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Studies of Triammonium Barium Pentachloride Crystals Grown by Slow Evaporation Technique

D. NALLAMUTHU*, P. SELVARAJAN† and T.H. FREEDA
Physics Research Centre, S.T. Hindu College, Nagercoil-629 003, India
E-mail: dnallamuthu@yahoo.com

Triammonium barium pentachloride dihydrate (TABPC) salt was synthesized using commercially available ammonium chloride and barium chloride. The synthesized salt was used to grow single crystals of triammonium barium pentachloride from aqueous solution by slow evaporation technique at room temperature. The grown crystals were characterized by X-ray diffraction (XRD), FTIR studies, TG/DTA studies and dielectric studies. The crystal structure of TABPC was identified as orthorhombic. The crystal planes of the TABPC have been identified by powder XRD studies. The functional groups of TABPC crystal have been identified. The thermal stability of the sample was analyzed. The dielectric constant and loss of the grown TABPC are observed to be increasing with increase in temperature and the activation energy for the conduction process is determined.

Key Words: Triammonium barium pentachloride crystals, XRD, FTIR, TG/DTA, Dielectric studies, Activation energy.

INTRODUCTION

Crystals of metal-halogen complexes of type $A_3BC_5 \cdot 2H_2O$ (where A is a monovalent metal, B is a divalent metal and C is a halogen) are insulating materials with unusual physical properties and they are known to possess structurally incommensurate phases[1-3]. It is reported that some of the metal-halogen systems show varying stoichoimetries and are known to exhibit five or six successive phase transitions[4,5]. Byrappa *et al*.[6] have grown crystals of trisodium barium pentachloride and characterized them through X-ray and thermal studies. Here the authors report the growth, structural, FTIR, TG/DTA and dielectric studies of triammonium barium pentachloride (TABPC) crystals.

EXPERIMENTAL

The materials used for the growth of triammonium barium pentachloride were commercially obtained AR grade ammonium chloride and barium chloride (Merck India). Ammonium chloride and barium chloride were taken in 3:1 molar ratio for

†Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628 216, India.

the synthesis of title compound. The calculated amounts of barium chloride and ammonium chloride were dissolved in deionized water and stirred well using a magnetic stirrer for about 3 h. The solution was heated at 50 ºC until the synthesized salt of TABPC was obtained. The chemical reaction for obtaining triammonium barium pentachloride dihydrate is written as

$$3NH_4Cl + BaCl_2 \cdot 2H_2O \rightarrow (NH_4)_3BaCl_5 \cdot 2H_2O$$

Slow evaporation of the saturated aqueous solution of the synthesized salt of TABPC yielded good quality crystals in about 20-25 days. The grown crystals were found to be transparent, colourless and the size of the crystals obtained was about 10 $mm^3 \times 4$ $mm^3 \times 3$ mm^3. The grown crystals are found to be polyhedron in shape and are stable, do not decompose in air and non-hygroscopic at ambient temperature. The grown crystals are observed to be transparent, colourless and the crystal faces and edges are well formed. To obtain large size crystals, seed crystal technique was also employed.

X-Ray diffraction (XRD) method helps in determining the arrangement and the spacing of atoms in a crystalline material. The grown single crystals of TABPC were subjected to single crystal X-ray diffraction (XRD) studies using an Enraf Nonius CAD4 diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) to identify the crystal. The powder X-ray diffraction pattern was obtained using an automated powder X-ray diffractometer (Model: Ritz-170 with nickel filtered CuK_α radiations (1.54056 Å), 35 KV, 10 mA).

In the present work, the FTIR spectrum of TABPC crystals was recorded in the wave number range 4000-450 cm^{-1} on a spectrophotometer (Bruker IFS-66V FTIR) using KBr pellet technique. The thermogravimetric and differential thermal analyses (TG/DTA) was carried out simultaneously using Seiko thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C/min for a temperature range of 25-900 °C.

Measurements of dielectric parameters like capacitance, dielectric constant (ε_r) and dielectric loss (tan δ) of crystals carried out using an LCR meter (Agilent 4284A) at frequencies 103 and 105 Hz at different temperatures ranging from 30-70 °C. Temperature was controlled to an accuracy of ± 0.1 ºC and it was measured using a digital thermometer. The sample crystals were cut, polished and silver-electroded. The observations were made while cooling the sample. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \left\{ \frac{C_{crys} - C_{air}(1 - A_{crys}/A_{air})}{C_{air}} \right\} \frac{(A_{air})}{(A_{crys})}$$

where C_{crys} = capacitance with crystal (including air), C_{air} = capacitance of air, A_{crys} = area of the crystal touching the electrode and A_{air} = area of the electrode[7,8]. Inaccuracy involved in the measurements of dielectric parameters was within ± 5 %. AC electrical conductivity of the grown crystals was determined using the data available from dielectric measurements on TABPC crystals.

