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Conventional synthesis and characterization of rare earth doped barium borophosphates, $BaBPO_5$:*RE* (Y, Gd and La)

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ABSTRACT

Purpose: of this research, our target is synthesis and characterization of rare earth metals such as Y, Gd and La doped barium borophosphate compounds which are applicable in non-linear optics industry.

Design/methodology/approach: The starting materials rare earth oxides, barium carbonate, boric acid and ammonium dihydrogen phosphate as analytically grade weighed 0.01:1:1:1 molar ratio and homogenized in an agate mortar. The mixture placed into a porcelain crucible to heat in high temperature oven step by step. First, mixtures were waited at 400°C for 2 hours for calcination process, subsequently heated 900°C with step rate 10°C/m for 8 hours, and finally cooled down to room temperature with step rate 10°C/m. After many grindings final product get ready for characterization. X-ray powder diffraction (XRD) analysis was performed using PANanalytical X'Pert PRO Diffractometer (XRD) with Cu Kα (1.5406 Å, 45 kV and 30 mA) radiation. Fourier transform infrared spectroscopy (FTIR) was taken on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm^{-1}. Scanning electron microscopy was achieved in SEM JEOL 6390-LV. Luminescence properties were performed by Andor Solis Sr 500i spectrophotometer. Conventional solid state syntheses were done in Protherm furnace.

Findings: The powder XRD patterns of the samples show that there is no impurity related to doping materials mean all diffractions corresponding to host material barium borophosphate crystallized in hexagonal system with unit cell parameters a=7.1003 and c=6.9705 Å. The unit cell parameters of rare earth doped barium borophosphates were calculated and display both increase and decrease depends on ionic Radius of rare earths. The other supporting methods confirm the crystal structure and luminescence properties.

Research limitations/implications: The synthesis method has some disadvantages such as low homogeneity, non-uniform product etc. We tried to minimize these negative aspects in our research and succeeded.

Practical implications: Phosphor materials Y:$BaBPO_5$, Gd:$BaBPO_5$ and La:$BaBPO_5$ (ICSD 51171) were synthesized by conventional solid state method and characterizations was mainly based on powder X-ray diffraction pattern. Also, morphological and luminescence properties were completed to get the highest knowledge.

Originality/value: Of the paper is first time conventional synthesis of Y, Gd and La doped $BaBPO_5$ compounds, calculation of unit cell parameters, and investigation of morphological and luminescent properties.

Keywords: Rare earths; Barium borophosphate; X-ray diffraction; Solid state chemistry; Rietveld refinement

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MATERIALS

1. Introduction

Borophosphate phosphors have been investigated both structurally and in terms of features since last ten years [1]. Bell et al. [2] reported that borophosphates are consisted of "BPO_7" group caused by B and P atoms connected with four oxygens in the structure as a result of building bridges with each other, creating a network of silica-like. Therefore, having a significant structural diversity of borophosphate crystal compounds blaze the trail for the studies aimed discovering new functional materials [3]. Adding alkaline earth metals to the structure can be basis for studies which aim forming new functional materials like non-linear optical materials by forming new structural units [4]. In literature, the mixture is homogenized after the preliminary calcination process for various periods in 400ºC, and the compounds were synthesized for various periods intervals 800-1150ºC [5,6].

Lanthanides which include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu elements are rare earth metals and located in the 6^{th} period of the periodic table. Lanthanide ions are luminescence materials highly used in imaging technologies, lasers and scintillators. Parametric crystal field model used to determine the energy levels of the lanthanide ions with 4f configuration was firstly developed in 1960's [7]. Crystal field model was applied successfully to low or high symmetry of the various lanthanides system. Model extended the configuration to 4fN-15d by using two [8] and trivalent [9] valence ions to analyse 4f → 4f 15d transition spectrum [10]. Rare earth metal doped alkaline earth borophosphates take place in many studies recently owing to their great structural diversity and also luminescence characteristic by doping process. Besides, rare earth metal doped materials are drawn interest with their intensive spectral gap which has a potential to be apply as optical data storage in high-density memory devices [11]. Y, Gd ve La rare earth ions were doped into barium borophosphate by conventional solid state technique to obtain phosphor non-linear optical materials.

