

Improvement of Mechanical, Thermal and Optical Properties of Barium Mixed Cobalt Tartrate Hydrate Crystals Grown by Gel MethodS. Vanaja^{1,*}, V. Selvamurugan², P.V. Chandrasekar³, R. Krishna Sharma², M. Alagar⁴¹ PSR Engineering College, Sivakasi-626140 Tamil Nadu, India² Mepco Schlenk Engineering College, Sivakasi, Tamil Nadu, India³ Institute optoelectronic display, Fuzhou University, Fuzhou 350002, People's Republic of China⁴ Ayya Nadar Janaki Ammal College, Sivakasi-626123, Tamilnadu, India

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In this present work, CTH and BCTH crystals have been prepared by gel technique by using single diffusion method at room temperature. The as grown crystals were characterized by using XRD, FT-IR, UV, TG / DTA and Micro hardness studies. X-ray powder diffraction results analyzed by using suitable software suggest that a CTH and BCTH crystals belong to cubic crystal system. The unit cell volume is observed to increase with increase in the concentration of barium in cobalt tartrate due to the lattice distortion. The band gap and optical properties have analyzed by UV-Visible spectrum. The functional groups and compound formation of the crystals have been studied by FT-IR spectrum. The mechanical properties of the grown crystals were tested by using Vicker's microhardness studies. The work hardening coefficient (n) was determined to be 3.7 for CTH, 5.3 for BCTH (1 : 1) and 6.4 for BCTH (2 : 1) and the stiffness constants for different loads were calculated and reported. Thermal analysis suggests that pure cobalt tartrate starts decomposing at 73.2 °C whereas the barium mixed cobalt tartrate brings about better thermal stability which increases with an increase in barium concentration.

Keywords: Cobalt Tartrate Hydrate (CTH), Barium mixed Cobalt Tartrate Hydrate (BCTH), XRD, FTIR, NLO, TG / DTA.

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1. INTRODUCTION

Growth of single crystals with high purity plays an important role in the development of modern scientific world. Particularly the tartrate crystals have highly attracted attention due to their interesting physical properties and technological applications. Some crystals of this family are used mainly, for their dielectric, ferroelectric, piezoelectric or nonlinear optical properties [1-3]. There are several research work have done by researcher in the crystal growth technique by using gel technique with different applications. Although, nowadays only have few number of literature in the cobalt tartrate crystals. V.Mathivanan et al [4], S.J.Nantre et al [5], S.Ariponnammal et al [6] were already reported about cobalt tartrate crystals by using gel technique. But, practically no information on the characteristics of pure and mixed cobalt tartrate crystals grown by gel technique is available. In this present paper we report the effect of pure and barium mixed cobalt tartrate crystals and their characterizations.

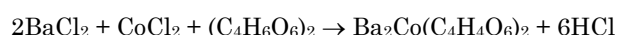
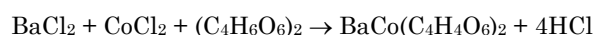
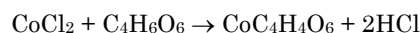
The grown BCTH single crystals were characterized by different techniques such as X-Ray Diffractometer (XRD), UV-Visible spectrum, Fourier Transform Infrared spectroscopy (FTIR) microhardness and thermal stability studies.

2. EXPERIMENTAL METHOD

Barium mixed cobalt tartrate ($\text{BaCo}(\text{C}_4\text{H}_4\text{O}_6)_2$) crystals were prepared by sol-gel method by using Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), L(+)-tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), Sodium meta silicate, Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$)

as the precursor materials. All the precursor materials were purchased and used without further purification.

In this work, Silica gel was prepared by adding a solution of sodium meta silicate to L(+) tartaric acid slowly with continuous stirring to avoid local ion concentration and to make the final homogeneous solution. A fixed amount of gel solution with desired value of pH was then transferred to several test tubes. The test tubes were sealed to prevent fast evaporation and contamination of the exposed surface of the gel. After a gel aging of one day 1M of cobalt chloride was added above it. The tube was kept undisturbed at room temperature. Crystals appeared near the gel column within three days and at the middle of the gel column within 1 week. All the crystals were harvested after 30 days. The following chemical reaction was employed in the growth of CTH and BCTH crystals.



