Structural, morphological and photoluminescence behaviour of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ hydroxyapatite

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Abstract. This paper reports synthesis of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ with different concentration of Ba$^{2+}$ ion by co-precipitation method. To enhance the intensity of photoluminescence properties of strontium hydroxyapatite, barium (Ba$^{2+}$) ions are incorporated into hydroxyapatite structure. XRD pattern analysis shows single phase hexagonal structure along with space group P6$_3$/m. SEM image depicts the deposition of apatite layer on the surface of agglomerated spheroidal grains. FTIR analysis reveals the presence of functional group (PO$_4$) in the synthesized hydroxyapatite. Photoluminescence spectra shows an intense green light emission at 523 nm under 230 nm UV light irradiation.

1. Introduction

Hydroxyapatite containing phosphate group have general formula $A_{10}(PO_4)_6X_2$, where A site belongs to the family of larger cations of alkali, alkaline earth or lanthanide metal (Ca$^{2+}$,Pb$^{2+}$,Ba$^{2+}$,Sr$^{2+}$,Mn$^{2+}$ etc.) and X site consists of anions of alkali halides (F$^-$,Cl$^-$,O$_2^-$ etc.) respectively. The crystal structure of hydroxyapatite was given by Mehmal and Naragszabo [1] in 1930. Its structure is hexagonal close packed bunch of spheres with space group P6$_3$/m, in which each sphere specify tetrahedral ion with octahedral interstitial site that form channel between cationic and anionic sites respectively. It is formed by the occupancy of two cationic sites A(I) and A(II). Four $A_4$(I) are fixed at the centre of narrow channels (4f sites), six $A_6$(II) are fixed around large channels (6h sites) [2].

In the midst of the family of apatite, hydroxyapatite with strontium as a host have captivated the interest of scientist and researchers in the field of environmental science, optoelectronics, and medical science [3]. Ba$^{2+}$ ion doped hydroxyapatite have been used as WLEDs because of its supremacy in high brightness, tensile design, strength and eco-friendliness [4]. In addition it shows several beneficial properties such as long fluorescence lifetime, high quantum yield, good luminescence efficiency and sharp emission peaks [5].

Apart from various wet and dry synthesis methods, co-precipitation is a wet synthesis technique which is used for the synthesis of nano dimension powder due to its reliability in controlling the stoichiometric ratio of the material [6]. Co-precipitation method have several advantages like it requires less time, temperature, solvents etc. [7].
2. Experimental Method
Sr(NO₃)₂.4H₂O, Ba(NO₃)₂.4H₂O, (NH₄)₂HPO₄ were taken as starting material. All the materials were taken in stoichiometric amount, mixed in 50ml of distilled water to form desired solution. The solution was placed on magnetic stirrer at 400 rpm for 1 hour. NH₄OH was added to the solution during stirring to maintain the pH value of solution at 10 [8]. After continuously stirring the precipitate was formed, which was filtered and washed several times by using ethanol. The obtained precipitate was placed in oven at 80°C for 3 hours, the evaporated precipitate was ground for 30 min and kept in high temperature furnace for calcination at 900°C for 4 hours (See figure1).

3. Results and discussions
3.1 Crystallography Analysis
The crystal structural analysis of Sr₁₀₋ₓBaₓ(PO₄)₆(OH)₂ samples as shown in figure 2 were taped by using 3kW PANalytical-XPERT-Powder X-ray diffractometer. The analysis of PXRD patterns confirm the formation of single phase hexagonal closed packed structure with space group P6₃/m [9]. The average crystallite size of the particle calculated by Debye Scherer formula is 31nm.
Figure 2. XRD patterns of $\text{Sr}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$ ($x = 0, 0.5, 1 \text{ mol\%}$) hydroxyapatite

3.2 Scanning Electron Microscopy (SEM) Study
SEM micrographs for the sample $\text{Sr}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$ ($x = 1 \text{ mol\%}$) were taken by using SEM analyser - ZEISS Ultraplus is shown in figure 3. It depicts the deposition of apatite layer on the surface of spheroidal grains [10].

Figure 3. SEM image of $\text{Sr}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$ ($x = 1 \text{ mol\%}$) hydroxyapatite

3.3 Fourier Transform Infrared (FTIR) Spectroscopy
The FTIR spectrum of $\text{Sr}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$ ($x = 0, 0.5$ and $1 \text{ mol\%}$) were recorded by using Bruker FT-IR Spectrometer in the range 500-4000 cm$^{-1}$ is shown in figure 4. The doublet bands obtained at 560 cm$^{-1}$ and 593 cm$^{-1}$ are symmetrical bending modes ($\nu_2$) of $\text{PO}_4^{3-}$ functional group [11]. Further because of symmetrical stretching ($\nu_1$) mode $\text{O} - \text{P}$, the bands were obtained at 854 cm$^{-1}$ and 941 cm$^{-1}$. The observed bands gathered at 1021 cm$^{-1}$ and 1075 cm$^{-1}$ corresponds to the unsymmetrical stretching
(ν3) mode of PO4 group. Uncertain bands obtained at 2850 cm⁻¹ and 2924 cm⁻¹ are because of O-H stretching [12]. Presence of OH group is observed by the band obtained at 3594 cm⁻¹.

Figure 4. FTIR spectra of Sr10-xBa(x)(PO4)6(OH)2 (x = 0, 0.5 and 1 mol%) hydroxyapatite

3.4 Photoluminescence (PL) Spectroscopy
Figure 5 display the photoluminescence spectra for Sr10-xBa(x)(PO4)6(OH)2 (x = 0, 0.5 and 1 mol%) phosphors, obtained by using RF-5301 PC spectrofluorophotometer. The broad emission peak obtained at 523 nm in the green region corresponds to 3S1/2→P1/2 transition [13].

Figure 5. PL spectroscopic spectra of Sr10-xBa(x)(PO4)6(OH)2 (x = 0, 0.5 and 1 mol%)

The CIE chromaticity coordinates (1931) of Sr10-xBa(x)(PO4)6(OH)2 (x = 1 mol%) was done by GoCIE software shows a good understanding with NTSC (National television standard committee) values. The broad emission peak obtained at 523 nm in the green region as shown in the figure 6 with coordinates value CIE X = 0.3 and CIE Y = 0.7.
Figure 6. CIE Chromaticity diagram for Sr_{10-x}Ba_x(PO_4)_6(OH)_2 (x = 1 mol%) 

4. Conclusion
The Ba^{2+} ions doped Sr_{10-x}(PO_4)_6(OH)_2 hydroxyapatite were prepared by co-precipitation technique. PXRD analysis explains the design hexagonal close packed structure with space group P6_3/m. SEM image depicts the formation of apatite layer over the spheroidal grains. FTIR spectroscopy shows the asymmetric and symmetric stretching and bending modes of phosphate (PO_4) group. PL spectroscopy reveals that the emission spectrum analogous to ^6S_{1/2}-^6P_{1/2} transition consist of an intense line at 523 nm in the green region. CIE coordinate values show a keen agreement with NTSC value showing a cool emission in green region.

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