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Synthesis and characterization of luminescent Er, Nd and Dy doped $Ba_3BP_3O_{12}$

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ABSTRACT

Purpose: Purpose of this study, our aim is high temperature based on synthesis method of barium borophosphate and doping with lanthanide type metals such as Er, Nd and Dy into the structure by solid state reaction.

Design/methodology/approach: The starting materials rare earth oxides, barium carbonate, boric acid and ammonium dihydrogen phosphate as analytically grade weighed 0.01:3:1:3 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 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 XRD patterns of the samples show that 0.01 wt.% Er:$Ba_3BP_3O_{12}$, 0.01 wt.% Nd:$Ba_3BP_3O_{12}$ and 0.01 wt.% Dy:$Ba_3BP_3O_{12}$ compounds were obtained as pure phase. When the pattern of the samples is compared to the International Centre for Diffraction Data (ICDD) cards, it gets along with $Ba_3BP_3O_{12}$ crystallized in tetragonal system In the XRD pattern of the samples, there is no reflection born of rare earth metal oxides.

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: Implications Luminescent Er:$Ba_3BP_3O_{12}$, Nd:$Ba_3BP_3O_{12}$ and Dy:$Ba_3BP_3O_{12}$ compounds were synthesized by conventional solid state method completely different from literature for the first time. The characterization was mainly based on powder X-ray diffraction pattern. Also, luminescence and morphological properties were determined.

Originality/value: Value of the paper is first time conventional synthesis of Er, Nd and Dy doped $Ba_3BP_3O_{12}$ compounds, calculation of unit cell parameters, and investigation of morphological and luminescent properties.

Keywords: Solid state synthesis; X-ray diffraction; $Ba_3BP_3O_{12}$; Solid state chemistry; Doped materials; Luminescence materials

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1. Introduction

The Borophosphate compounds have a structural diversity caused by the localized binding scheme of basic components B_2O_3 and P_2O_5 groups [1]. In borate structure; boron atoms form planar or pyramidal BO_3 structure by bounding from four oxygen atoms with trigonal sp^2 bonds or tetrahedral BO_4 group by bonding from for oxygen atoms with tetragonal sp^3 bonds [2]. Additionally, borates do not contain just these basic two groups, they can also contain complex groups such as B_3O_6, B_3O_7 or $(BO_3)_n$ [3-5]. Phosphate structure is formed by relatively basic tetrahedral PO_4 group and complex two groups P_2O_7 which includes two distorted tetrahedral PO_4 groups bonded with non-linear P-O-P bond [6]. $Ba_3BP_3O_{12}$ compound is a medium product in forming process of $BaBPO_5$ compound which is an alkaline earth borophosphate and consisted of single-chains which are occurred from bonding of two free tetrahedral group BO_4 extending parallel to [1 0 0] plane to tetrahedral PO_4 group by corners [7]. This compound is consisted of various canals where the barium ions are located inside [7,8]. These types of compounds were firstly synthesized by conventional high temperature solid state method and hydrothermal method [9].

The meaning of the photoluminescence can be defined as the using of photons as stimulating source in light propagation. A look to the formation of molecule orbitals to understand the luminescence is an essential requirement. Binding and opposite binding molecular orbitals occur with the combination of two atomic orbitals. Binding orbitals are chosen by electrons because they have lower energy. All the molecule orbitals have lower vibration energy sublevels. These transitions can be impossible in some molecules, because the energy gap between these levels is wide. However, this transition still has several ways to make it possible. One of them is to form inorganic luminescence materials. These materials are consisted of host molecule, crystal spaces of this molecule and dopant elements which will locate in this holes. Host molecules are inorganic structures like Y_2O_3, $Y_3Al_5O_{12}$ chosen by considering excitation energy, absorbance, chemical environment and temperature. And the dopant is an element chosen according to execution area and host molecule, like Cr^{3+}, Mn^{3+}, Eu^{3+}, Ce^{3+} with constant oxidation [10]. The basic investigation of this research is doping rare earths such as Er, Nd and Dy into multifunctional $Ba_3BP_3O_{12}$ compound to integrate luminescent property and increase usage area more and more.

