

INVESTIGATION ON PRASEODYMIUM INCORPORATION IN THE STRUCTURAL, MORPHOLOGY, THERMAL AND OPTICAL PROPERTIES OF BARIUM HYDROGEN PHOSPHATE CRYSTALS

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Abstract

Barium hydrogen phosphate and praseodymium doped barium hydrogen phosphate crystals prepared by single diffusion growth process in silica gel medium were studied. The influence of growth parameters such as gel density, gel ageing, gel pH, concentration of reactants etc were examined. By X-ray diffraction analysis, the crystal structure was identified and found to be in orthorhombic system. The major functional groups expected to be present in the crystals were identified and confirmed by Fourier transform spectroscopy. The scanning electron microscopy and the energy dispersive X-ray analysis have been done to find the morphology and stoichiometric composition of the crystals. By thermal analysis, thermal behaviour and stability of the crystals were investigated. The optical response and band gap of these crystals have been obtained by UV-Visible spectroscopy at room temperature. The optical absorption region and the lower cut off wavelength of the crystals have been identified.

Keywords: Single diffusion technique, Pr doped Barium Hydrogen Phosphate Crystals, Thermal analysis, Optical bandgap.

1. INTRODUCTION

Crystallization is the process of formation of solid crystals deposited directly from gas, precipitating from solution, melts, or by solid state reaction. Crystal growth in gels [1] is an effective and simple technique for growing good quality single crystals. Due to its simplicity, it can be used successfully at room temperature to suppress nucleation centres and is suitable for the materials that have low solubility [2].

Extensive researches have been carried out over the decades on the growth of defect free single crystals as the subject is a key for fundamental research and it plays a vital role in the fields of optoelectronics, solid state lasers, remote sensing etc [3,4].

Due to its application in various fields such as bioceramics, ionic conductivity, ferroelectrics and luminescence, the alkaline earth phosphates such as barium hydrogen phosphate (BHP),

calcium hydrogen phosphate (CHP), strontium hydrogen phosphate (SHP), etc have been given considerable attention [5,6]. Barium hydrogen phosphate (BHP) crystal consists of tetrahedral phosphate groups, linked by hydrogen bonds and Ba^{2+} ions. For this alkaline earth phosphate, ferroelectricity is expected to occur in the orthorhombic structure [7,8]. Recently, rare earth doped crystals are also being studied extensively due to their potential application as optical fibre amplifier, visible lasers, optical communication and display devices [9-12]. Study on rare earth based single crystals have intensified on account of their high radiative transition rates which increases the quantum efficiency [13]. Considering the significance of rare earth in modifying and altering various physical and chemical properties of host materials, an attempt is made to synthesis, crystal structure, FTIR, SEM, thermal and optical properties of new praseodymium doped barium hydrogen phosphate crystals by single diffusion technique.

2. EXPERIMENTAL PROCEDURE

The crystallization of barium hydrogen phosphate (BHP) and praseodymium doped barium hydrogen phosphate (PrBHP) were carried out by single diffusion system. The crystallizer was glass tube of 25 mm diameter and 150 mm long for single diffusion method. The chemicals used were: pure Sodium Meta Silicate AR grade $Na_2SiO_3 \cdot 9H_2O$ (SMS) (CDH, New Delhi, India), Orthophosphoric acid- H_3PO_4 , Barium Chloride $BaCl_2 \cdot 2H_2O$ and

Praseodymium Nitrate $Pr(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9 wt.%). The gel was set up by mixing SMS of specific gravity $1.04g/cm^3$ with aqueous 0.5M ortho phosphoric acid in proper ratio such that the pH of the solution was set at 6.5 for the growth of crystals at room temperature, in which the orthophosphoric acid acts as lower reactant. Constant stirring with magnetic stirrer was preferred, in order to avoid premature local gelling which in turn make the final medium inhomogeneous. The three dissociation equilibrium representing the dissociation of orthophosphoric acid system that provide various ions at various pH values were reported [6]. Thus orthophosphoric acid acts as the source of anions needed for crystallization of the compound. The gel of given pH was then allowed to set and once the gel got set, an aqueous solution of barium chloride of a particular molarity was added to it slowly. Slow diffusion of the upper reactant ions passes through the narrow pores of silica gel which initiate the reaction between these ions and the ions present in the gel as lower reactant. The BHP crystals started growing in different regions of the crystallizer in about a week time.

