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Growth and Characterization of Barium Chloride Dihydrate Crystal

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Abstract: ***An inorganic barium chloride dihydrate, alkanine earth metal halide single crystal, was grown by a slow solvent evaporation technique in solution growth method. Highly transparent crystals were grown with the aid of phosphorous acid, which control the optimum pH of the aqueous solution and optimize the growth faster. The harvested crystals were subjected to characterization for revealing its structural, optical, mechanical and thermal properties. Barium chloride dihydrate crystal was confirmed by single crystal X-ray diffraction analysis and the functional groups present in it were identified using Fourier transform infrared analysis, and reported. The linear optical transmittance in the ultraviolet, visible and infrared radiation of wavelength ranging from 200 to 1100 nm was studied and explained in detail. Dielectric studies were made on the crystalline compound to find dielectric permittivity. In order to find mechanical properties such as surface hardness, yield strength, and other relevant properties, Vicker's microhardness testing was done on the as grown crystal. The thermal stability of the crystalline material was found out using thermal analysis such as Thermogravimetric and Differential thermal analysis.***

Keywords: Crystal growth; Optical property; X-ray diffraction; Thermal analysis; Inorganic compound

PACS: 81.10; 74.25.Gz; 61.05.Cp; 81.70.Pg; 61.66.Fn

1. Introduction

Crystal growth has become an important technology, due to the fact that many of today's technological systems in the fields of information, communication, energy, transportation, medical and safety technologies depend critically on the availability of suitable crystals with tailored properties and their fabrication [1]. Many modern technological devices would not exist without the use of synthetic single crystals. Inorganic compounds have good thermal and mechanical properties and so they can withstand high temperature during their utilization in device. Many researchers are focusing to grow inorganic single crystals possessing nonlinear optical and other physical properties due their high melting point and durability. Barium chloride dihydrate combine with other organic compound to produce their compound exhibiting nonlinear optical and photoluminescence properties [2]. Barium chloride dihydrate coordinate with l-histidine, l-alanine and glycine to produce the corresponding amino acid barium chloride dihydrate nonlinear optical crystalline compounds [3-5]. Barium bromide dihydrate crystals were grown from the aqueous solution in the presence of nitrogen atmosphere and reported its structural analysis [6]. In this paper the growth of the title compound at normal atmosphere and its optical, mechanical, dielectric and thermal properties are presented.

2. Crystal Growth

Barium chloride dihydrate single crystals were grown from a supersaturated aqueous solution of barium chloride dihydrate (AR grade) in distilled water as a solvent by a slow solvent evaporation method. Barium chloride dihydrate is hygroscopic and toxic in nature and highly soluble in water. A homogeneous aqueous solution of barium chloride dihydrate was prepared in a glass beaker by continuous stirring using a magnetic stirrer. Its pH value was tested by a digital pH meter as 5.8. The process was continued until it becomes supersaturated solution at room temperature. Then it was filtered using Whatman filter paper and kept in a dust free atmosphere. After 10 days, small crystals were found to be formed, but they were not transparent for linear optical characteristic analysis. In view of developing good crystals, phosphorous acid (AR grade) was added into the solution in an equimolar ratio. The presence of electronegative atom in the phosphorous acid tends to strengthen the acidic property and hence the pH value of the prepared solution became 0.8. The finally prepared solution was kept on a vibrationless table and closed by a polythene cover with few holes for evaporation at room temperature. After 8 days, optically transparent and regularly shaped barium chloride dihydrate (BCD) single crystals were harvested with a dimension of 35 x 22 x 4 mm^3. Phosphorous acid exists in the solution and activates to form transparent barium chloride dihydrate crystal. The photograph of the grown crystal is shown in the Fig.1.

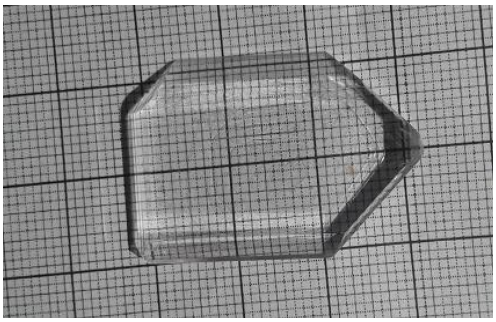

Figure 1: Photograph of Barium chloride dihydrate crystal

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3. Experimental Methods

A single crystal X-ray diffractometer is used to determine the structure of the grown crystals. In order to determine the structure of the grown barium chloride dihydrate (BCD) single crystal, the crystal was subjected to X-ray diffraction studies using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated MoKα (λ= 0.7107Å) radiation. Fourier transform interferometry confirms the presence of functional groups in the crystalline materials. Spectroscopic methods are widely used for qualitative and quantitative analyses of chemical compounds of grown single crystals. Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. This technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. In order to analyze the presence of functional groups in barium chloride dihydrate crystal qualitatively, Fourier transform infrared spectrum was recorded between 4000 and 450 cm^{-1} using Perkin-Elmer spectrum one FTIR spectrometer. The UV-Vis spectrum gives the optical transmittance and absorption of the grown crystals. To determine the transmission range and to know the suitability of BCD single crystals for optical applications, the UV-Vis-NIR transmission spectrum was recorded in the range of 200 to 1100 nm using Perkin-Elmer Lamda 35 UV-VIS spectrometer. The crystal of 3mm thickness was used for recording the spectrum.

