Growth kinetics and thermo-opto properties of manganese doped barium phosphate crystals

Delma D'Souza[1], Jagannatha N.[1] , Nagaraja K. P.[1] and Ganavi A. S.[2]*

[1] Department of Physics, FMKMC College (A constituent college of Mangalore University), Madikeri, Karnataka, India
[2] Department of Physics, Mangalore University, Mangalagangothri, Karnataka, India

Email: jagannathnettar@yahoo.co.in

Abstract

Manganese doped barium phosphate (MDBP) crystals were grown by gel technique. Phosphoric acid impregnated silica (PIS) gel was optimized by varying gel parameters: pH, specific gravity of sodium meta silicate, concentration of acid and temperature of gelling solution. In an optimized growth environment, Ba^{2+}-Mn^{2+} cationic mixture was made to diffuse through the set PIS gel to nucleate with intrinsically available $(PO_4)^{3-}$ ions, which yielded high quality MDBP crystals. Energy dispersive X-ray analysis confirmed the constitution of MDBP crystal by the prime elements Ba, Mn, P and O with cationic distribution 8.784 : 1 (Ba^{2+} : Mn^{2+}). Fourier transform infrared spectral studies identified the phosphate group, water of crystallization and M-O (M= Ba^{2+}, Mn^{2+}) bonds in the crystal armature. Thermogravimetric analysis demonstrated the degradation behavior and ensured the thermal stability upto 500°C in the phosphorus pentoxide state. MDBP crystals exhibited high crystalline nature and adjoined to orthorhombic geometry. The crystals being insulators, ingrained with high band gap energy of 6.08 eV.

Keywords: *impregnated, doped crystals, spectral studies*

1. Introduction

In modern days, search for new materials is one of the prime concerns in the field of Material Science [1]. The physical and chemical properties of new materials can be better understood when it exists in the most ordered crystalline form [2]. In particular, gel technique supports doping and using it variety of doped, co-doped and mixed crystals were grown. Crystals advanced from gel technique exhibit relatively low solubility, well defined morphology, purity, high surface fineness and offer very good corrosion resistance [3].

Studies on gel crystal growth unveil inherent physical and chemical properties of phosphate crystals [4]. Flexibility and adaptability of $(PO_4)^{3-}$ anions to co-ordinate with monovalent, divalent and trivalent cations of alkaline/ transition metals is a supporting feature for the synthesis of new crystalline materials [5]. Phosphate crystals are well known for exhibiting NLO properties and luminescence. Inorganic phosphate

crystals behave as catalysts and solid electrolytes in batteries [6, 7]. Potassium dihydrogen phosphate crystal exhibits piezoelectricity. Potassium titanyl phosphate crystals are used in optical waveguides [8]. In view of the above, our investigation was aimed at the growth of manganese doped barium phosphate (MDBP) crystals using gel technique and studies on thermal and optical properties.

2. Materials and methods

2.1 Growth of MDBP crystals

Chemicals used for growing MDBP crystals are sodium meta silicate (SMS-$Na_2SiO_3.9H_2O$), phosphoric acid (H_3PO_4), manganous chloride ($MnCl_2.6H_2O$) and barium chloride ($BaCl_2.2H_2O$) of AR grade. Phosphoric acid impregnated silica (PIS) hydro gel was used to grow MDBP crystals. It was prepared by mixing SMS solution of specific gravity 1.04 g/cm^3 with 1N phosphoric acid in the ratio 5:4. PIS gel sets in 24 hours. To the set gel, the reactant mixture of 0.5M $BaCl_2$ and 0.5M $MnCl_2$ were added in the ratio 4.25: 1.75. Ba^{2+} ions diffused through the porous polymerized gel and communicated with PO_4^{3-} ions. Mn^{2+} ions also diffused adjacently and occupied the vacancies of Ba^{2+} ions, which resulted in the formation of MDBP crystal. Chemical process involved in the formation of MDBP crystals is as follows.

$$3Mn^{+2} + 3BaCl_2.2H_2O + 4H_3PO_4 \rightarrow (Mn : Ba)_3(PO_4)_2.3H_2O + 2POCl_3 + 9H_2O.$$

Fig. 1 illuminates the growth and extraction of MDBP crystal. Table 1 records the optimum growth conditions. Crystals showed exponential growth; exhibiting rapid growth in the initial stages and as growth advances growth rate decays finally halts at 7 days and follow the growth equation

$$Cs = Cs_0 [1 - e^{-t/nk}];$$

where, Cs = crystal size at any instant of time t, Cs_0 = maximum size acquired when growth saturated in t_0 number of days, k = constant of proportionality (Cs_0/t_0) and n = 5 is an integer.