For the growth of PrBHP crystals, praseodymium nitrate solution was mixed with the aqueous solution of barium chloride of a particular molarity and then poured over the set gel. The diffusion of Pr^{3+} and Ba^{2+} ions through the narrow pores of the silica gel initiate the reaction between these ions and the HPO_4^{2-} ions present in the gel acts as lower reactant. The

Condition	BHP	Pr:BHP
Gel Density	1.04	1.04
Conc. of H_3PO_4	0.5M	0.5M
pH of gel	6.5	7
Gel setting time	4 days	5 days
Conc. of $BaCl_2$	1M	0.9M
Conc. of $Pr(NO_3)_3$	--	0.1M

with gel density, pH of the gel, concentration of the reactants and acidity of the feed solution [14-18]. By varying these parameters, the optimum condition for getting good quality crystals were found and was shown in the Table 1.

Table 1 Optimum condition for obtaining good quality BHP and PrBHP single crystals
 Optically transparent good quality single crystals of well-defined rectangle type morphology were grown during a time period of three weeks and can be seen in Fig 1.

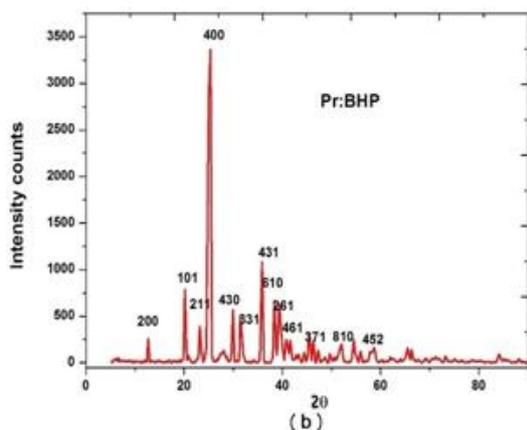
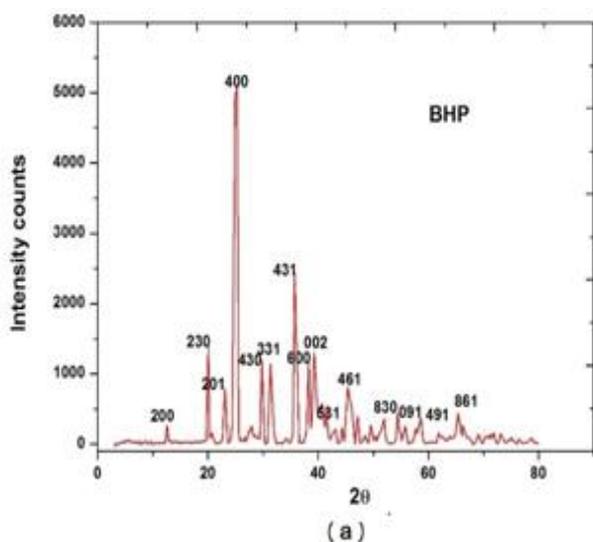


Fig. 1 PrBHP single crystals grown in gel system

reaction led to the formation of PrBHP crystals in test tubes. It was found that the morphology, quality, size and the number of crystals vary

d-spacing (Å)		2theta (Θ)		[hkl] planes	
BHP	PrBHP	BHP	PrBHP	BHPPrBHP	
7.035	6.988	12.571	12.666	200	200
4.430	4.409	20.025	20.120	230	101
3.847	3.830	23.097	23.676	201	211
3.580	3.508	24.846	25.366	400	400
2.997	2.986	29.786	29.890	430	430
2.850	2.842	31.351	31.451	331	331
2.511	2.504	35.721	35.822	431	431
2.348	2.343	38.292	38.379	600	610
2.293	2.286	39.252	39.367	002	261
1.993	1.990	45.343	45.452	461	461
1.684	1.68	54.408	54.541	830	452
1.426	1.424	65.374	65.452	861	662

III. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION ANALYSIS (XRD)

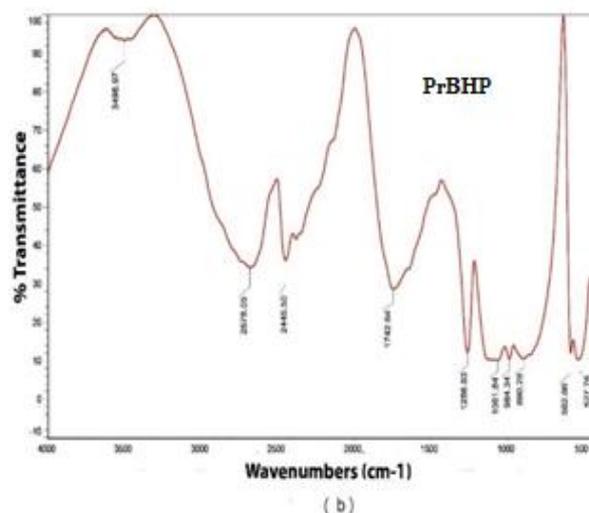
The powder X-ray diffraction patterns of the samples were obtained using a powder X-ray diffractometer (model: Ritz-170 with nickel filtered $\text{CuK}\alpha$ radiations (1.54056\AA), 35KV,10mA). The X-ray diffractogram of both BHP and PrBHP single crystals were shown in fig 2(a) and (b) respectively using ICDD data file (Card no.72-1370) and was found that the crystal belongs to orthorhombic system having space group $\text{Pn}2_1\text{a}$.

Fig. 2(a) X-ray diffractogram of BHP crystal (b) X-ray diffractogram of PrBHP crystal

The crystal system of the sample was also obtained from single crystal diffractometer

which turned out to be the same as calculated from the powder XRD pattern. The occurrence of well-defined peak at specific 2Θ Bragg angles in both the crystals indicates the crystalline nature of the grown crystals. The dopant Pr^{3+} ions have been selected for the modification because the ionic radii of Pr^{3+} (1.12\AA) was close to that of Ba^{2+} (1.35\AA) ion. The ions having similar size easily replace each other but it affects the unit cell volume of the parent compound [19]. The details of PXRD plot illustrating interplanar 'd' spacing and corresponding {hkl} planes for BHP and PrBHP are given in the table 2.

Table 2 Compiled data of various hkl planes corresponding to different Bragg angle 'Θ' and

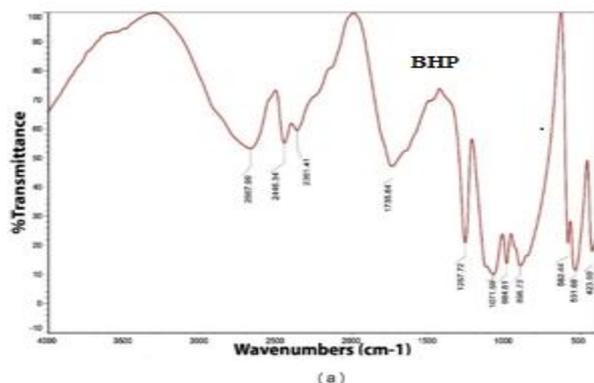


interplaner spacing 'd' for BHP and PrBHP
 From the table 2, it is evident that the peak values of PrBHP shift towards higher angle when compared with BHP. This may be because of Pr^{3+} ion in the composition of BHP crystal system. This indicates a decrease in the value of lattice constants and cell volume of PrBHP. The lattice parameters obtained for pure BHP crystal