In addition to that, barium mixed cobalt tartrate crystals were grown and characterizations in two different concentrations (1 : 1) and (2 : 1) for comparing with cobalt tartrate results. The grown crystals were dark brown in color.

3. X-RAY DIFFRACTION STUDIES

Fig. 3 shows the powder XRD patterns of pure and barium mixed CTH crystals. Powder X-ray diffraction

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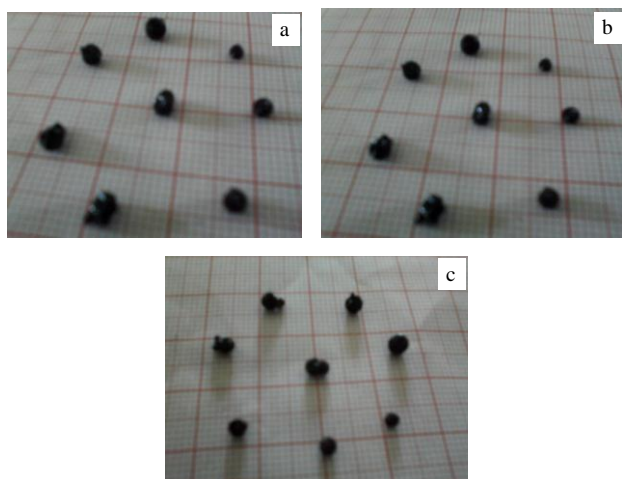


Fig. 1 – Photographs of grown crystals (a) CTH (b) BCTH (1 : 1), (c), BCTH (2 : 1)

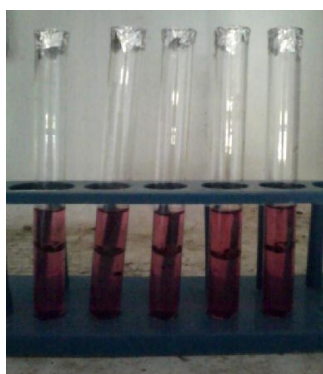


Fig. 2 – The grown crystals in test tubes

analyses for the grown crystals were performed by using XPERT- PRO X-ray diffractometer with CuK α -radiation ($\lambda = 1.54051 \text{ \AA}$) at 30 kV, 15 mA and resolution 0.5 degree.

In the XRD figure the very sharp Bragg's peaks with high intensities show the fine crystalline nature of the grown crystal. All the observed diffraction peaks were indexed and very well matched with the JCPDS card no: 23-0187. From these XRD pattern, ' d ' values and (hkl) were calculated, and these calculated values are compared with JCPDS values. The calculated hkl values from peak indexing method are (100), (011), (111), (200), (210), (211), (220), (311), (222), (321), (400), (332), (431) and (432) of 2θ values 14.438, 19.588, 22.088, 24.644, 27.888, 31.583, 36.481, 44.438, 46.938, 50.183, 53.368, 64.269, 68.719 and 74.990 respectively. The calculated hkl values are very well matched with JCPDS hkl values. In the PXRD pattern, the appearance of slight shift in the 2θ values of doped crystals suggest that the crystal structure was slightly distorted compared to pure cobalt tartrate hydrate.

With the comparison of CTH and BCTH crystals, the additional peaks occurred in the BCTH crystals at the 2θ value of 24.644, 64.269, 68.719 and 74.990. These peak formations are attributed to the mixing of barium. The crystallite sizes of the most intense peaks (200) were calculated by using Scherer's formula. The crystallite sizes of the grown crystals were 59 nm, 54 nm, 50.29 nm for CTH, BCTH (1 : 1) and BCTH (2 : 1) respectively.