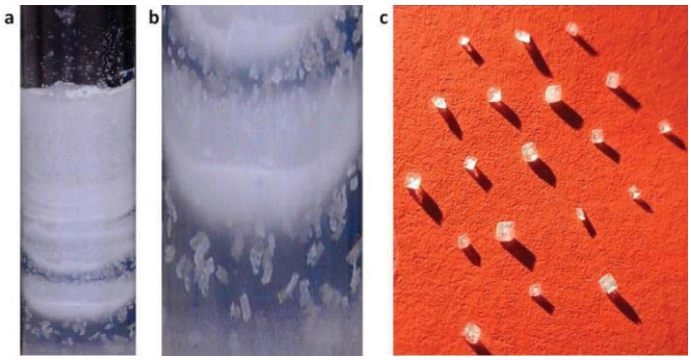

FIG 1. (a,b) Growth and (c) extraction of MDBP crystals.

Table 1. Optimum growth conditions.

Parameter	Optimum condition
Specific gravity of SMS (g/cm^3)	1.04
Gel pH	6.5
SMS: phosphoric acid	5:4
Cationic mixture ratio	$BaCl_2$: $MnCl_2$ 4.25:1.75
Growth period	7 days
Chemical formula	(Mn**:** Ba)$_3(PO_4)_2$ $3H_2O$
Physical appearance	Hard and transparent

2.2 Characterization

Chemical constituents of the MDBP crystals were estimated using CARL ZEISS FESEM attached with EDS system (Oxford instruments). Bruker (Alpha) KBr Fourier transform infrared spectrophotometer (FTIR) was used to identify the functional groups associated with doped crystals. The spectrum was recorded for the wave number range 400-4500 cm^{-1}. TG measurements were carried out using DSC-TGA TA (SDT-Q600). Percentage weight loss and decomposition behavior of crystals were explored until 500^oC. Minflex 600 Rigaku (X-ray Cu-K alpha-wavelength 1.54A^o) at a scan speed of 1°/minute was used to study the X-Ray diffraction patterns. Impact of UV-visible light on crystals were analyzed with the aid of UV-visible spectrophotometer (UV-1800SHIMADZU) in the wavelength range 200-1200nm. Electrical conductivity measurements of the crystals were recorded using Roy instruments (IR- 503, Sl. No. CDM-17076) operated for the conductivity range 0-1000 mMho/cm. Dielectric studies were performed using Mittal instruments 2151/T-7C calibrated to attain sine wave of frequency 253.88 kHz in DSO.

3. Results and discussion

3.1 EDAX spectral measurements

Intense peaks of EDAX spectrum identified the presence of barium, manganese, oxygen and phosphorous in MDBP crystal (Fig. 2). The SEM image at 20 µm resolution (Fig. 3) showed different ordered layers with valley regions. The weight and atomic percentages of elements present in MDBP crystals were listed in Table 2. MDBP crystal constituted with cationic distribution of 8.784: 1 (Ba^{2+}:Mn^{2+}).

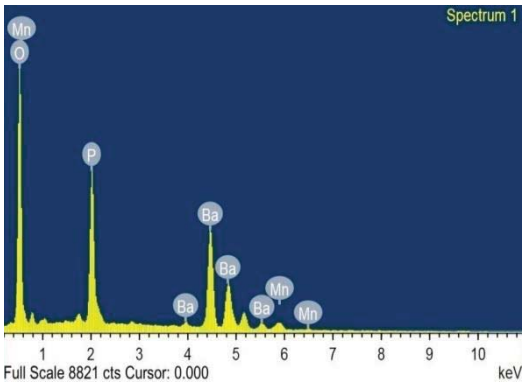

FIG 2. EDAX spectrum of MDBP crystal.

