions to prepare phosphors used in different lighting devices including computer and television screens as well as in phototherapy lamps. The rare earth ions act as efficient emitters of luminescence as well as sensitizing agents. Hydroxyapatite ($Ca_5(PO_4)_3OH$), with a band gap of ~5 eV, is considered to be an effective generic host because its Ca sites can readily be occupied by different types of rare-earth cations.

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In this work, the luminescence properties of hydroxyapatite co-doped with gadolinium ($Gd^{3+}$) and praseodymium ($Pr^{3+}$); that is, $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$; have been studied using thermoluminescence (TL), a widely documented technique for monitoring changes in the density of point-defects in insulators and semiconductors (McKeever, 1985). Thermoluminescence is emitted from an irradiated material when it is heated at a controlled rate. The ionizing radiation produces free electrons and holes some of which may be trapped at certain imperfections in the lattice. During heating, some of the trapped charges are stimulated from the traps and make radiative transitions to luminescence centres via the conduction band. The emission appears as a glow-curve, that is, a temperature dependent set of peaks with each peak associated with a particular electron trap. The position, shape and intensity of the glow-peaks are therefore characteristic of the specific material, impurities and point-defects present. The particular features of the electron traps such as their activation energy may be determined using kinetic analysis.

The aim of this work is to characterize the TL features of $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$, a material prepared as a phosphor for application in phototherapy lamps. It should be noted that this report is not concerned with the influence of the dopants $Gd^{3+}$ and $Pr^{3+}$ on the TL of $Ca_5(PO_4)_3OH$. For phototherapy lamp application, $Gd^{3+}$ produces ultraviolet B (UVB) narrowband emission at ~313 nm. This emission is ideal for treatment of various skin diseases such as psoriasis, vitiligo, and hyperbilirubinemia related ailments as previously reported (Mokoena et al., 2014a). The advantage of the narrowband emission is that it covers only the therapeutic wavelengths range specific to the treatment of these skin diseases without side effects as opposed to the conventional UVB broadband that includes shorter wavelengths that can cause sunburn thereby increasing the risk of skin cancer. $Pr^{3+}$ is incorporated to act as a sensitizer to improve the intensity of signal from $Gd^{3+}$. The incorporation of $Gd^{3+}$ and $Pr^{3+}$ in the $Ca_5(PO_4)_3OH$ host lattice was demonstrated in our data published elsewhere (Mokoena et al., 2014a).

This paper reports the kinetic analysis of the thermoluminescence of the main glow-peak in $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$.

## 2. Experimental

$Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ was prepared in powder form by the co-precipitation method. Stoichiometric amounts of 0.6 M $Ca(NO_3)_2\cdot 4H_2O$, 0.4 M $(NH_4)_2HPO_4$, 10 M $Gd(NO_3)_3\cdot 6H_2O$ and 2 M $Pr(NO_3)_3\cdot 6H_2O$ were dissolved in distilled water at room temperature to form a homogeneous solution. The pH of the system was adjusted from 6.5 to 10.8 by adding dropwise 0.1 M NaOH solution with vigorous stirring for 12 h until a white precipitate was formed. The precipitate was separated by centrifugation and dried at 80 °C for 24 h. The dry powder was then ground using a mortar and pestle. Good crystallinity of $Ca_5(PO_4)_3OH$ co-doped with gadolinium and praseodymium was achieved after post-precipitation calcination of the powder at 900 °C in air. This is the same sample $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ used in Ref. (Mokoena et al., 2014a). The concentrations of $Gd^{3+}$ and $Pr^{3+}$ in the host lattice were 10 and 2 mol% respectively. Concentration data are presented for charge materials, and the concentration of impurities in the lattice is not measured.

Thermoluminescence was measured in a nitrogen atmosphere using a RISØ-TL/OSL-DA-20 Luminescence Reader from samples prepared as a monolayer on stainless steel discs of diameter 10 mm and thickness 0.3 mm. The luminescence was detected by an EMI 9235QB photomultiplier tube through a 7 mm Hoya U-340 filter (transmission band 250–390 nm FWHM). Samples were irradiated to different doses using a $^{90}Sr/^{90}Y$ beta source at a dose rate of 0.10 Gy $s^{-1}$. Glow-curves were corrected for the background signal. All data is shown in degrees Celsius unless otherwise specified.

## 3. Results and discussion

### 3.1. X-ray diffraction spectra

Fig. 1 shows the X-ray diffraction pattern of undoped $Ca_5(PO_4)_3OH$ powder. The spectrum corresponds to the hexagonal phase of $Ca_5(PO_4)_3OH$ as evident in the reference standard JCDPS Card No. 73-0293. In particular, the sharp and narrow diffraction peaks are consistent with the powder being crystalline. The average crystal size $D$ was calculated using Scherrer equation,

$$D = \frac{k\lambda}{\beta \cos\theta}, \quad (1)$$

where β is the full width at half maximum, $k$ is a constant that refers to the crystalline shape factor, $\lambda$ is the X-ray wavelength (1.542 Å for copper) and θ is the Bragg angle at the peak maximum. By using the two peaks at (002) and (222), the average crystal size was estimated to be 49 nm.

### 3.2. General features of thermoluminescence of hydroxyapatite

Fig. 2(a) shows the glow-curve of $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ measured at 5 °C $s^{-1}$ from 20 to 500 °C after irradiation to 12 Gy, and for comparison, the natural TL recorded at the same heating rate. This rate enabled suitably defined glow-peaks thus avoiding the problem of very wide but improperly defined peaks at too slow heating rates. The glow-curve consists of an apparently single peak at 88 °C. The peak is quite broad, a feature probably caused by overlapping of closely spaced components as will be examined later in the text. In the natural TL, the main peak is barely visible but comparatively weak TL appears above 150 °C. The natural TL peak is also very wide, again suggesting that the prominent peaks in $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ may in fact be a collection of closely collocated components.

Fig. 2(b) shows a glow curve measured at 5 °C $s^{-1}$ from 20 to 500 °C from an undoped sample ($Ca_5(PO_4)_3OH$) of similar mass as

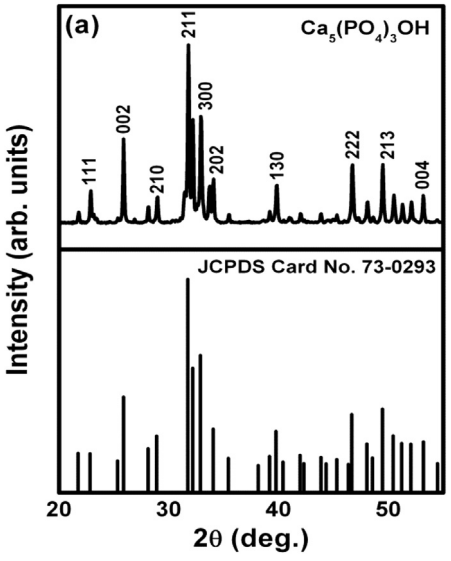


**Fig. 1.** The X-ray diffraction pattern for $Ca_5(PO_4)_3OH$. The standard reference, JCDPS card No. 73-0293, is shown for comparison.