2. Material and methods

The starting materials rare earth oxides, barium carbonate, boric acid and ammonium dihydrogen phosphate as analytically grade weighed 0.01:3:1:3 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 waited at 400 °C for 2 hours for calcination process, subsequently heated 800°C with step rate 10°C/m for 4 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 (PL). Conventional solid state synthesis was done in Protherm furnace. Perkin Elmer thermogravimetric analyser was used to determine thermal behaviour of the compounds.

3. Results and discussion

The XRD patterns and data of the samples are shown in Figure 1 and Table 1, respectively. 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$ compounds were obtained as pure phase. When the patterns of the samples are compared to the International Centre for Diffraction Data (ICDD) cards, they get along with $Ba_3BP_3O_{12}$

crystallized in tetragonal system with defined unit cell parameters given in Table 2. In the XRD pattern of the samples, there are no reflections based on rare earth metal oxides. The unit cell parameters of the samples were calculated by Rietveld Refinement Method benefiting from X-ray powder diffraction data.

Table 1.
The XRD data of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$

$d_{obs.}$, Å Er:$Ba_3BP_3O_{12}$	$d_{calc.}$, Å Er:$Ba_3BP_3O_{12}$	$d_{obs.}$, Å Nd:$Ba_3BP_3O_{12}$	$d_{calc.}$, Å Nd:$Ba_3BP_3O_{12}$	$d_{obs.}$, Å Dy:$Ba_3BP_3O_{12}$	$d_{calc.}$, Å Dy:$Ba_3BP_3O_{12}$
4.19499	4.19084	4.25557	4.17205	4.15432	4.14852
3.72365	3.72200	3.69130	3.69056	3.68025	3.68432
3.58134	3.59490	3.54548	3.54462	3.54413	3.54142
3.41776	3.41949	3.39890	3.39973	3.39191	3.39670
3.17874	3.17518	3.15812	3.15772	3.16035	3.15245
3.05184	3.06865	3.07102	3.05278	3.07024	3.05020
2.83028	2.83418	2.81547	2.82111	2.81275	2.81869
2.58046	2.58083	2.56752	2.55750	2.56666	2.56454
2.33841	2.34037	2.32842	2.32976	2.30697	3.32876
2.31553	2.30039	2.30611	2.28250	2.29087	2.28237
2.21645	2.22207	2.20971	2.21155	2.20600	2.21020
1.94090	1.94127	1.93117	1.94947	1.93237	1.93230
1.71201	1.70975	1.70618	1.70090	1.67783	1.67398
1.41154	1.41280	1.39742	1.39135	1.40856	1.39818