are: $a=14.088\text{\AA}$, $b=17.00\text{\AA}$, $c=4.586\text{\AA}$ and $\alpha=\beta=\gamma=90^\circ$ and volume of unit cell being 1098.32\AA^3 are in good agreement with the reported values [20,21]. Similarly, the lattice parameters obtained for doped PrBHP crystals are: $a=14.058\text{\AA}$, $b=16.399\text{\AA}$, $c=4.572\text{\AA}$ and volume of unit cell being 1054.01\AA^3 . The cell parameters were also obtained from single crystal diffractometer which turned out to be same as calculated from the powder XRD pattern. The unit cell parameters and cell volume of Pr-doped BHP crystal are slightly different from that of BHP crystal. The changes in lattice parameters are due to incorporation of Pr^{3+} ions in the lattice of BHP crystal. Since the ionic radii of praseodymium and barium are comparable, one can expect identical crystal system for both BHP and PrBHP crystals. Hence it can be confirmed that both the crystals belong to orthorhombic crystal system.

3.2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR was widely used for identifying the chemical bonds, functional groups and internal structure of molecules. Fig 3(a) and (b) represent



the FTIR spectrum of pure BHP and PrBHP crystals respectively.

Fig. 3(a) FTIR spectrum of BHP crystal shows all the major functional groups expected to be present in the crystals (b) FTIR spectrum of PrBHP crystal

Fundamental IR frequencies reported in other phosphate compounds were found in the present case, which confirms the presence of phosphate group in the grown crystal. The peaks at 3498cm^{-1} in PrBHP crystals is due to weakly H bonded O-H vibrations [22]. The bands at 2667 and 2446cm^{-1} in BHP crystal related to the intermolecular Ba-O phonon bands and O-H stretching of the hydrogen phosphate anions respectively. These bands are shifted towards 2678 and 2445cm^{-1} in the case of PrBHP crystal. The band centred at 2361cm^{-1} in BHP and PrBHP confirms the presence of Si-H bond. The bands located at 1735 and 1257cm^{-1} are referred to vibration of hydrogen ions in HPO_4^{2-} and in plane P-O-H bending respectively. The P=O stretching in the PO_4 section of BHP are characterized by two bands at 1071 and 984cm^{-1} . The bands at 896cm^{-1} in BHP and 890cm^{-1} in PrBHP reveal the P-O(H) stretching and liberation of H_2O molecules [23]. The peaks occurring at 531 and 527cm^{-1} , are due to the presence of metal oxygen bond in BHP and PrBHP crystals respectively. There are no additional peaks or bands present in praseodymium modified BHP, but slight shifting and broadening of peaks occurred. This shift in some of the characteristic vibration frequency of

the PrBHP spectrum suggests the co-existence of Pr^{3+} ions in BHP crystal. The lattice strain developed due to the difference in mass of barium and praseodymium ions leads to change in molecular geometry and mechanical vibrations. This causes the broadening and shifting of bands [24]. The effect of doping can also be seen clearly in FTIR spectrum where the transmittance percentage decreases in case of PrBHP crystals. The vibration frequencies corresponding to other functional groups were also present and comparative assignment of prominent peaks of FTIR spectra is given in the Table 3.

