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Physico-chemical characterization of $BaHPO_4$ crystals

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Abstract. Characterization of the gel-grown barium hydrogen phosphate (BHP) crystals was performed by utilizing the techniques of chemical analysis, X-ray diffraction, infrared and thermal behaviour. The results show that BHP crystals had chemical composition $BaHPO_4$ at room temperature. TG and DTA studies revealed the BHP crystals to be anhydrous at room temperature and decomposed at temperatures above 370°C and the decomposition was an endothermic process. Magnetic susceptibility measurements indicate the material to be diamagnetic.

Keywords. Barium hydrogen phosphate; infrared; thermal; magnetic.

1. Introduction

Characterization of synthesized crystals is essential for practical applications, to confirm the purity and to identify the material. BHP crystals are of considerable interest for their ferroelectric, piezoelectric and other characteristics. This paper reports our observations and results on the characterization of BHP crystals grown in silica hydrogel. The gel technique is well established, simple and inexpensive and the quality of the grown crystals are good.

2. Experimental details

The growth process involves controlled diffusion of barium chloride solution into gel made up of sodium meta silicate and orthophosphoric acid at ambient temperature. Good quality BHP crystals were obtained at gel density 1·03, pH 6, and concentration of $BaCl_2$ solution at 0·5 M. Some of the crystals grown of size $5 \times 4 \times 2$ mm are displayed in figure 1. To confirm the presence of Ba^{++} and PO_4^{-3} ions the crystal was subjected to physical and chemical analysis. X-ray powder diffraction pattern of BHP crystals was recorded with Philips-PM 9920 X-ray diffractometer using CuK_α radiation of wavelength 1·5148 Å. The IR spectrum was recorded using a Hitachi -AA spectrometer. Thermogravimetric (TG) and differential thermal analysis (DTA) of BHP crystals were carried out simultaneously using DT-30 Shimadzu-instrument at a heating rate of 10°C min^{-1}. The magnetic susceptibility of the material was performed by using Faraday's method (Bates 1951).

3. Results and discussion

3.1 *Chemical analysis*

The estimated concentration of Ba^{++} ions in BHP crystals by gravimetric method

with error ±2% indicated that the chemical composition for BHP crystal was $BaHPO_4$. This was further confirmed by atomic absorption spectral analysis (table 1).

The difference between expected and observed values of concentration of Ba^{++} ions in BHP crystal could be due to the impurities present in the feed materials $BaCl_2$ or due to the incorporation of gel in the crystal (Patel and Bhat 1977). The average density of BHP crystal was found to be 4·295.

3.2 *X-ray powder diffractometric studies*

The X-ray diffractogram recorded showed the crystallinity of the sample. The observed *d* values for BHP crystals was compared with standard values (Joint Committee 1972) and the deviations from the standard values were found to be only in second decimal place, which confirmed the purity of BHP crystal. From the standard values (Burley 1958) the following data of BHP crystals were computed: Chemical formula: $BaHPO_4$; crystal system: orthorhombic; space group: $Pn_1^2a(33)$.

3.3 *Magnetic susceptibility measurements*

The gram magnetic susceptibility X_g characteristic of a material was calculated using the formula,

$$X_g = (\alpha + dW)/W$$

where α, is a constant which represented a correction factor due to the displacement

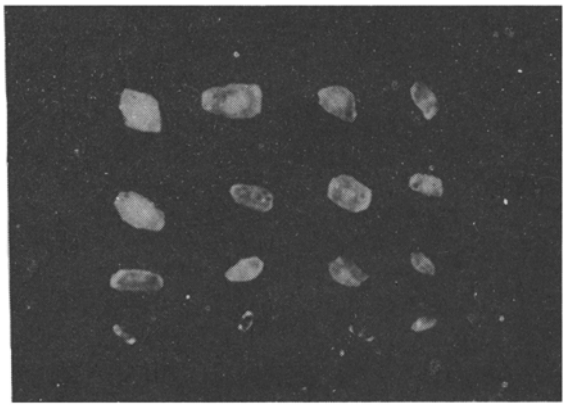

Figure 1. Barium hydrogen phosphate crystals.

Table 1. Atomic absorption spectral analysis results of BHP crystals.

	Ba^{++} wt %		
Proposed formula	Expected	Observed	Purity (%)
$BaHPO_4$	58·66	58·83	98·89

of air; β, a constant for the glass container at a given current; W, mass of the material and dW the change of mass when a magnetic field was applied. For BHP crystals the susceptibility obtained at room temperature is shown in table 2. The magnetic susceptibility of BHP was found to be $-92{\cdot}93 \times 10^{-6}$ e.m.u. The negative value showed that BHP was a diamagnetic material.

3.4 *Thermal characteristics*

Figures 2 and 3 represent the TG and DTA plots of BHP crystals. By taking initial weight as the standard the course of decomposition was analysed comparing their molecular weights. From the TG curve, it was observed that $BaHPO_4$ did not contain water of crystallization and was stable up to 370°C and began to

Table 2. Magnetic susceptibility of BHP crystals.