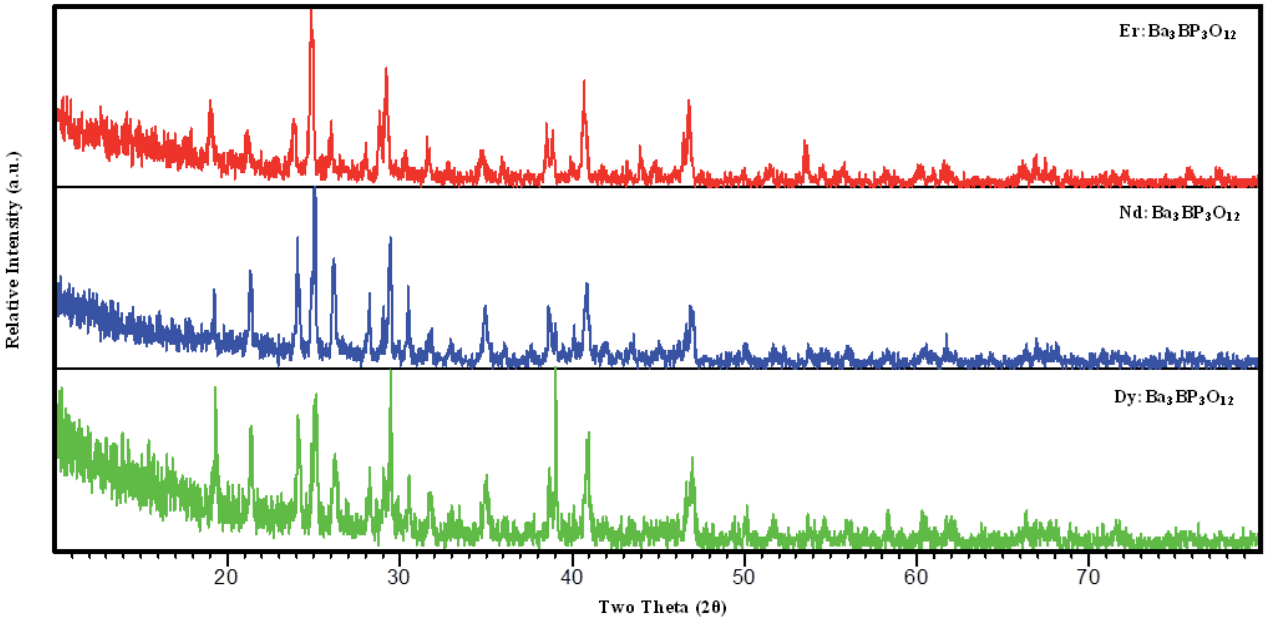

Fig. 1. The XRD patterns of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$

Table 2.
The unit cell parameters of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$ calculated by Rietveld Refinement Method

Compound	Lattice parameters		
	a, Å	b, Å	c, Å
Er:$Ba_3BP_3O_{12}$	7.0897	14.2932	22.1929
Nd:$Ba_3BP_3O_{12}$	7.0984	14.3057	22.1731
Dy:$Ba_3BP_3O_{12}$	7.1091	14.3084	22.1913

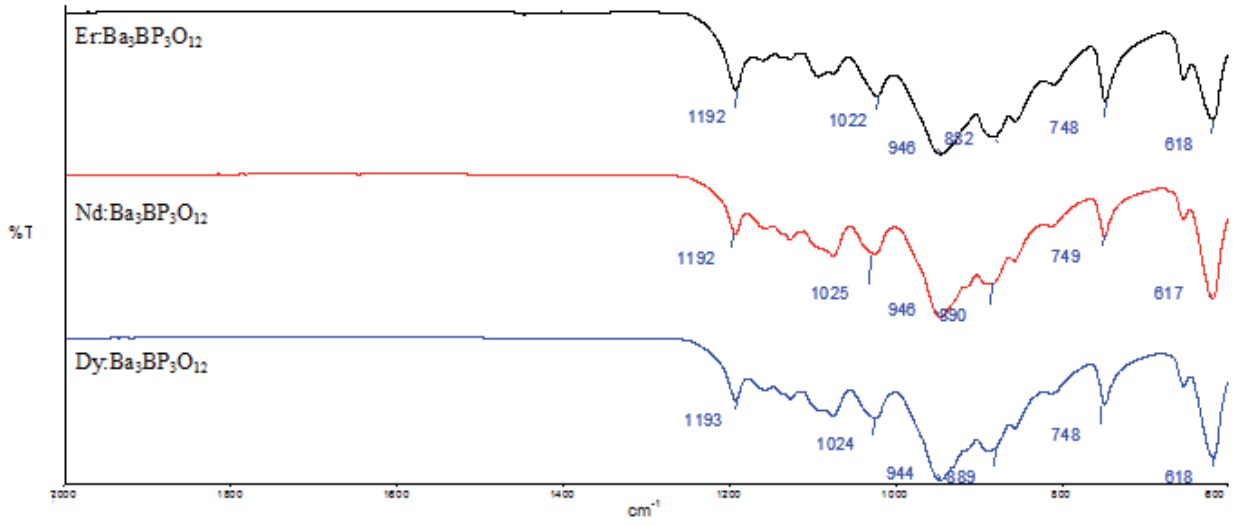

Fig. 2. FTIR spectrums of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$

In Figure 2 and Table 3, fourier transform infrared spectrum and data are given respectively. The B-O, P-O and B-P-O vibrations are present in the related spectrum and vibration frequencies of the compounds in data table.

