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Crystal Structure, Dielectric Response and Thermal analysis of Ammonium Pentaborate (APB)

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ABSTRACT. Nonlinear optical material Ammonium Pentaborate (APB) crystals have been grown using slow evaporation method from aqueous solution. From Powder XRD analysis the orthohrombic crystal structure was found. Various vibrations in FTIR spectrum were assigned. Thermo gravimetric analysis suggested that the crystal remained stable up to 173°C and then decomposed through various stages and endothermic reactions were identified by DTA. The variation of dielectric constant, dielectric loss and ac conductivity with frequencies was studied at room temperature. Further investigation of dielectric properties with higher temperature is under progress.

Introduction. Borate crystals have received much attention because of their excellent physical and chemical properties. Alkali borate crystals generally possess chemical stability as well as wide range of optical transparency extended into the ultraviolet due to large difference in the electro negativities of B and O atoms [1]. For majority of borates, it is necessary to use complex and long lasting high temperature solution top-seeding methods [2]. In the current study, authors have employed inexpensive and relatively simple slow solvent evaporation method to grow ammonium pentaborate (APB) crystals. The grown crystals were characterized by Powder XRD, FTIR, thermal and dielectric analysis.

Experimental. Commercially available, 32 gm ammonium pentaborate octahydrate powder (AR grade) was dissolved in 200 ml distilled water at 50^0C and stirred well and solvent was allowed to evaporate. By using Whatmann filter paper the grown crystals were recovered. This process was repeated three times in order to increase purity of compound. This recovered crystalline material was dissolved in 200 ml distilled water and poured in a glass beaker, which was covered with porous sheet of polymer material to allow controlled evaporation. Within a period of 35 days, prismatic, colourless and transparent crystals were grown. The crystal of maximum size 15mm x 13mm x 9mm was grown as shown in fig.1.

Powder XRD of APB crystal has been carried out using Pan Analytical system with Cu Kα radiation (λ = 1.5405Å). The data were analyzed by software Powder X. The FTIR spectrum has been recorded at 300K on Bruker setup in the range of 450 to 4000 cm^{-1} with Attenuated Total Reflectance (ATR) technique. The thermal analysis was performed using Linseis STA- PT1600 set up in atmosphere of air at heating rate of 10K/min. The initial mass of the material subjected to the analysis was 22.6 mg. The dielectric study was carried out on pelletized APB using Agilent Technologies E4980A LCR meter in the frequency range from 20 Hz to 2 MHz at room temperature.

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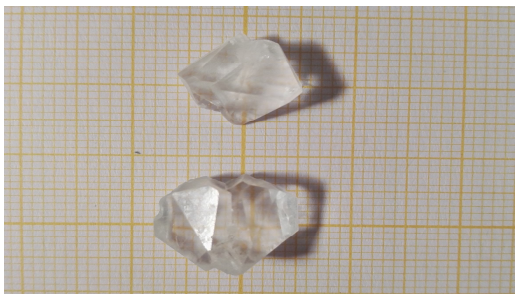

Fig. 1. Crystals of Ammonium Pentaborate (APB).

Result and discussion

XRD Analysis

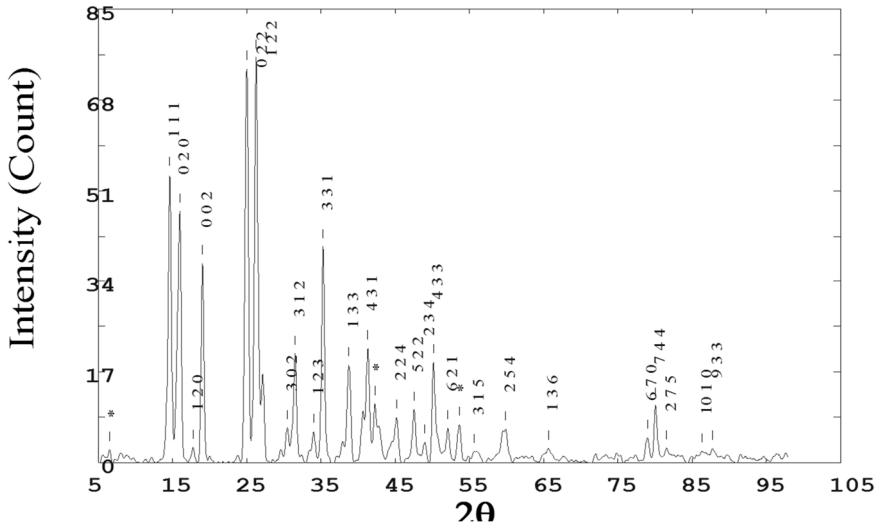

Fig. 2. Powder X-ray diffraction of APB.