2. Material and methods

The rare earth oxides, barium carbonate, boric acid and ammonium dihydrogen phosphate (Analytically grade) were weighed 0.01:1:1:1 molar ratio and homogenized in an agate mortar. The mixture placed into a porcelain crucible to heat in high temperature oven subsequently described steps; firstly, mixtures waited at 400°C for 2 hours to complete calcination process, then heated 900°C with step rate 10°C/m for 8 hours, and finally cooled down to room temperature with step rate 10°C/m. After many grindings final product get ready for characterization.

PANanalytical X'Pert PRO Diffractometer (XRD) with Cu Kα (1.5406 Å, 45 kV and 30 mA) radiation was used to determine X-ray powder diffraction (XRD) pattern and data. Perkin Elmer Spectrum 100.

FTIR Spectrometer was used to take fourier transform infrared spectrum (FTIR) in the range 4000 to 650 cm^{-1}. Scanning electron micrographs were achieved in SEM JEOL 6390-LV. Luminescence properties were performed by Andor Solis Sr 500i spectrophotometer. Protherm furnace was used to conventional solid state synthesis.

3. Results and discussion

The XRD patterns and data of Y:$BaBPO_5$, Gd:$BaBPO_5$ and La:$BaBPO_5$ compounds are shown in Figure 1 and Table 1, respectively. When the patterns of the samples are compared to the International Centre for Diffraction Data (ICDD) cards, there is no impurity related to doping materials mean all diffractions corresponding to host material barium borophosphate crystallized in hexagonal system with calculated unit cell parameters a=7.1003 and

c=6.9705 Å by Rietveld refinement method (Table 2). The unit cell parameters of rare earth doped barium borophosphates were calculated and display both increase and decrease depends on ionic radius of dopant rare earths.

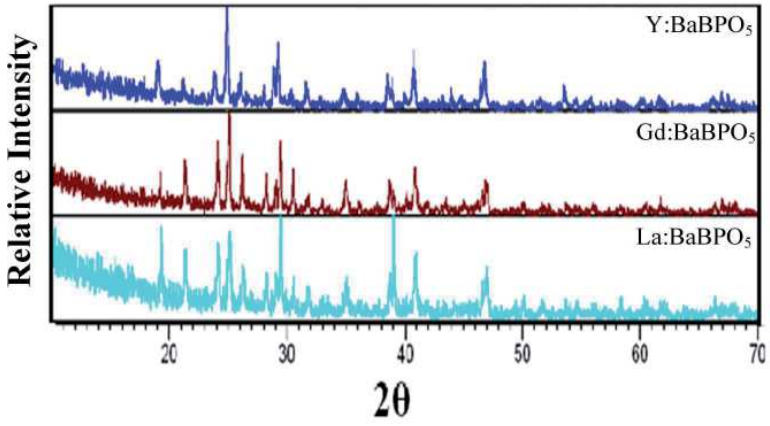

Fig. 1. The XRD patterns of 0.01 wt.% Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt. % La:$BaBPO_5$

Table 1.
The XRD data of $BaBPO_5$, 0.01 wt. % Y:$BaBPO_5$, 0.01 wt. % Gd:$BaBPO_5$ and 0.01 wt. % La:$BaBPO_5$

I/I_o	h k l	$BaBPO_5$	$Y:BaBPO_5$	$Gd:BaBPO_5$	$La:BaBPO_5$
		$d_{calc.}$ (Å)	$d_{obs.}$ (Å)	$d_{obs.}$ (Å)	$d_{obs.}$ (Å)
40.7	0 1 1	4.62006	4.65151	4.68764	4.62745
-	-	-	4.20909	4.20459	4.18009
-	-	-	3.72666	3.73120	3.69487
100.0	1 1 0	3.55450	3.57440	3.58329	3.57081
-	-	-	3.42843	3.43394	3.54558
8.6	1 1 1	3.16838	3.18869	3.19177	3.39991
17.4	0 2 0	3.07829	3.08847	3.09770	3.16655
79.7	1 0 2	3.03940	3.05179	3.06275	3.03469
14.0	2 0 1	2.81720	2.83222	2.83766	2.93518
-	-	-	2.57878	2.58016	2.82358
12.4	1 1 2	2.49211	2.49965	2.50687	2.56503
11.1	0 0 3	2.33000	2.32931	2.34045	2.33379
23.2	2 1 1	2.20784	2.21749	2.21812	2.20890
4.5	0 3 0	2.05219	2.05543	2.05950	2.15081
27.7	2 1 2	1.93693	1.94273	2.02360	2.05040
-	-	-	1.82805	1.94472	1.93342
6.7	1 3 0	1.70753	1.70926	1.77877	1.77383
8.7	2 2 2	1.58419	1.58751	1.71193	1.70679
4.4	3 1 2	1.53421	1.53441	1.68387	1.67991
4.3	4 0 1	1.50314	1.50316	1.58780	1.64097