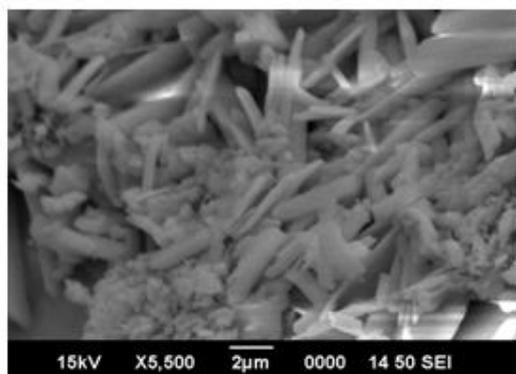
Assignment of bands	Peaks for BHP	Peaks for PrBHP
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Weakly H bonded O-H vibrations	3498
Intermolecular Ba-O phonon bands	2667	2678
O-H stretching of the hydrogen phosphate anion	2446	2445
Si-H bond	2361	2361
Vibration of hydrogen ions in HPO_4^{2-}	1735	1742
Vibration of hydrogen ions in plane P-O-H bending	1257	1256
P=O stretching vibrations	1071,984	1061,984
P-O(H) stretching vibration	896	890
P-O bending of PO_4^{3-}	582	582
Metal oxygen bond	531,423	527

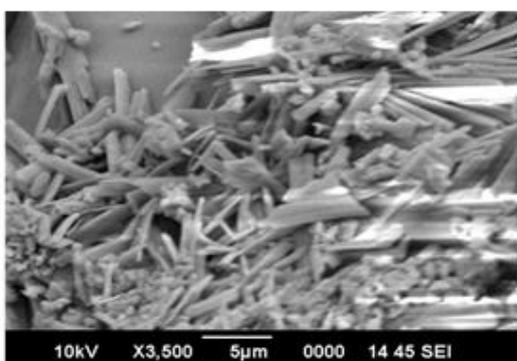
Table 3 FT-IR wavenumbers and vibrations assignment of BHP and PrBHP crystal

3.3. SCANNING ELECTRON MICROSCOPY (SEM)

Electron microscopy is an efficient tool to investigate the microstructure of single crystals. Fig 4(a) and (b) shows the SEM pictures of pure and Pr added BHP crystals respectively. The micrograph indicates that both the crystals have irregularly arranged needle shaped bundles like morphology. Figure suggest that doping of BHP with Pr does not result any changes in the basic morphology of the crystal.



(a)

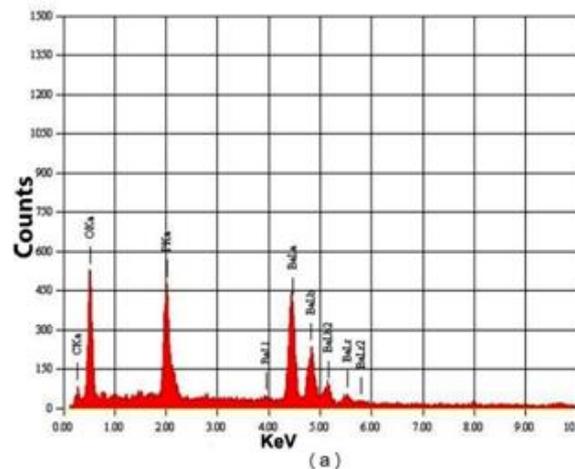


(b)

Fig. 4(a) SEM image of BHP crystal (b) SEM image of PrBHP crystal

3.4. ENERGY DISPERSIVE X RAY ANALYSIS (EDAX)

EDAX technique aid us to identify elements present and know their concentrations by analysing the energies of X ray photons emitted as a result of bombardment by an electron beam. The spectrum obtained from EDAX analysis for BHP and PrBHP were shown in fig 5 (a) and (b) respectively. EDAX pattern shows peaks constituting all the major elements present in the grown crystals as expected. The spectrum of PrBHP crystal shows peaks indicating all major elements along with Pr thereby suggesting that Pr^{3+} ion has entered into the crystal lattice of BHP. Hence the presence of Pr in the doped specimen was confirmed by EDAX analysis and the concentration of incorporated Pr^{3+} ion into the BHP crystal system can be seen in Fig 5(b).