RESULTS AND DISCUSSION

Single crystal XRD studies: Single crystal XRD data of TABPC crystals were collected from a single crystal X-ray diffractometer with graphite monochromated Mo K_α radiation. From the data, it is observed that the grown crystals crystallize in orthorhombic system. The lattice parameters are found to be a = 6.701(2) Å, b = 7.119(3) Å, c = 10.897(2) Å, $\alpha = \beta = \gamma = 90^o$. The number of molecules per unit cell (Z) for the crystal of this work is found to be 4. The volume of the unit cell is observed to be 519.83(4) $Å^3$.

Powder X-ray diffractometric studies: The powder X-ray diffraction (XRD) pattern of TABPC crystals is shown in Fig. 1. From the X-ray diffractogram, the 2θ values were read directly and the relative intensities of the diffraction peaks were estimated. The d-spacings, corresponding to different peak positions were reported by default calculation using the Bragg's relation 2d sin θ = nλ where d is the inter planar spacing, θ is the Bragg's angle, n is the order of diffraction and λ is the wavelength of X-rays. When X-rays penetrate through the powdered sample, a number of particles can be expected to be oriented in such a way as to satisfy the Bragg's condition for reflection from every possible interplanar spacing. All the reflections of powder XRD pattern of the grown crystals in powder form were indexed using the TREOR software package following the procedure of Lipson and Steeple[9].

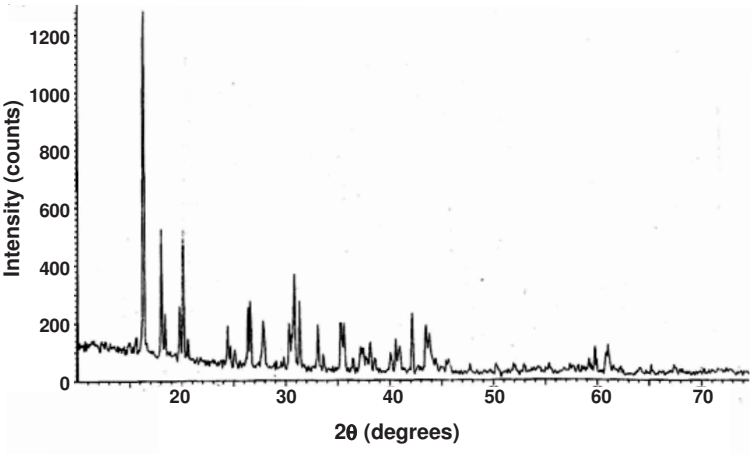

Fig. 1. Powder XRD pattern of TABPC crystals

The values of 2θ, d-values, hkl values and relative intensity for various reflections of powder XRD pattern of TABPC crystals are provided in the Table-1. When hkl values and 2θ values are used in the UNIT CELL software package, the unit cell parameters of the sample could be obtained. It is observed that the unit cell parameters obtained from powder XRD analysis are almost same as the values obtained from single crystal XRD studies.

TABLE-1
POWDER XRD DATA FOR TABPC CRYSTALS

S. No.	2θ (degrees)	d-values (Å)	hkl	I/I_{max} (%)
1	16.3212	5.4262	020	100.00
2	18.0400	4.9132	101	34.26
3	27.8436	3.2015	210	12.70
4	30.4425	2.9338	211	8.18
5	30.7664	2.9037	131	17.30
6	33.0923	2.7047	122	12.12
7	35.4098	2.5328	032	7.65
8	37.3150	2.4078	202	5.33
9	38.0701	2.3617	003	7.33
10	40.9376	2.2027	310	6.55
11	42.1126	2.1439	042	15.64
12	43.4443	2.0812	051	12.58
13	59.7786	1.5457	134	5.40
14	60.9302	1.5192	071	4.85

FTIR Spectroscopis studies: The FTIR spectrum of the sample is shown in the Fig. 2. The band assignments were given in accordance with the data reported in the literature[10,11]. The presence of water of crystallization in the sample is established by revelation of well-pronounced broad intense peaks at 3461 and 3379 cm^{-1} relating to asymmetric and symmetric OH stretching. This band indicates that the stretching frequencies of water molecules overlap. The peaks at 1637 and 1603 cm^{-1} are related to the bending vibrations of water molecules. The water molecule has three vibrational modes (wagging, twisting and rocking) and these modes are more sensitive to interactions involving hydrogen bonds and less sensitive to metal-oxygen coordinations[12,13]. The band at 703 cm^{-1} is attributed to the presence of metal bonds in the crystal. The observed FTIR bands from the spectrum and their assignments are displayed in the Table-2.