Fig.2 shows the powder XRD pattern and the cell parameters are calculated using the software powder X, which are found to be a= 11.325 Å, b= 11.066 Å , c = 9.320Å and cell volume 1167 $Å^3$. This suggests orthorhombic structure of APB crystal. The APB crystal structure belongs to non-centrosymmetric space group Aba2 [4]. The data of present work are in good agreement with the reported work [3, 4].

FTIR Studies. The FT-IR spectrum of APB is presented in Fig.2. Various absorptions and corresponding assignments are summarized in Table 1. A broad envelope of comparatively less absorption between 2850 cm^{-1} and 3750 cm^{-1} corresponds to the O-H stretching of BO-H, water between and outside the lattice and NH stretching of NH_4^+ ion. The similar peaks with higher absorption are reported by others where KBr is taken as reference for FTIR, which contains higher absorption of O-H due to K+ ions.

The NH_4 symmetric stretching is observed at 1327 cm^{-1}. The very strong absorption peak at 1021cm^{-1} is attributed to B-O terminal symmetric stretching. The other assignments are summarized in Table 1.

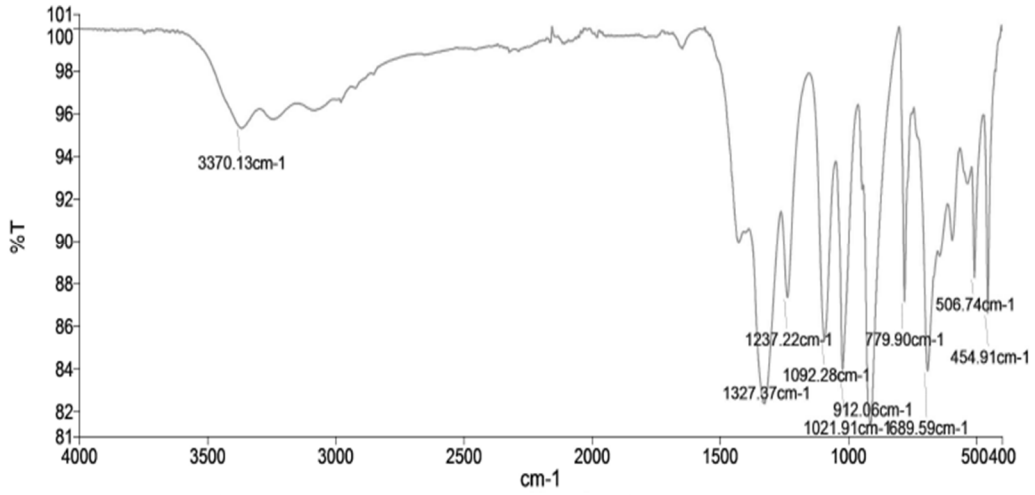

Fig. 3. FT-IR Spectrum of APB.

Table 1. Band Assignment of APB.

Band Assignment	**Absorptions (in cm^{-1})**	**Band Assignment**	**Absorptions (in cm^{-1})**
O-H symmetric stretching	3370	B-O ring stretching	912
NH_4 symmetric stretching	1327	B-O ring stretching	779
CH_2 Torsion	1237	O-B-O ring asymmetric stretching	689
B-O terminal asymmetric stretching	1092	O-B-O ring bending	506
B-O terminal asymmetric stretching	1021	O-B-O ring bending	454

Thermal Analysis. Complete decomposition of Ammonium pentaborate octahydrate in form of stochiometric expression can be given as :

$$(NH_4)_2O{\bullet}5B_2O_3{\bullet}8H_2O \longrightarrow 5B_2O_3+2NH_3+9H_2O$$

From analysis, three major stages [5] can be assigned to thermal decomposition of Ammonium Pentaborate octahydrate are as follows:

(i) Dehydration: Three endothermic peaks are observed in relevance to three stages of dehydration from 71.2°C to 110°C; 114°C to 142°C and 173.7°C to 241.7°C, which corresponds to release of, total seven crystal water molecules.

(ii) Decomposition: The endothermic peak observed between 285.1°C to 332.5°C corresponds to release of two water molecules as molecular water that was difficult to remove during dehydration.

(iii) Deammination: during this stage, two molecules of NH_3 are released between 428.3°C to 458.4°C and finally APB is transformed into five molecules of boric oxide.

TGA Curve (fig. 4) and DTA curve (fig. 5) shows good agreement with each other. Comparison of observed mass loss with calculated mass loss corresponds to these stages is given in Table 2.