Table 3.
The unit cell parameters of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$ calculated by Rietveld Refinement Method

Observed wave numbers, cm^{-1}	Vibration type
1193	$\upsilon(BO_4)$ [11]
1024	$\upsilon_s(PO_2)$ [12]
944	υ_{as}(P-O-P) [12]
889	$\upsilon(BO_4)$ [11,13]
748	υ_{as}(BOP) [1,2]
618	δ(BOP) [1,5]

Figure 3 exhibits SEM micrographs of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$ compounds. The distribution of the sample size display changes from place to place in a range of 2-20 μm dimensions. There are homogeneous dispersions as the overview. Also, the results of EDX analysis are in accordance with chemical composition of the samples.

PL spectrums of the compounds in ultraviolet zone are given in Figure 4. In the photoluminescence spectrum of Er:$Ba_3BP_3O_{12}$, broad emission at 400-600 nm are belong to $^2H_{11/2}\rightarrow {}^4I_{15/2}$ and $^4S_{3/2}\rightarrow {}^4I_{15/2}$ transitions. The emissions at 660 and 805 nm are related to $^4F_{9/2}\rightarrow {}^4I_{15/2}$ and $^4S_{3/2}\rightarrow {}^4I_{15/2}$ transitions [14,15], respectively. When we checked the VUV-PL spectrum of Nd:$Ba_3BP_3O_{12}$, the emissions at 462, 518, 594, 803 and 889 nm are belonging to $^4G_{7/2}\rightarrow {}^4I_{9/2}$ [16], $^4G_{5/2}\rightarrow {}^6H_{5/2}$, $^4G_{5/2}\rightarrow {}^6H_{7/2}$ [17], $^4F_{5/2} + {}^2H_{8/2} \rightarrow {}^4I_{9/2}$ [18] and $^4F_{3/2}\rightarrow {}^4I_{13/2}$ [19] in order. The emission peaks of Dy:$Ba_3BP_3O_{12}$ are at 486, 582, 668 and 756 nm are correspond to $^4F_{9/2}\rightarrow {}^6H_{15/2}$, $^4F_{9/2}\rightarrow {}^6H_{13/2}$ [20], $^4G_{5/2}\rightarrow {}^6H_{9/2}$ and $^4G_{9/2}\rightarrow {}^6H_{11/2}$ [15], respectively.

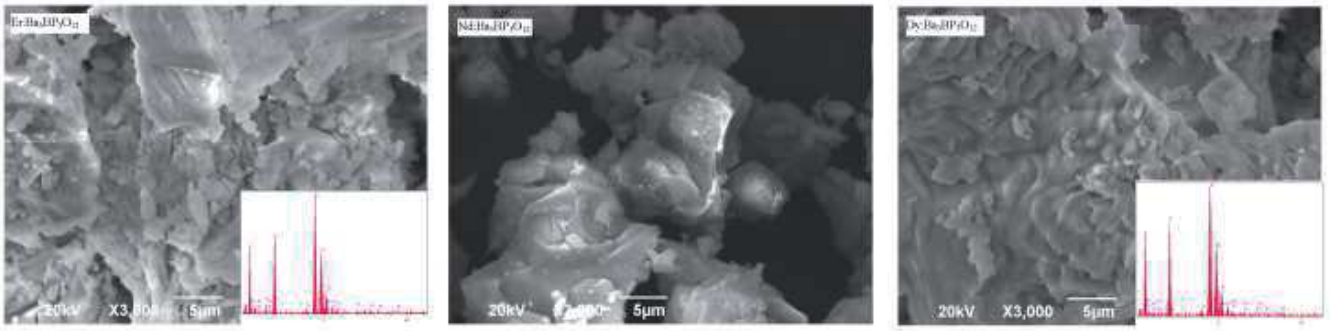

Fig. 3. SEM micrographs and EDX results of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$