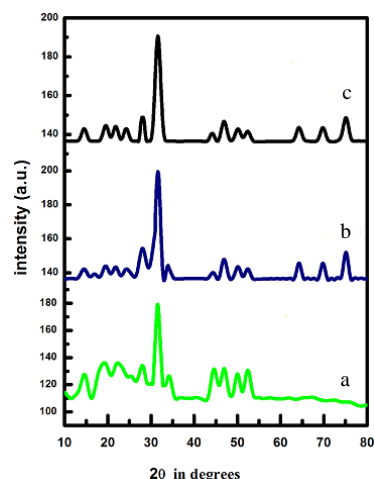


Fig. 3 – XRD patterns of grown crystals (a)CTH, (b) BCTH (1 : 1) and (c) BCTH (2 : 1)

The cubic unit cell parameters calculated by Rietveld refinement program, according to the values of 2θ in XRD pattern are tabulated in Table 3. The experimental results of the unit cell parameters are in good agreement with the theoretically calculated values by using the formula $a = d (h^2 + k^2 + l^2)^{1/2}$.

Table 1 – Lattice parameters for CTH and BCTH crystals

Compound	Theoretically calculated cell parameters	Experimental cell parameters
CTH	$a = b = c = 6.922 \text{ \AA}$	$a = b = c = 6.911 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 335.85 \text{ \AA}^3$
BCTH (1 : 1)	$a = b = c = 6.934 \text{ \AA}$	$a = b = c = 6.984 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 337.88 \text{ \AA}^3$
BCTH (2 : 1)	$a = b = c = 6.984 \text{ \AA}$	$a = b = c = 6.895 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 340.65 \text{ \AA}^3$

From Table 1, we confirm that all the grown crystals exhibit cubic crystal system. The lattice parameters of the grown crystals decrease with the increasing of barium mixing. This is due to the lattice distortion of atoms.

The strain, stress and dislocation density can be calculated by using the formula:

Strain (ϵ) = $\beta \cos \theta / 4$, Stress = $1 / \text{strain}$ and Dislocation density (δ) = $1 / D^2$ [10, 11] respectively.

Table 2 – Stress, Strain and Young's modulus of CTH and BCTH crystals

Grown crystal	Intense peak	Stress $\times 10^{-3} \text{ m}^{-2}$	Strain	Dislocation density $\times 10^{14} \text{ m}^{-2}$	Young's modulus (10 ⁻⁷)
CTH	31.583	0.5870	1703.5	2.873	3.445
BCTH (1 : 1)	31.638	0.6375	1568.6	3.429	4.064
BCTH (2 : 1)	31.638	0.675	1481.5	4.00	4.556

The above table suggests that the variation in the stress, strain, dislocation density of the prepared crystals depending upon the barium mixed with CTH.

4. UV-STUDIES

Fig. 4 demonstrates absorption spectra of CTH and BCTH crystals. The spectrum indicates that the crystal has a wide optical transmission window range from 250-900 nm. There is no remarkable absorption in the entire region of the spectra. The transmission region and lower cut-off wavelength increases with the increasing of barium mixing due to the crystal free defects and also confirms the good quality of the crystal is good. Also the spectrum shows, the presence of lower cut off wavelength in the UV spectrum.

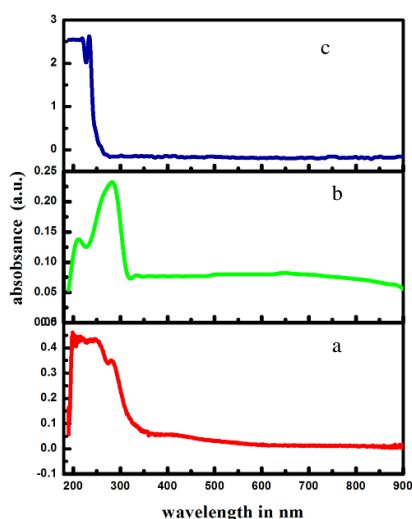


Fig. 4 – UV absorption spectrum of grown crystals (a) CTH, (b) BCTH (1 : 1) and (c) BCTH (2 : 1)

The UV spectrum confirms the NLO activity, electro-optic applications of grown crystals from its lower cut off wavelength and the wide optical transmission window range [12-13]. The optical transparency of BCTH crystal is higher than pure CTH.