(a)

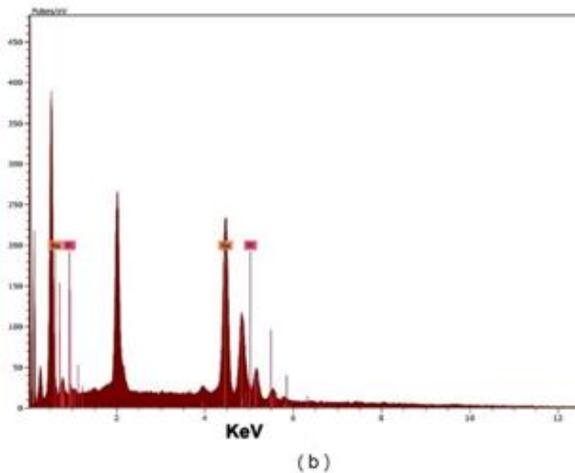


Fig. 5(a) EDAX pattern of BHP crystal (b) EDAX pattern of PrBHP crystal

3.5. THERMAL STUDIES

Thermal decomposition stages of BHP and PrBHP were investigated by thermo gravimetric analysis (TGA) along with differential thermo gravimetry (DTG). The TGA was carried out in the temperature range 25–800°C at a heating rate of 25°C/min. Fig 6(a) and (b) shows simultaneously recorded TG and DTG curves for BHP and PrBHP crystals respectively.

The thermal stability of the grown material can be explained in two steps. The TGA curve of BHP crystal shows that the crystal was stable upto 330°C with slight weight loss. This was due to the removal of adsorbed water molecules, which was negligible for all samples [25]. The decomposition begins from 330°C and continues upto 520°C and thereafter the sample tends to be stable. The decomposition process results in a

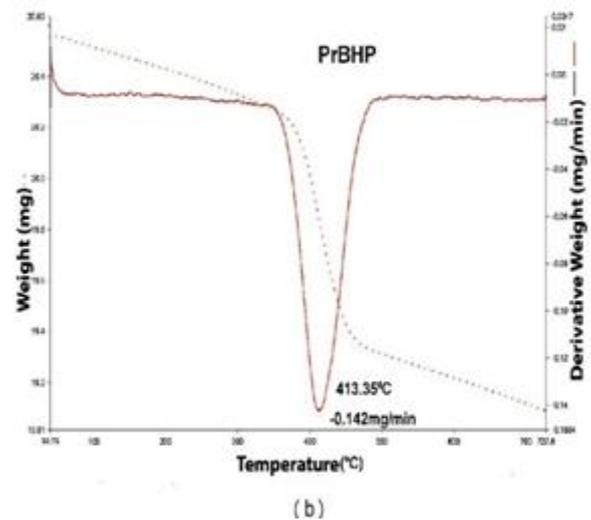
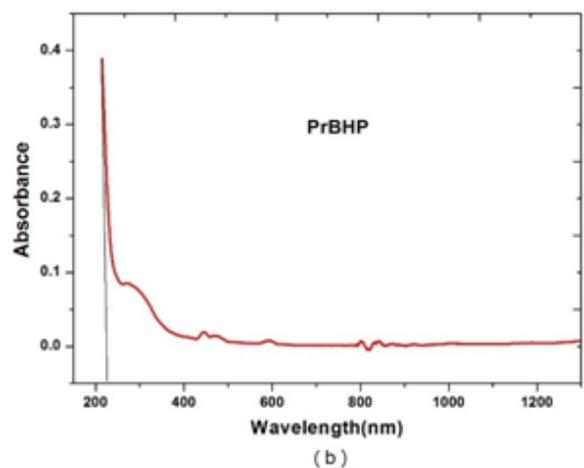
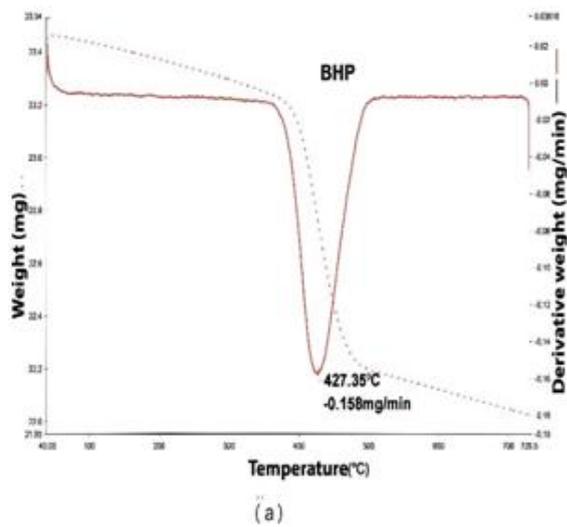