Table 2.
The unit cell parameters of % Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt.% La:$BaBPO_5$ calculated by Rietveld Refinement Method

Compounds	Y:$BaBPO_5$	Gd:$BaBPO_5$	La:$BaBPO_5$
a (Å)	7.096161	7.095432	7.097284
c (Å)	6.972474	6.978899	6.975303

In Figure 2, Fourier transform infrared spectrums of the compounds are given. The vibrations at 65-673 cm^{-1}, 681-750 cm^{-1} and 796-850 cm^{-1} ranges are belongs to δ(BOP) [12-14], ν_s(BOP) [12-14] and ν_s(BOP) groups, respectively. The vibrations except the related groups are related to CO_2 born of atmosphere [15,16].

Figure 3 exhibits SEM micrographs of 0.01 wt. Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt.% La:$BaBPO_5$ compounds. The investigation of the micrograph shows a homogeneous distribution of the sample with particle size 6-7 μm.

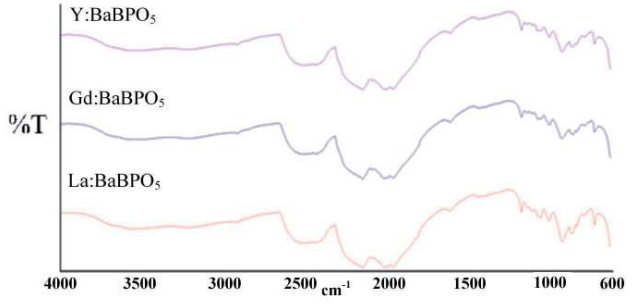

Fig. 2. FTIR spectrums of 0.01 wt.% Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt.% La:$BaBPO_5$

VUV-PL spectrums of the compounds are given in Figure 4. The luminescent properties of these compounds were investigated for the first time with significant intensity. The phosphorescing peak nearly 625 nm of La doped $BaBPO_5$ corresponds to $5D_0 \rightarrow 7F_2$ transition [17]. The peak around 575 nm of Y doped $BaBPO_5$ is originated by structural defects [18,19].