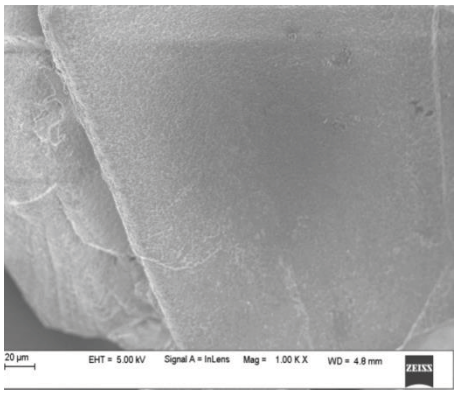

FIG 3. SEM image of MDBP crystal.

Table 2. EDAX results of MDBP crystal.

Crystal	Elements present	Weight%	Atomic%	Cationic distribution
MDBP	O	72.05	28.86	Ba^{2+} : Mn^{2+} 8.784 : 1
	Mn	01.46	02.67	
	Ba	12.83	58.65	
	P	13.66	09.82	
	Total	100	100	

3.2 FTIR studies

FTIR spectral analysis was used to identify various functional units and bond formations in MDBP crystals. Fig. 4 gives the FTIR spectrum of MDBP crystals. Spectral absorption bands identified water of crystallization, PO_4 group and metal oxygen bonds. Absorption bands at 3770 cm^{-1}, 3543 cm^{-1} and 3159 cm^{-1} are attributed to symmetric and asymmetric stretching of O-H group. Bending vibration of water molecules appeared at 1603 cm^{-1}. The absorption band at 1400 cm^{-1} corresponds to P=O stretching. Asymmetric and symmetric stretching of P-O bond appears at 1105 cm^{-1} and 946 cm^{-1} respectively. Absorption bands at 574 cm^{-1} and 429 cm^{-1} correspond to O-P-O asymmetric and symmetric bending. Fingerprint region showed M-O (M: Mn, Ba) stretching at 448 cm^{-1} and 492 cm^{-1} respectively [9]. Table 3 records the FTIR results of MDBP crystal.

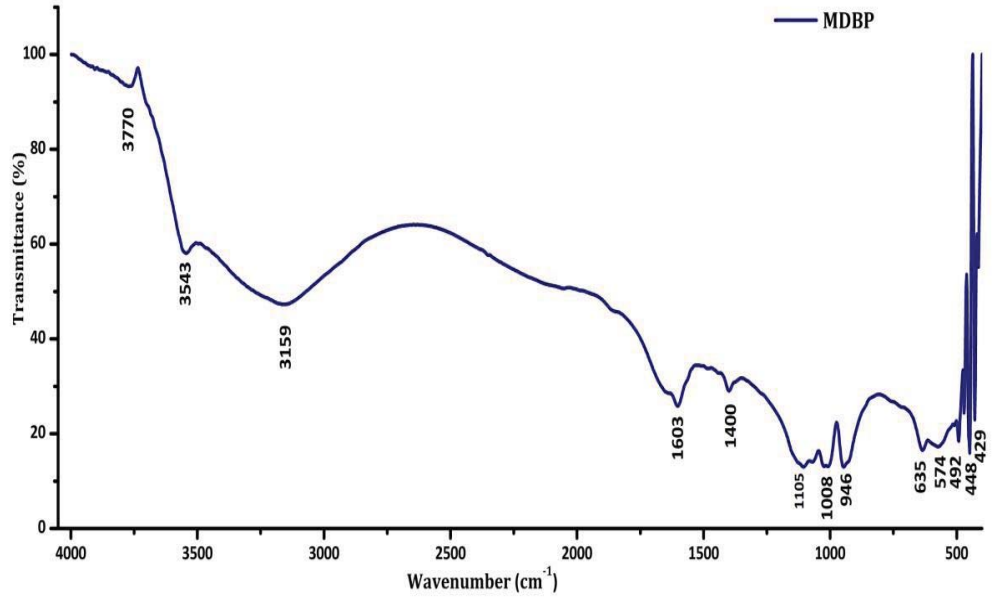

FIG 4. FTIR spectrum of MDBP crystal.

Table 3. FTIR results of MDBP crystal.