Fig. 6(a) TGA/DTG curves of BHP crystals (b) TGA/DTG curves of PrBHP crystal

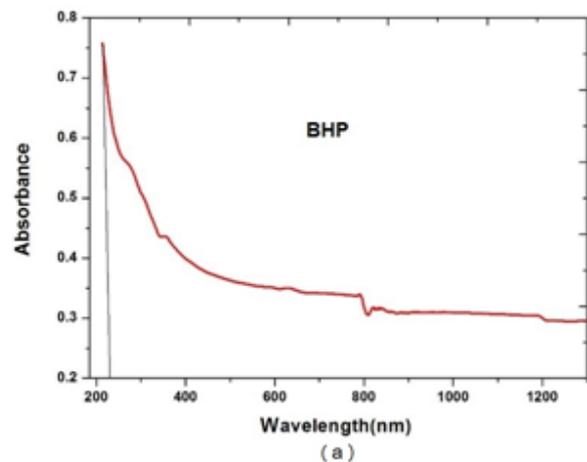




weight loss of 4.5% which arises due to the condensation of two HPO_4 molecule to P_2O_7 group as reported [26]. The sharp peak in the DTG curve at $427^\circ C$ supports the single step decomposition. In the case of PrBHP crystal, the decomposition starts from $290^\circ C$ and ends at $498^\circ C$ with a weight loss of 5.1% and after that the sample tends to be stable. This weight loss is due to the loss of water molecule from grown crystal. It can be mentioned here that, in PrBHP crystal the decomposition process starts and ends at a temperature lower than that of pure BHP. The temperature for the formation of stable product after decomposition was at $520^\circ C$ and $490^\circ C$ in BHP and PrBHP crystals respectively. This means that the temperature for the formation of end product decreases with praseodymium substitution which establishes a reduction in thermal stability of PrBHP crystal. This is due to decrease in bond energy caused by the incorporation of dopants in the lattice of BHP crystals.

3.6. OPTICAL ABSORPTION PROPERTIES

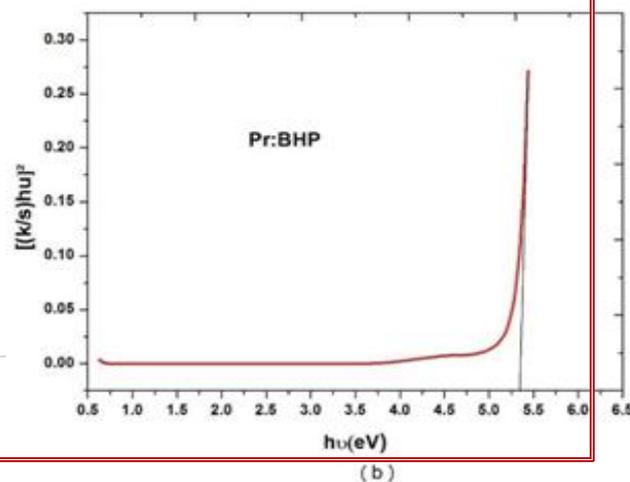
The UV-Vis transmittance of crystals were recorded with a Varian Cary 5000 UV-Vis spectrometer in the range 200-1200nm to study the transmission range and hence to know the suitability of the material for optical applications. The optical properties of crystalline materials provide information regarding the composition, behaviour and quality of the



crystal. Hence a good optical transmittance is an essential requirement for crystals. Fig 7(a) and (b) shows UV- Vis spectrum of BHP and Pr doped BHP crystals respectively.