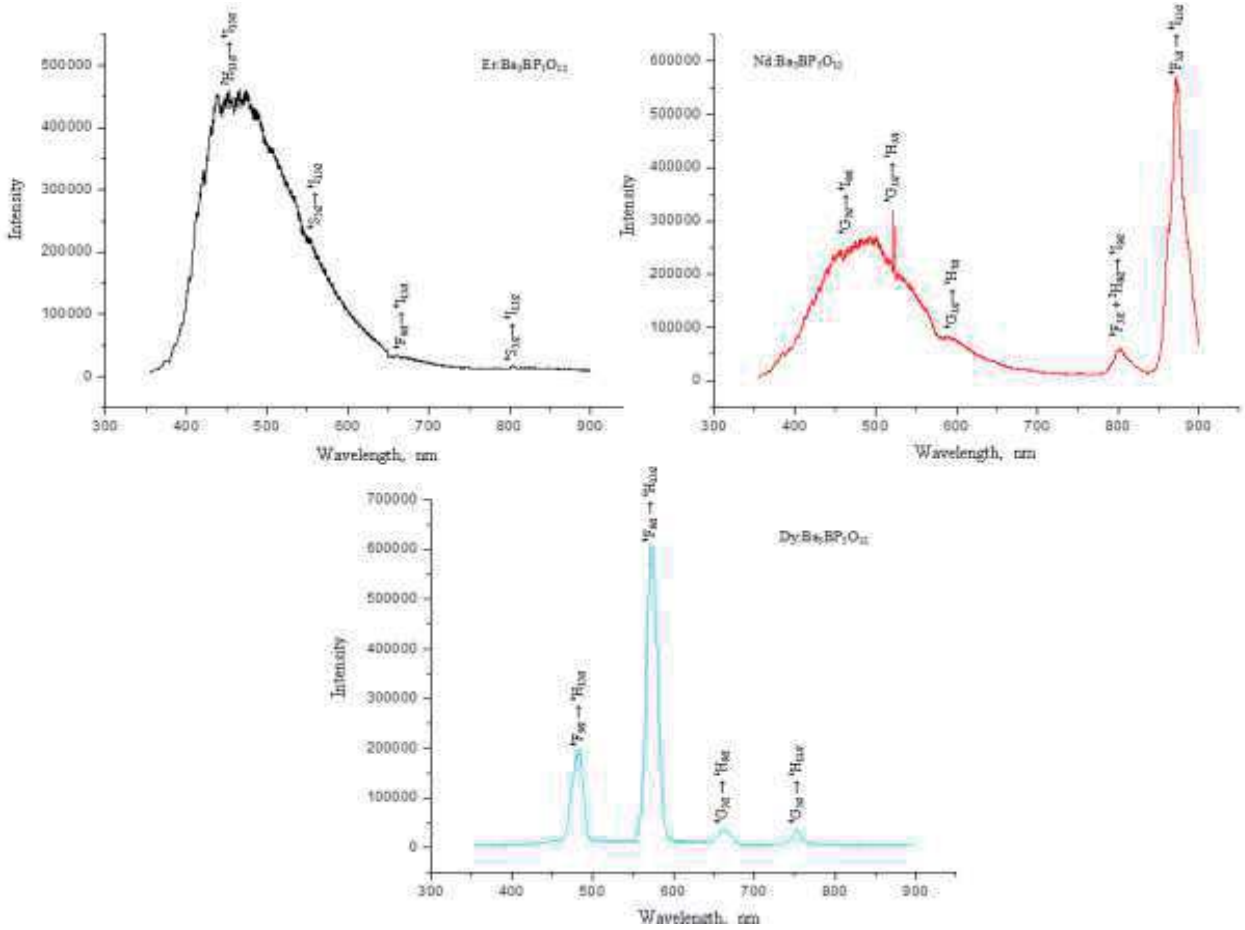

Fig. 4. VUV-PL spectrums of 0.01 wt. % Er:$Ba_3BP_3O_{12}$, 0.01 wt. % Nd:$Ba_3BP_3O_{12}$ and 0.01 wt. % Dy:$Ba_3BP_3O_{12}$

4. Conclusions

Luminescent Er:Ba_3BP_3O12, Nd:$Ba_3BP_3O_{12}$ and Dy:$Ba_3BP_3O_{12}$ compounds were synthesized by conventional solid state method completely different from literature for the first time. The characterization was mainly based on powder X-ray diffraction pattern. Also, luminescence and morphological properties were determined.

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