Band assignments	Wave number (cm^{-1})
Symmetric and asymmetric O-H stretching (water of crystallization)	3770 3543 3159
Internal bending vibration of water molecules	1603
P=O stretching	1400
Asymmetric P-O stretching	1105 1008
Symmetric P-O stretching	946
Asymmetric O-P-O bending	635 574
Symmetric O-P-O bending	429
M-O stretching	448 492

3.3 Thermal studies

The decomposition behaviour and thermal stabilities of MDBP crystals were investigated by thermo gravimetric (TG) analysis. The TG plot (Fig. 5) of MDBP crystals consists of TG, derivative thermo-gravimetry (DTG) and differential thermal analysis (DTA) curves. The TG studies determined the degradation temperatures, matter released, rate of weight loss (%) and chemical processes involved during decomposition of crystals. Fig. 5 shows the thermogram of MDBP crystal. The crystal encompasses two stages of structural transformation between the T_D range 45 - 400°C. The crystal lost three units of crystalline water in the first stage comprising a weight loss of 8.12% (calculated loss: 8.56%). This occurs in the T_D gradient of 45 -127°C, T_{DTG} 71.56°C and endothermic T_{DTA} at 77.57°C. The dehydrated MDBP crystal undergone second decomposition phase between the temperature range 245-400°C with a weight loss of 21.89% (calculated loss:22.50%) evolving phosphorous pentoxide; rectified by T_{DTG} peak at 311.38°C and exothermic T_{DTA} peak at 322.54°C. On heating above 400°C the crystal exhibited thermal stability in oxide state. The decomposition profile of MDBP crystal is recorded in Table 4. The degradation process is unveiled in Table 5.

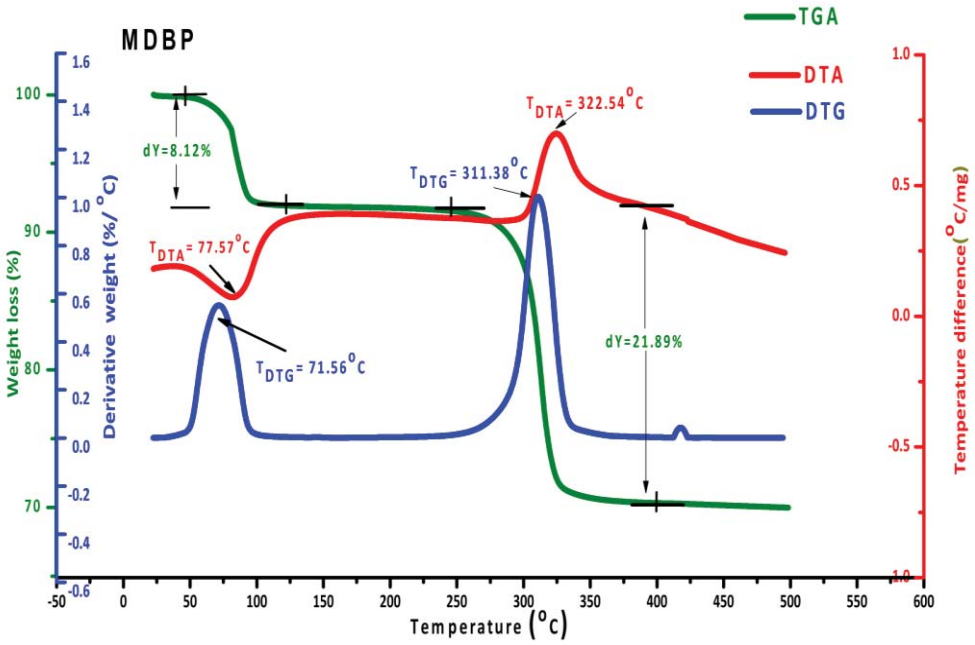

FIG 5. TG plot of MDBP crystal.

Table 4. TG results of MDBP crystal.

Crystal	Molecular weight	Phase	T_D range (°C)	T_{DTG} (°C)	T_{DTA} (°C)	Weight loss analysis	
						Observed (%)	Calculated (%)
MDBP	630.714	I	45 – 127	71.56	77.57	08.12	08.56
		II	245 - 400	311.38	322.54	21.89	22.50

Table 5. Decomposition behavior of MDBP crystal.