Fig. 7(a) UV-Vis spectrum of BHP crystals. (b) UV-Vis spectrum of PrBHP crystals.

The crystals show a good transmittance in the visible region, which makes the material suitable



for optoelectronic applications. It can also be noted that less absorbance in the entire visible region is an essential requirement for non-linear optical applications [27]. No characteristic absorption was observed in the visible region of the spectrum. Hence the crystals exhibiting good transmittance lead to the generation of both second and third harmonics of light.

From the fundamental absorption wavelength, the band gap energy (E_g) of the material is calculated from the standard formula, $E_g = hc/\lambda_{max}$ [28]. The E_g of BHP crystal for $\lambda_{max}=229\text{nm}$ was found to be 5.41eV. In the case of PrBHP crystal, $E_g =5.43\text{eV}$ for $\lambda_{max}=228\text{nm}$. From the fig 7(b) of PrBHP crystal, it can be seen that, there exist an additional less intense absorption peak for $\lambda=284\text{nm}$ which was absent in BHP crystal. This leads to an $E_g=4.37\text{eV}$ due to decrease in binding energy as a result of Pr incorporation in lattice site.

The estimation of band gap energy was also been done using Diffuse Reflectance Spectra(DRS) proposed by Kubelka and Munk. A graph between $h\nu$ and $[(\frac{k}{s})h\nu]^2$ is plotted in fig 8(a) and (b) where $\frac{k}{s} = (1 - R)^2/2R$ in which k is the absorption coefficient and s is the scattering coefficient [29,30].

The E_g was estimated by extrapolating the straight line in the graph at $k=0$. The band gap energy for BHP and PrBHP were calculated and found to be 5.39eV and 5.4eV respectively.

Fig. 8(a) Graph between $h\nu$ and $[(\frac{k}{s})h\nu]^2$ for BHP (b) For PrBHP crystal

4. CONCLUSION

Optical good quality single crystals of pure and praseodymium doped barium hydrogen phosphate crystals were grown by employing slow and controlled ionic diffusion at room temperature. By single crystal and powder X-ray diffraction analysis, the diffraction planes of both the crystals were identified and hence confirmed that there was no change in the basic structure of BHP crystal due to doping. The grown crystals were identified as in orthorhombic $Pn2_1a$ space group crystal system and the lattice constants for BHP and PrBHP crystals are $a=14.088\text{\AA}$, $b=17.00\text{\AA}$, $c=4.586\text{\AA}$ and $a=14.058\text{\AA}$, $b=16.399\text{\AA}$, $c=4.572\text{\AA}$ respectively. The volume of unit cell being 1098.32\AA for BHP and 1054.01\AA for PrBHP. It was evident from the results that due to praseodymium doping peak value shifts towards higher angle, indicating a decrease in the value of lattice constants and cell volume. The presence of various functional groups such as Ba-O, P=O, P-O(H), etc associated with the grown pure and Pr doped BHP crystals were identified by FTIR spectral analysis. The SEM and EDAX analysis helped to find the morphology and stoichiometric composition of the crystals which confirms the presence of praseodymium in the grown crystal. The thermal stability of BHP and PrBHP crystals were analysed by TG/DTG studies. The substitutional

occupancy of praseodymium ion in the parent lattice can be established from the decomposition temperatures. From the result it was noticed that the thermal stability of PrBHP crystal was less than that of BHP crystal due to decrease in bond energy. UV–Vis absorption spectrum has been recorded to determine the cut-off wavelength of the crystal. The value of bandgap estimated from both absorbance and DR spectra are found to be in good agreement with each other. The high value of bandgap indicates the crystals are insulators by nature. The wide range of transparency in UV and the entire visible region shows that these crystals will be potential candidates for optoelectronic applications.

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