The band gaps of the grown crystals are 2.56 eV, 3.75 eV and 4.0 eV for CTH and BCTH (1 : 1) and BCTH (2 : 1) respectively. The band gap increases with the increasing of barium mixing. The increase in band gap was due to the replacement of cobalt ions by barium ions.

5. FT-IR STUDIES

In this present work, the FTIR studies for the CTH and BCTH crystals by using the FTIR spectrum of which obtained from the FTIR instrument, 8400 SHIMADZU.

Fig. 5 shows the FT-IR spectrum of CTH and BCTH crystals grown in gel medium. The broad trough positioned band in between the region $3861.32\text{-}3169.04\text{ cm}^{-1}$ corresponds to O-H bonding which confirms the hydrous nature of the compound.

The C=O stretching and plane bending of C-O-H of tartaric acid were noted in the peak of around 1602.81 cm^{-1} and 1441.29 cm^{-1} for pure CTH and is shifted to 1608.77 cm^{-1} and 1439.48 cm^{-1} respectively for the mixed crystals[14-15]. The peak shifted due to the lattice distortion.

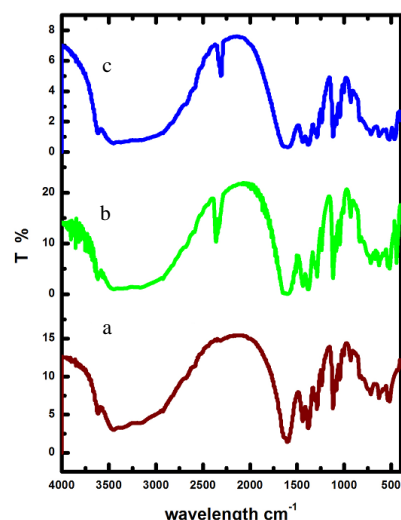


Fig. 5 – FTIR Spectrum of grown crystals (a) CTH, (b) BCTH (1 : 1) and (c) BCTH (2 : 1)

The peaks at $929.01\text{-}935.62\text{ cm}^{-1}$ and 628.60 cm^{-1} are confirm the M-O stretching vibration and M-H bending vibrations of cobalt tartrate crystals. Formation of new peaks are observed at wave number 444.34 cm^{-1} in BCTH (1 : 1) and are shifted to 463.26 cm^{-1} in BCTH (2 : 1) crystals [16]. This may be due to the formation of barium with cobalt, so when the amount of barium increasing, the sharpness of the absorption band changes.

The presence of cobalt is confirmed from the peak around at 517.52 cm^{-1} . The presence of barium is confirmed from the peak around 444.34 and 463.26 cm^{-1} . Hence the entry of dopants in the pure cobalt tartrate crystal is evident from this study.

The shift in wave number is due to the difference in mass number of barium (137.32) and cobalt (58.93) ions. It is reported in the literature that the difference in mass of ions leads to a change in molecular geometry and mechanical vibrations, which results in a shift in bands [17].

6. THERMAL BEHAVIOUR

6.1 Thermal Stability

The Thermal stability of the compound was identified by thermo gravimetric (TGA) and differential thermal analysis (DTA) studies simultaneously. The initial weight of the sample was taken to be 7.613 mg. Fig. 6 (a-c) show the record of TG /DTA curves of grown crystals.

The first stage of decomposition starts at $73.2\text{ }^{\circ}\text{C}$, $81.4\text{ }^{\circ}\text{C}$, $83.9\text{ }^{\circ}\text{C}$ for CTH, BCTH (1 : 1), and BCTH (2 : 1) with an observed weight loss of 17.9 %, 18 %, 18.3 % respectively. This result shows that the BCTH crystals have more stable than CTH. Also, the temperature for the formation of stable metal oxide product increases with the increase in the concentration of barium. It suggests that the thermal stability is linked to the incorporation of foreign ions in the modified (barium) in the mixed cobalt tartrate crystals [20].