Crystal	Phase	Decomposition process	Molecule decomposed
MDBP	I	$(Mn_{0.1022}\,Ba_{0.8978})_3\,(PO_4)_2.\ 3H_2O \rightarrow (Mn_{0.1022}\,Ba_{0.8978})_3\,(PO_4)_2 + 3H_2O$	$3H_2O$
	II	$(Mn_{0.1022}\,Ba_{0.8978})_3\,(PO_4)_2 \rightarrow 3\ Mn_{0.1022}\,Ba_{0.8978}\ O + P_2O_5$	P_2O_5

EDAX, FTIR and TGA studies reveal that, MDBP crystal ingrains a chemical formula of $(Mn_{0.1022}\,Ba_{0.8978})_3(PO_4)_2.3H_2O$ and possesses a molecular weight of 630.714.

3.4 Powder X-ray diffraction studies

The Bragg's diffraction pattern of MDBP crystal was shown (Fig. 6) for specific 2θ values ranging from 0-80°. The sharp well defined peaks illuminate high crystalline nature of doped MDBP crystal. Powder XRD pattern of the crystal was studied using PowderX software and indexed using N-TREOR09 program. After refinement with Chekcell software, the *d*-spacing and lattice parameters were measured (Table 6). MDBP crystal belongs to orthorhombic geometry [10].

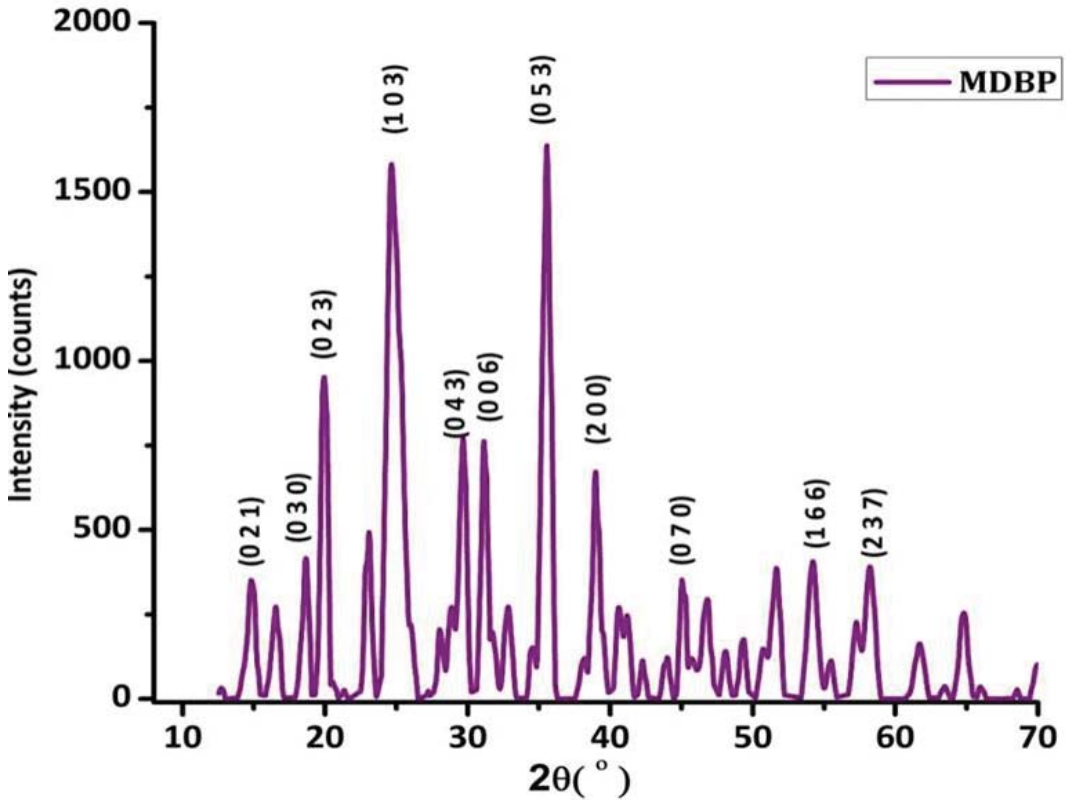

FIG 6. Powder XRD pattern of MDBP crystal.