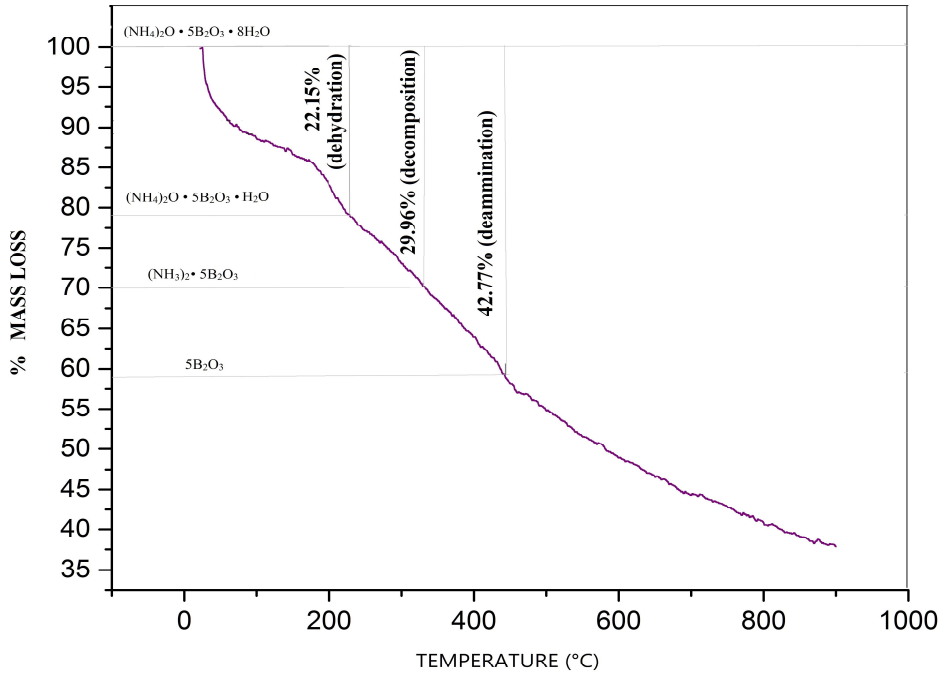

Fig. 4. TGA graph of APB.

Table 2. Thermal decomposition stages of APB.

Phase	Temp. (℃)	Experimentally observed Mass Loss (wt%)	Theoretically obtained Mass Loss (wt%)	Remark
Dehydration	up to 242	22.15	23.10	Loss of Seven water molecules.
Decomposition	295 to 332	29.96	29.80	Loss of two water molecules which can only be removed by decomposition.
Deammination	428 to 458	42.77	36.05	Removal of two NH_3 molecules.

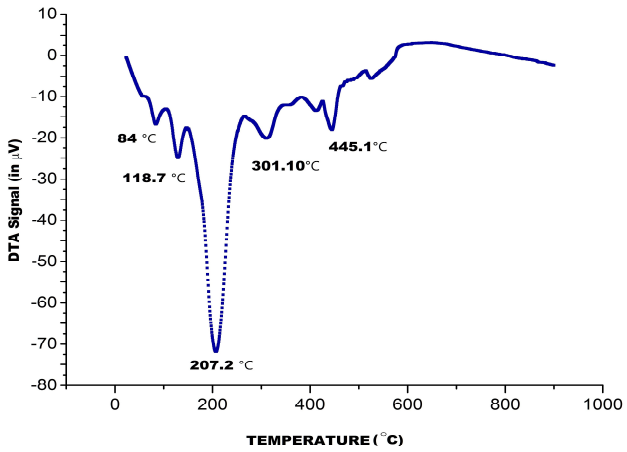

Fig. 5. DTA trace of APB.

Dielectric analysis:

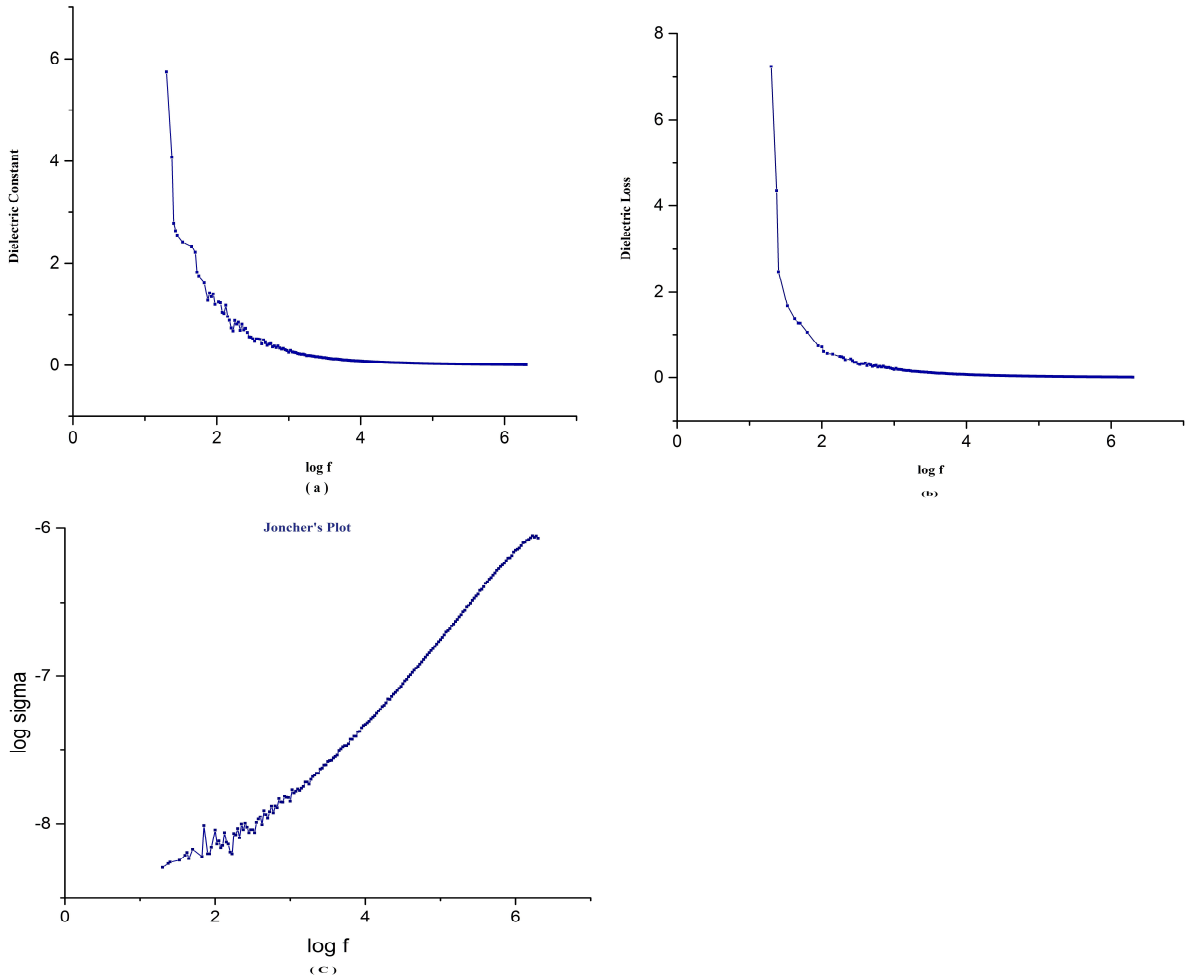

Fig. 6. (a) Dielectric constant vs. log f (b) Dielectric loss vs. log f (c) Joncher's plot.

Figs. 6 (a) and (b) show variation of dielectric constant and dielectric loss with frequency. High dielectric constant at lower frequency may be attributed to the contribution of all types of polarisation like electronic, ionic, orientational and space charge [6]. As frequency increases polarisation decreases since dipoles are unable to comply with variation of alternating field. Dielectric loss shows the similar behaviour. Fig. 6(c) indicates high frequency dispersion curve.

The Joncher's power law is

$$\sigma_{tot} = \sigma_{dc} + A\omega^n$$

where A indicates strength of polarisibility and is dependent on temperature, n is degree of interaction of mobile ions with lattice.

From Fig. 6 (c) the values of parameters A and n for joncher's equation , are obtained as $2.421X10^{-10}$ and 0.574, respectively. The AC conductivity increases with increment in frequency.Stella Mary et al [7] suggested polaron hopping mechanism for high conduction at higher frequencies. Analysis of dielectric properties including Joncher's plot with various temperature range is under progress.

Summary. Ammonium Pentaborate (APB) crystals were grown successfully using slow solvent evaporation technique. The Powder XRD pattern indicated orthorohmbic crystal structure. The FT-IR spectrum confirmed the presence of various functional groups. The TGA suggested the APB thermally remained stable up to 173 ^{0}C and then decomposed through various stages. Nine water molecules were found to be associated with the crystal. The dielectric study indicated decrement of dielectric constant and dielectric loss as increment in frequency. Joncher's plot suggested that AC conductivity increased with frequency.

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