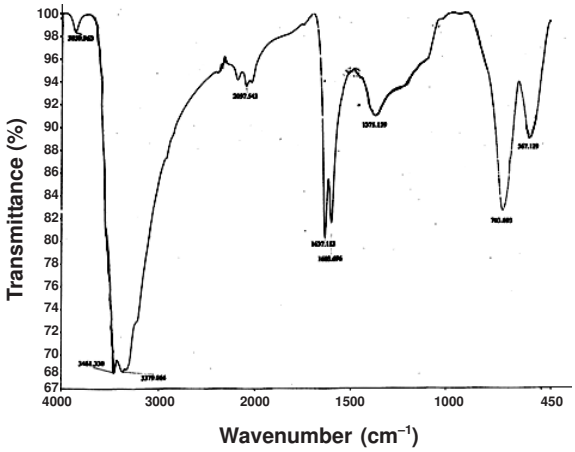

Fig. 2. FTIR spectrum of TABPC crystal

TABLE-2
ASSIGNMENTS FOR THE FTIR BANDS

Band $(cm)^{-1}$	Assignments
3461 s	Asymmetric OH stretching
3379 s	Symmetric OH stretching
1637 m	HOH bending
1603 m	HOH bending
703 m	Metal bond stretching
547 w	Liberational modes of water

DTA and TG studies: DTA and TG studies on the grown crystals have been carried out using Netzsch-DTA/TG thermal analyser. The TG and DTA thermograms of the grown crystals are shown in the Fig. 3. It is noticed that the sample loses water of hydration and it becomes anhydrous at 180 ºC. The sample loses one molecule of water of crystallization at 120 and at 180 ºC, it loses another molecule of water of the crystallization. TG thermogram shows that the grown crystals are unstable and there is no physical transformation independent of mass changes or decomposition of the grown crystals beyond 200 ºC.

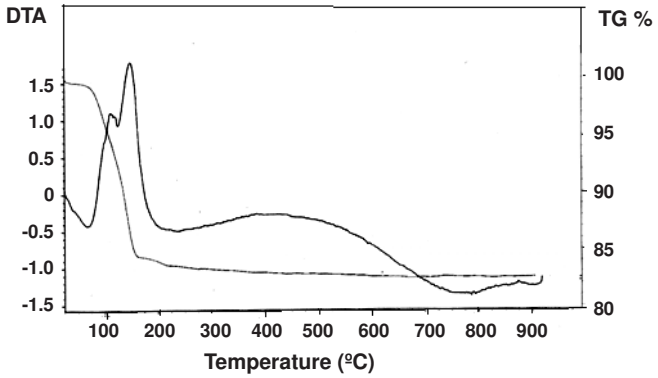

Fig. 3. TG/DTA curves for the grown TABPC crystals

Dielectric studies: The dielectric parameters like dielectric constant (ε_r) and dielectric loss (tan δ) are the basic electrical properties of insulating solids. The measurement of dielectric constant and loss as a function of frequency and temperature gives the ideas of electrical processes that are taking place in materials and these parameters were measured for the samples of this work. Variations of dielectric constant and dielectric loss of TABPC crystal with various temperatures ranging from 30-70 ºC and at frequencies 10^3 and 10^5 Hz are presented in the Figs. 4 and 5. The results suggest that the dielectric constant and loss depend on the frequency of applied field and the temperature of the sample. It is observed from the figures that both dielectric constant and loss are high at 10^3 Hz and they are observed to low at 10^5 Hz. When temperature of the sample is increased, the dielectric parameters are

found to be increased. The high values of dielectric constant (ε_r) and dielectric loss (tan δ) of TABPC crystal at low frequency (10^3 Hz) are ascribed to space charge polarization due to charged lattice defects. It is to be noted here that space charge polarization is dominant and electronic and ionic polarizations are not very much active in low frequency region. The nature of decrease of ε_r and tan δ with frequency suggests that the crystals of this work seem to contain dipoles of continuously varying relaxation times. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the dielectric constant and loss tangent (tan δ) are low at higher frequencies[14,15]. Variation of the dielectric parameters with temperature is generally attributed to the crystal expansion, the electronic, space charge and ionic polarizations and the presence of impurities and crystal defects. The increase in the values of dielectric parameters at temperatures is mainly attributed to the thermally generated charge carriers and impurity dipoles. As far as polarization is concerned, the increase in dielectric constant with temperature is essentially due to the temperature variation of ionic and space charge polarizations and not due to the temperature variation of orientational polarization.