Table 6. Cell parameters of MDBP crystal.

Cell parameters	MDBP
a	4.6194 Å
b	14.0777Å
c	17.1914Å
α	90°
β	90°
ϒ	90°
Space group	*Pnma*
Geometry	orthorhombic

3.5 Opto- electrical properties

Optical properties of MDBP crystal was investigated with the aid of UV-visible spectrum. MDBP crystal is brought into solution form by dissolving known amount (10mg) in 1.5N sulphuric acid at 25°C. The crystal solution exhibited transparency in visible region and showed absorption maxima (A_{max} = 0.867) in UV region (λ=196 nm). Fig. 7a shows UV-visible spectrum. Using Tauc plot (Fig. 7b**),** the band gap energy of the crystal was determined. MDBP crystal possesses E_g of 6.08 eV.

Electrical conductivity measurements of MDBP crystal (solution form) were undertook for the temperature range of 40-80°C. The instrument was calibrated to neutralize the conductivity of blank solution (1.5 N sulphuric acid). Fig. 8 shows electrical conductivity plot of the crystal. The doped crystal exhibited linear growth of conductivity with temperature. Slope of the straight line gives conductivity coefficient of temperature (σ_k). MDBP crystal possesses σ_k of 0.108S/m/°C.

Dielectric properties of the crystal were studied by forming circular crystal pellet of dimension equivalent to that of gold plated dielectric cell. Comparing the voltage developed across the crystal pellet (V_p) and $V_{Sc}$of standard capacitor (C_s), the capacitance of the crystal pellet was measured using:

$$C = \frac{V_{Sc}}{V_p} C_s$$

Capacitance of air C_o is calculated accordingly:

$$C_o = \frac{\epsilon_o A}{d}$$

Where, ϵ_O is absolute permittivity of free space.

The dielectric constant (ϵ_r) of MDBP crystal pellet was measured as [3]

$$\epsilon_r = \frac{C}{C_o} = \frac{141.55\times10^{-12}}{1.741\times10^{-12}} = 81.26$$

The opto-electrical parameters of MDBP crystals were recorded in Table 7.

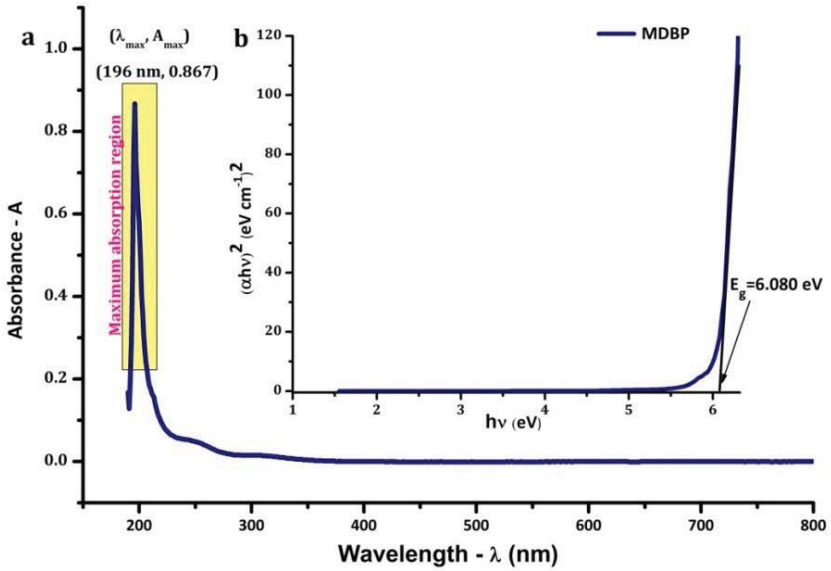

FIG 7. UV–visible spectrum of MDBP crystal.