Material	Current (A)	dW (g)	α ($\times 10^{-6}$)	β ($\times 10^{-3}$)	X_g ($\times 10^{-6}$) (emu)	X_M ($\times 10^{-6}$) (emu)
$BaHPO_4$	2	−0·0004	0·01463	1·135	−0·386	−89·68
	4	−0·0012	0·01463	0·414	−0·423	−96·19

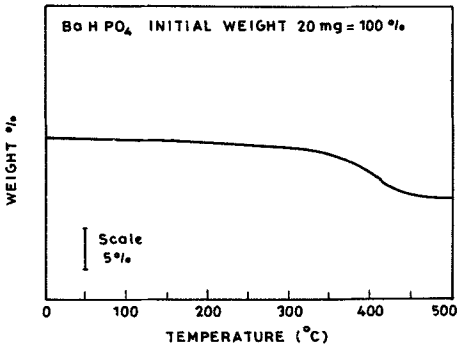

Figure 2. TG plot: weight % vs temperature.

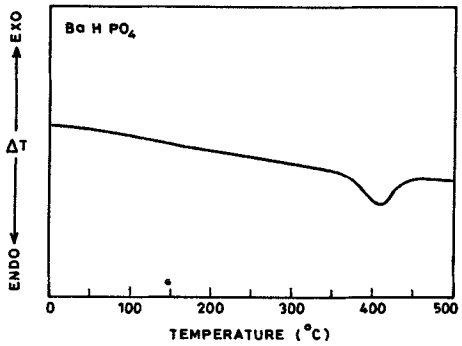

Figure 3. DTA curve for BHP crystals.

decompose at this temperature. The decomposition process was completed at 430°C with a total weight loss of 7·9 wt% which accounted for the loss of hydrogen with oxygen resulting in the formation of barium pyrophosphate at 430°C. No further changes were noticed beyond this temperature. The formation of barium hydrophosphate was also confirmed by this analysis and by comparing their molecular weight with TG data. From DTA curve it was observed that the thermal decomposition taking place in this crystal was endothermic.

On the basis of TG and DTA studies, the following tentative mechanism was proposed for the thermal decomposition of BHP crystals.

$$2BaHPO_4 \xrightarrow{370°C–430°C} Ba_2P_2O_7 + H_2O.$$

3.5 *IR absorption spectral characteristics*

IR spectra of BHP crystals are presented in figure 4. The observed infrared band and their assignments are shown in table 3. The assignments were made by

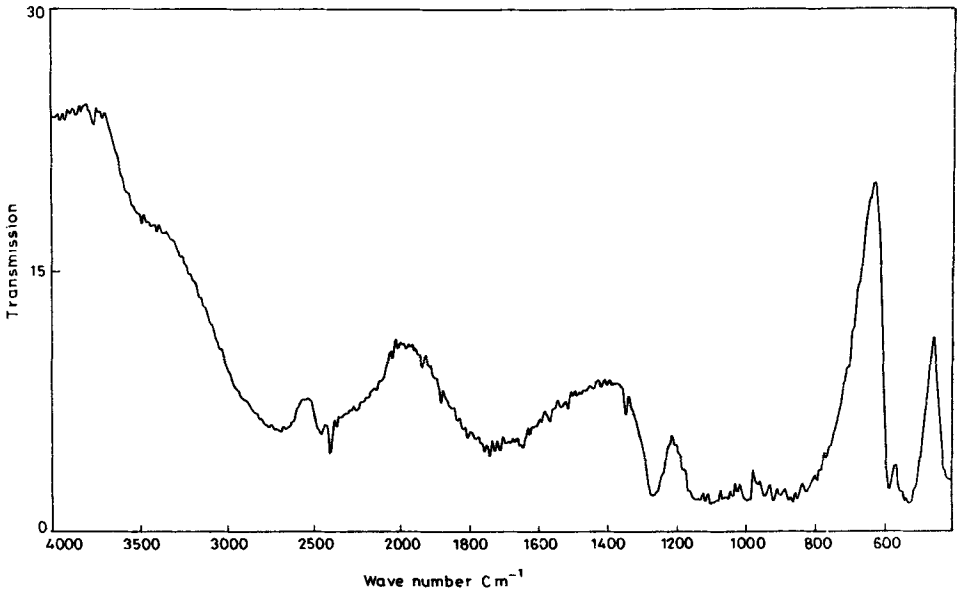

Figure 4. Infrared spectra of BHP crystals.

Table 3. Infrared spectral analysis of BHP crystals.

IR peaks (cm^{-1})	Intensity	Assignment
2700	Strong, broad	OH-stretching
2386	Strong	OH-stretching combination
1750	Strong, broad	
1266	Strong	P-O-H in-plane deformation
940	Weak, broad	P-O-H out-of-plane deformation
590	Weak	O-P-O bending-mode
525	Weak	O-P-O bending-mode

comparison with the earlier report (Champman and Thinlwell 1964) on the spectra of hydrogen phosphates.

The two strong bands around 2700 cm^{-1} and 2386 cm^{-1} corresponded to O-H stretching mode of vibrations. The band at 1266 cm^{-1} was associated with P-O-H in-plane deformational vibrations. The bands near 940 cm^{-1} were assigned for the P-O-H out-of-plane deformational vibrations whereas the weak bands around 590 cm^{-1} and 525 cm^{-1} were associated with O-P-O bending-mode of vibrations.

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