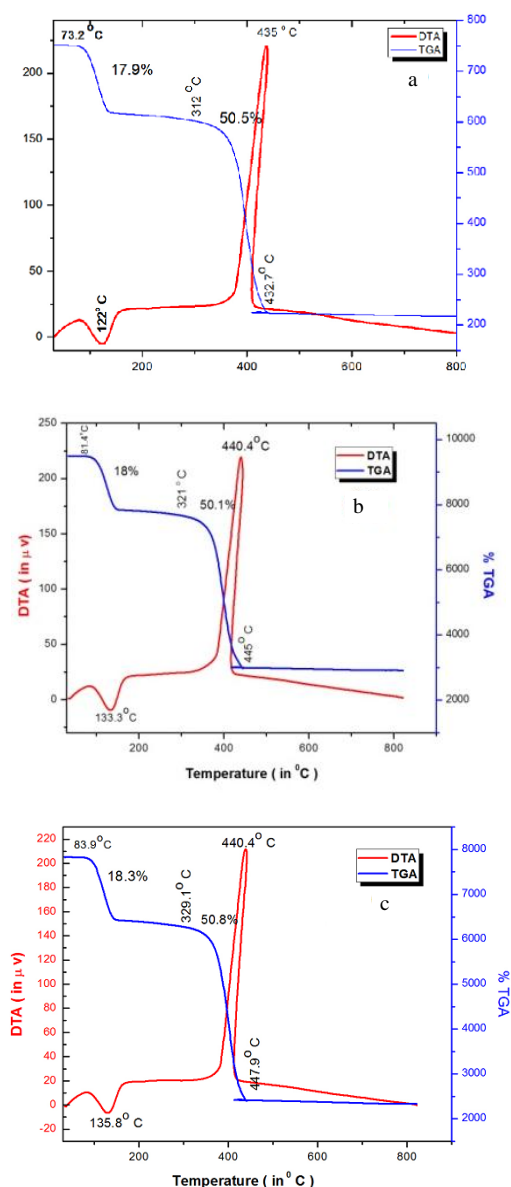


Fig. 6 – TG / DTA image of (a) CTH crystals, (b) BCTH (1 : 1), (c), BCTH (2 : 1)

The first stage of weight loss confirms the presence of 5.H₂O water molecules of the grown crystals in the temperature range 73.2 °C to 135.8 °C. Second stage weight loss confirms the elimination of CO, CO₂ and H₄. The second stage of weight loss shows the major decomposition of the grown crystals.

According to literature [5], thermal study of Cobalt tartrate shows the first decomposing started at 30 °C. But in the present study decomposing started at 73.2 °C, 81.4 °C, 83.9 °C for CTH, BCTH (1 : 1) and BCTH (2 : 1) respectively. This confirms that grown crystals have more stable in the present work.

In the DTA curve the peak at 122 °C, 133.3 °C and 135.8 °C corresponds to the decomposition of hydrated cobalt tartrate to anhydrous cobalt tartrate, whereas the peak at 435 °C, 440.4 °C may be attributed to the decomposition of cobalt tartrate to cobalt oxide. The weight loss observed in TGA is thus supported by the peak in the DTA [14, 19].

7. MECHANICAL BEHAVIOR OF BCTH CRYSTALS

7.1 Hardness Studies

The hardness measurement of the crystals CTH and BCTH have been carried out using HMV2T Vickers micro hardness tester. The measurements were made at room temperature and loads ranging from 10g to 50 g have been used for making indentations, keeping the time of indentation constant at 5 seconds for all the cases. Due to release of internal stresses generated locally by indentation, above 50 g the cracks developed on the smooth surface of the crystals.