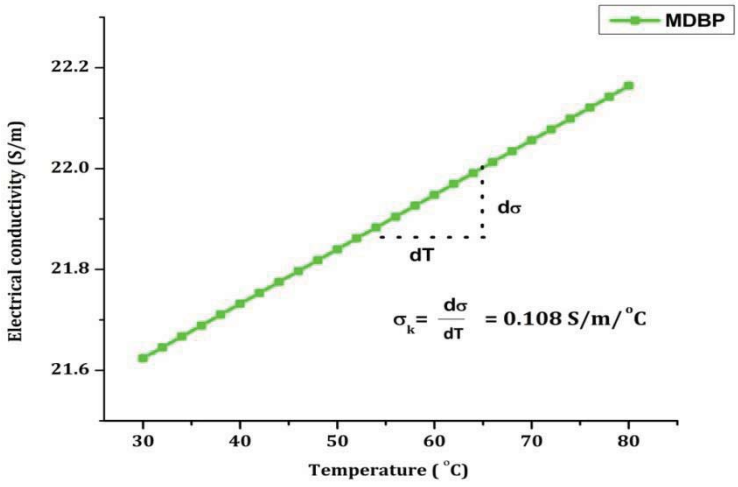

FIG 8. Conductivity plot of MDBP crystal.

Table 7. Opto-electrical parameters of MDBP crystals

Band gap energy E_g (eV)	6.08
Conductivity coefficient of temperature σ_k (S/m/°C)	0.108
Dielectric constant ϵ_r	81.26
Capacitance C (pF)	141.55

Extremely high band gap energy, linear growth profile of electrical conductivity with temperature, good dielectric properties ensured insulating behaviour of the MDBP crystals. Due to thermal stability above 500°C and high dielectric constant, the MDBP crystallites could be moulded as fillers in laminates; which may provide good dielectric strength, resistance to hot solder and flame resistance. Purity, high surface fineness and water insolubility are the unique features of MDBP crystals, which offer very good corrosion resistance.

4. Conclusion

MDBP crystal was grown by adopting gel diffusion technique in phosphoric acid impregnated silica hydro gel. EDAX measurements identified the existence of Ba^{2+} and Mn^{2+} ions in the crystal. FTIR studies confirm the association of phosphate group, water molecules and metal oxygen bonding in the crystal armature. The MDBP crystal possesses a chemical formulae of $(Mn_{0.1022}\,Ba_{0.8978})_3\,(PO_4)_2.3H_2O$. UV-visible spectral studies revealed high band gap energy of 6.08eV in MDBP. Further, the crystal exhibited good dielectric strength and possessed capacitance of 141.55pF. Good thermal stability, water insolubility, insulating behavior and extended dielectric strength possessed by the crystal may find a spectrum of applications in high temperature and microelectronics.

5. Acknowledgements

The authors are grateful to UGC, New Delhi for the financial support under MANF scheme. The authors are also thankful to Principal, FMKMC College Madikeri; Director, University science instrumentation center, Mangalore University and Scientific officer, DST- PURSE laboratory, Mangalore University, Mangalore for providing laboratory facilities.

REFERENCES

[1] Abeer Samy Yousef Mohamed, Energy Procedia 115, 139 (2007)

[2] Vinnik D A, Zherebtsov D A, Mashkovtseva L S, Nemrava S, Semisalova A S, Galimov D M, Gudikova I A, Chumanov I V, Isaenko L I and Niewa R, Journal of Alloys and Compounds 628, 480 (2015)

[3] Nagaraja K P, Pampa K J, Kumaraswamy S R, and Lokanath N K, Journal of Applicable Chemistry 7, 863 (2018)

[4] Justin Raj C, Mangalam G, Mary Navis Priya S, Mary Linet J, Vesta C, Dinakaran S, Milton Boaz B and Jerome Das S, Crystal Research and Technology 42, 344 (2007)

[5] Bamzai K K, Suri S and Singh V, Materials Chemistry and Physics 135, 158 (2012)

[6] Onoda H, Nariai H, Maki H and Motooka I, Phosphorus Research Bulletin 9, 69 (1999)

[7] Xiao-Bo Chen, Xian Zhou, Trevor B A, Mark A E and Nick Birbilis, Surface and Coatings Technology 217, 147 (2003)

[8] Iyappan G, Rajesh P and Ramasamy P, Optoelectronics and Advanced Materials - Rapid Communications 13, 217 (2019)

[9] Fernandes K S, Alvarenga E de A, Brandão P R G and Lins V de F C, Rem: Revista Escola de Minas 64, 45 (2011)

[10] Suri S, Bamzai K K and Singh V, Ferroelectrics 423, 94 (2011)