The study of dielectric constant of a material gives out line about the nature of the atoms, ions and their bonding in the material. Dielectric constant will depend on the manner in which the atoms are assembled to form a crystal. It is necessary to find the dielectric constant of any kind of materials which are to be used for device application such as capacitor and sensor. In this point of view dielectric studies of barium chloride dihydrate crystal were carried out at various frequencies and temperatures using Precision LCR meter AGILENT 4284A model. The as grown crystal whose thickness is about 2mm and 1x1 cm^2 surface area was taken and it's both the surfaces were made carbon coating in order to make a contact with the electrodes. Then the sample was placed in between the electrodes whose diameter is equal to 1 cm and the sample was heated from ambient temperature to 120 °C with the function of frequency ranges from 100 Hz to 1 MHz. Capacitance and dielectric loss were measured and hence dielectric constant of the grown was calculated with respect to temperature and frequency. The material should posses sufficient wear resistance in the fabrication of any device. Vicker's microhardness plays an important role in such kind of device fabrication. In order to find the surface hardness of the grown barium chloride dihydrate single crystal, Vicker's microhardness tests were conducted using Reichert-Jung MICRO-DUROMAT 4000 E microhardness tester. Microindentation is a widespread technique used to determine the hardness of bulk materials. The measurements of indentation size were performed using the optical system of the apparatus consisting of an indenter known as Vickers diamond pyramid. Impressions were made on the sample with loads ranging from 10 g to 100 g. A set of two indentations were measured for each load level by the same operator. Both diagonals were measured to take into account the eventual asymmetry of the indentation. It was carried out on the on-growing crystal plane using microhardness tester provided with a Vicker's diamond pyramidal indenter. The hardness values were calculated from the formula H_v = 1.8544 P/d^2 kg/mm^2, where P is the applied load, d is the mean diagonal length of the indentation and 1.8544 is a constant of a geometrical factor for the diamond pyramid. Thermal properties of barium chloride dihydrate single crystal such as dissociation and melting temperature were studied by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) respectively. These were carried out between 30 °C and 1500 °C in nitrogen atmosphere at a heating rate of 10 °C/min using SDT Q600 V20.9 Build 20 TG/DTA instrument by stepwise isothermal method.

4. Results and Discussions

The title compound barium chloride dihydrate single crystal crystallizes primitive monoclinic structure with the centrosymmetric space group of $P2_1/n$. The unit cell parameters obtained in the single crystal X-ray diffraction are a = 6.75 Å, b = 10.95 Å, c = 7.17 Å, α = 90˚, β = 91.12˚, γ = 90˚ and volume V = 530 $Å^3$. When the cell parameters are compared with the crystallographic data [7], the result is highly agreed with them. The resultant Fourier transform infrared spectrum is shown in the Fig.2, where medium intensity of O-H stretching band is found to be at 3963, and 3793 cm^{-1}. These are due to the asymmetric stretching vibration of O-H in water molecule present in the compound. There are two sharp and strong intense stretching band assigned at 3542 and 3412 cm^{-1}, which are due to the symmetric stretching of O-H molecule in the molecule.

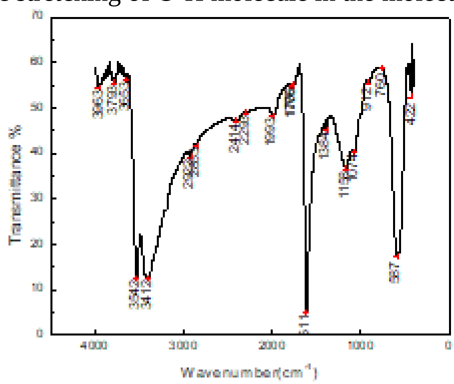

Figure 2: FTIR spectrum of Barium chloride dihydrate crystal

These asymmetric and symmetric vibrations show very precisely the presence of water molecule in the grown compound. A strong stretching vibration of Ba-Cl is obtained at 1611 cm^{-1} and its bending band takes place at 1158 cm^{-1}. The strong peak at 587 cm^{-1} corresponds to Cl-Cl and 422 cm^{-1} for Ba-Cl in-plane bending band. All the functional group assignments are

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Table 1: Frequencies of the fundamental vibrations of Barium chloride dihydrate crystal

Frequency in wavenumber (cm^{-1})	Assignment of vibration [8-10]
3963	O-H Asymmetric Stretching band
3793	O-H Asymmetric Stretching band
3542	O-H Symmetric stretchind band
3412	O-H Symmetric stretching band
1611	Sharp stretching for Ba-Cl
1158	Ba-Cl bending band
587	Strong vibration for Cl-Cl
422	Ba-Cl in-plane bending band

summarized in the table 1. Fig.3 shows the resultant optical transmittance curve, in which it is observed that there is a steady transmittance in the visible region and the lower cut off region is obtained at 260 nm. Further it is found that the maximum transmittance of the grown barium chloride dihydrate single crystal is 97% in the ultraviolet region and it has sufficiently higher transmittance about 94% throughout the visible region. Hence the barium chloride dihydrate crystal has very high transmittance in the visible region. The absorption peak found at 370 nm is due to the excitation of electron from lower to higher energy level [11].