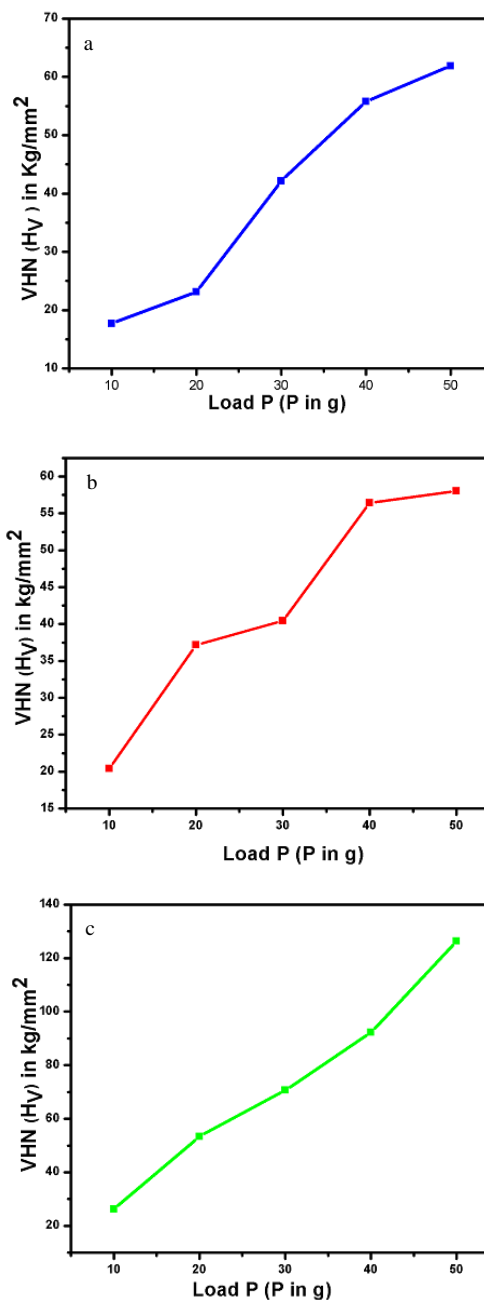


Fig. 7 – Plot of $\log P$ vs hardness number for CTH (a), BCTH (1 : 1) (b) and BCTH (2 : 1) (c) respectively

The hardness number has been calculated using the relation $H_v = 1.8544 \cdot P/d^2$ in kg/mm^2 where ' P ' is applied load in grams, ' d ' is the arithmetic mean of two diagonals of the indentation made. The calculated values of hardness number for the grown crystals are presented in Table 3. A plot between the hardness number (H_v) and the load (P) is depicted from Figure 7a-7c. These figures clearly infer that the hardness number increases with the increase of load, due to the Reverse Indentation Size Effect (RISE).

Because of the dopant ions enter into the lattice and hinder the formation of dislocations, micro hardness number (H_v) increases on mixing of barium [21].

Plots of $\log P$ versus $\log d$, for both CTH and BCTH crystals are shown in Fig. 8a-8c. The slope of $\log P$ versus $\log d$ yields the value of Meyer's index n using the