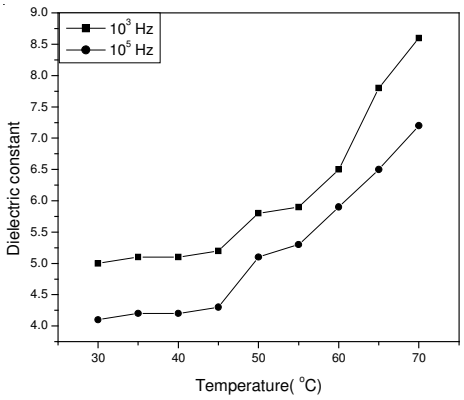

Fig. 4. Variation of dielectric constant with temperature for TABPC crystals at 10^3 and 10^5 Hz

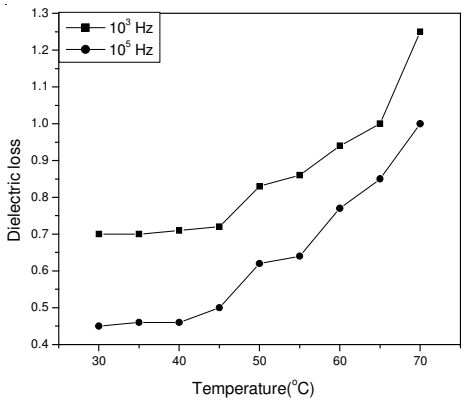

Fig. 5. Variation of dielectric loss with temperature for TABPC crystals at 10^3 and 10^5 Hz

AC Conductivity of the samples: The AC conductivity of the samples was determined using the relation, $\sigma_{ac} = 2\pi f \varepsilon_o \varepsilon_r \tan \delta$ where f is the frequency of AC. Signal, ε_o is the permittivity of free space or vacuum, ε_r is the dielectric constant and tan δ is the dielectric loss of the sample. Since the sample is an insulating material, the values of AC conductivity (σ_{ac}) are fitted in the equation $\sigma_{ac} = \sigma \exp(-E_{ac}/k_BT)$ and the activation energy (E_{ac}) was calculated. Here k_B is the Boltzmann's constant, T is the absolute temperature, σ is a constant depending on the material. Activation energy is the energy required for charge carriers to take part in the conduction process of the sample. A graph of ln σ_{ac} *versus* 1/T is depicted in the Fig. 6(a-b) and the activation energy was found to be 0.251 and 0.240 eV for TABPC

crystal at frequencies 10^3 and 10^5 Hz, respectively. It is observed that conductivity increases with temperature for the sample. Since conductivity is more at 10^5 Hz and less at 10^3 Hz for TABPC crystal, the activation energy at 10^5 Hz is less than that at 10^3 Hz[16].

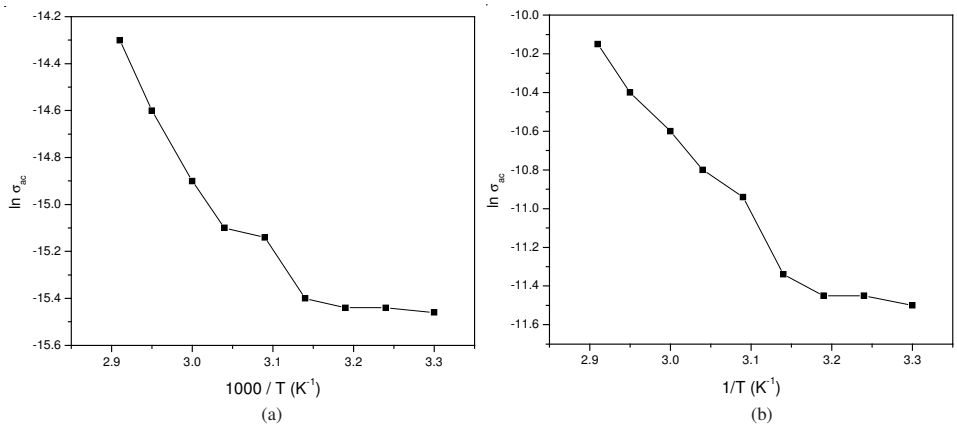

Fig. 6. (a) Plot of ln σ_{ac} *versus* 1/T for TABPC crystal at 10^3 Hz, (b) Plot of ln σ_{ac} *versus* 1/T for TABPC crystal at 10^5 Hz

Conclusion

Single crystals of triammonium barium pentachloride (TABPC) were grown by solution method with slow evaporation technique. The grown sample crystallizes in orthorhombic crystal system and various diffracting planes of the crystal have been identified. TG/DTA studies reveal the thermal stability of the grown TABPC crystal. The water of crystallization was observed in the sample by FTIR studies. The dielectric constant and dielectric loss and hence AC conductivity of TABPC crystal were determined and they were found to be increasing with increase in temperature. The activation energy of the sample of this work for AC conduction process was determined.

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