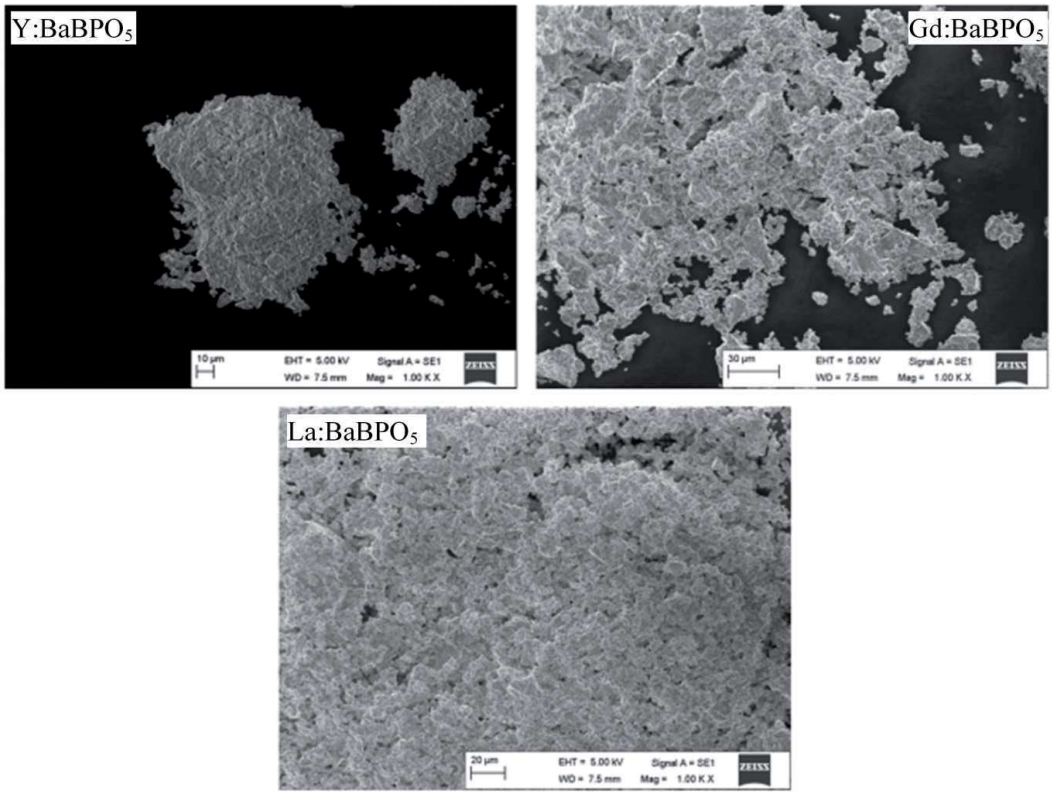

Fig. 3. SEM micrographs of 0.01 wt.% Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt.% La:$BaBPO_5$

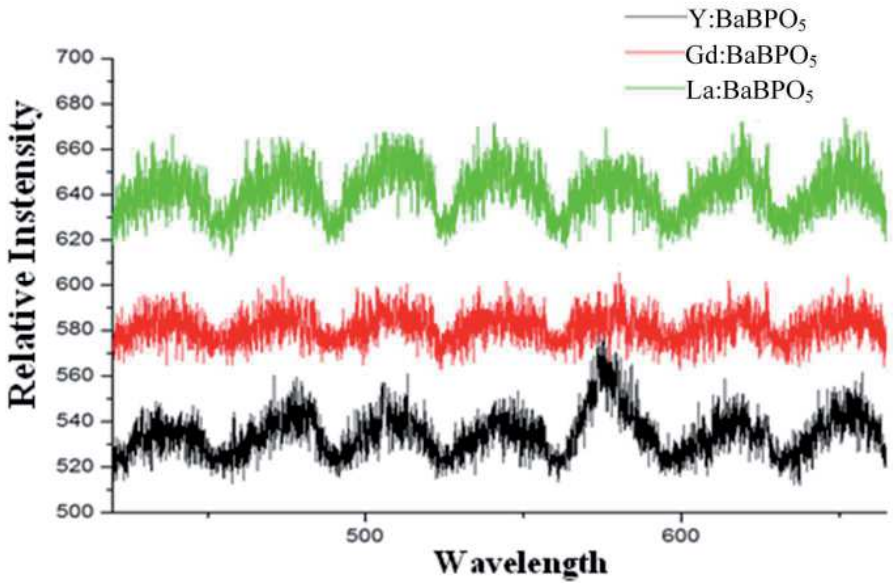

Fig. 4. VUV-PL spectrums of 0.01 wt.% Y:$BaBPO_5$, 0.01 wt.% Gd:$BaBPO_5$ and 0.01 wt.% La:$BaBPO_5$

4. Conclusions

Originality of the presented paper is first time conventional synthesis of Y, Gd and La doped $BaBPO_5$ compounds, calculation of unit cell parameters, and investigation of morphological and luminescent properties.

The phosphor materials Y:$BaBPO_5$, Gd:$BaBPO_5$ and La:$BaBPO_5$ (ICSD:51171) were synthesized by conventional solid state method at 900°C for 4 hours and characterizations was mainly based on powder X-ray diffraction pattern and unit cell parameters of the compounds were calculated by Rietveld refinement method for the first time. Also, morphological and luminescence properties were achieved to support the crystal structure and nature of the compounds.

Acknowledgements

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