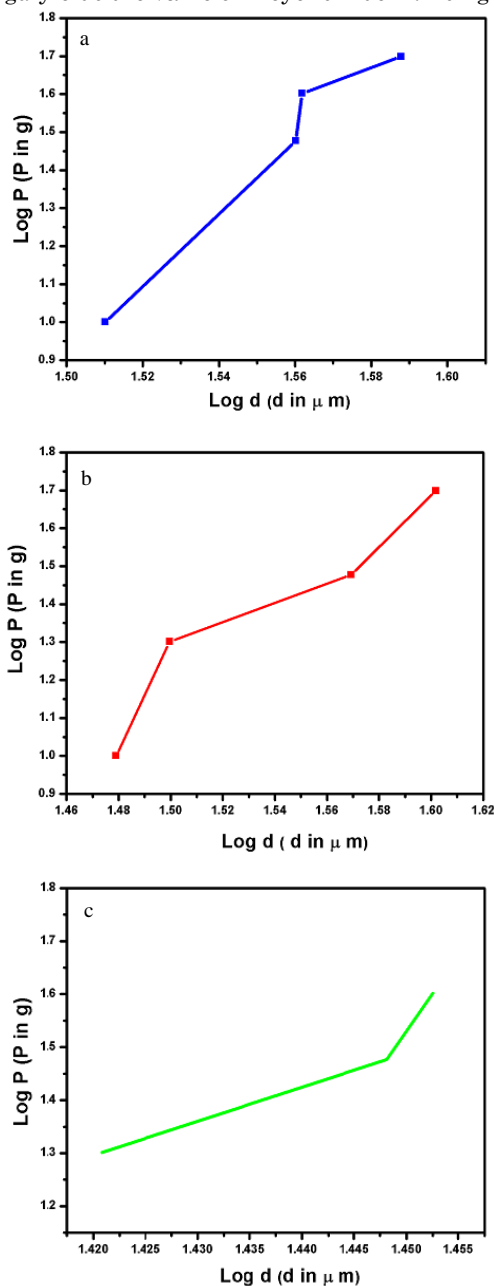


Fig. 8 – Plot of $\log d$ versus $\log P$ for pure CTH (a), BCTH (1 : 1) (b) and BCTH (2 : 1) (c)

relation $P = A \cdot n \cdot d$, where A is a material constant. From the hardness studies Meyer's index number ' n ' was calculated to be 3.7 for CTH, 5.3 for BCTH (1 : 1) and 6.4 for BCTH (2 : 1) respectively. According to Onitsch and Hanneman the values of n [15], the grown CTH and BCTH crystals belong to soft material category.

7.2 Elastic Stiffness Constant

The elastic stiffness constant (C_{11}) for different loads calculated using Wooster's empirical formula $C_{11} = H_v^{7/4}$. This formula gives the idea about the tightness of bonding between neighboring atoms. The table shows that the BCTH 2 : 1 has tightly bound to neighboring atoms [22].

Table 3 – Hardness number (H_v) for pure and Barium mixed CTH crystals

Load (g)	H_v for pure CTH (kg/mm^2)	H_v for BCTH (1 : 1) (kg/mm^2)	H_v for BCTH(2 : 1) (kg/mm^2)
10	17.70045	20.4206	26.2017
20	23.1452	37.1553	53.409
30	42.15615	40.4250	70.6462
40	55.7806	56.42	92.3112
50	61.8833	68.019	126.307

Table 4 – Elastic stiffness constant (C_{11}) for pure and Barium mixed CTH crystals

Load (g)	C_{11} for pure CTH $\times 10^{14}$ (Pa)	C_{11} for BCTH (1 : 1) $\times 10^{14}$ (Pa)	C_{11} for BCTH (2 : 1) $\times 10^{14}$ (Pa)
10	2.62	3.37	5.21
20	4.19	9.61	18.12
30	11.98	11.13	29.57
40	19.56	19.95	47.22
50	23.45	27.67	81.74

8. CONCLUSION

CTH and BCTH single crystals were successfully grown by sol-gel method by using sodium meta silicate. The structure of grown crystals identified through powder XRD pattern. Disorder of crystal structure, hkl values and lattice parameters also confirmed through powder XRD pattern. UV-Visible spectrum suggest that, the grown crystals have high transparency region due to the lower cutoff wavelength and wide optical transmission region. Thermo gravimetric analysis shows the grown crystal has stable up to 81.4 °C. Due to the influence of foreign ions BCTH crystals have more stable than CTH. M-O, M-H, C-O, OH stretching functional groups of grown crystals identified through FTIR spectrum. Micro hardness number increases with the increase of barium, because of Donar ions enter into the lattice and hinder the formation of dislocations. According to Onitsch and Hanneman values, the grown CTH and BCTH crystals belongs to soft material.

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