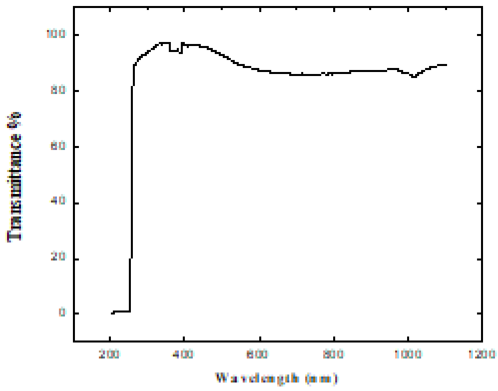

Figure 3: UV-VIS-NIR spectrum of Barium chloride dihydrate crystal

Fig. 4 shows the plot of dielectric constant of the sample, in which it is observed that the dielectric constant increases with the increase of the temperature and decreases with the increase of frequencies. At higher frequency its dielectric constant becomes less. Dielectric constant is maximum 14.5 at 100 Hz in the given temperature range since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at lower frequency. Due to the inertia of the molecules and ions at high frequencies, the orientation and ionic contribution of polarization are small [12]. This is the reason why the dielectric constant decreases with the increase of frequencies. Fig. 5 shows the plot of dielectric loss which is corresponding to the dielectric constant. The graph of microhardness as a function of load in gram is shown in the Fig.6. It is very precisely observed from the graph plotted between load and Vicker's microhardness that the hardness value increases with the increase of load and attain maximum hardness 255 kg/mm^2 at 90 gram load and thereafter it decreases. In the barium chloride dihydrate crystal, the atoms arranged in a regular order get dislocated along the slip plane. The dislocated atoms restrict the plastic deformation when load is increased further. This is the reason why the Vicker's microhardness increases with the increase of up to a certain load.

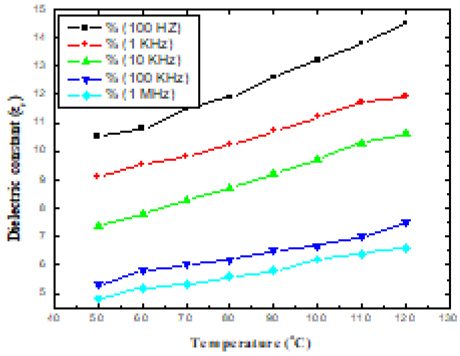

Figure 4: Dielectric constant of Barium chloride dihydrate crystal

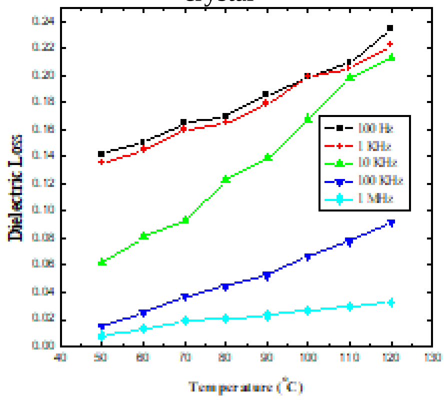

Figure 5: Dielectric Loss of Barium chloride dihydrate crystal

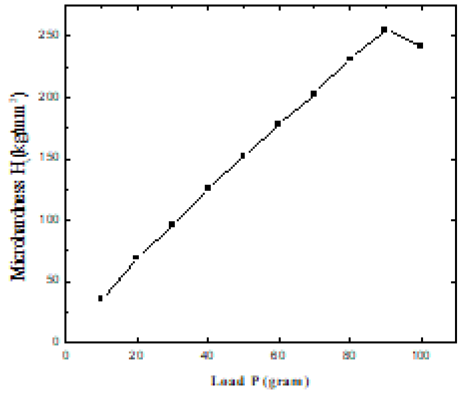

Figure 6: Vicker's Microhardness of barium chloride dihydrate crystal

The strengthening of a material by plastic deformation is known as work hardening. This strengthening of a crystalline material occurs due

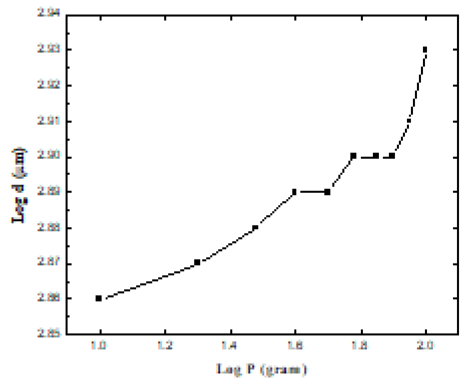

Figure 7: Plot of log P and log d of barium chloride dihydrate crystal

to dislocation of atomic movements within the crystal structure along the slip plane. The material becomes stronger and more difficult to undergo further deformation, and hence it requires more stress to produce additional plastic deformation. This is due to the restriction of slipping of atoms along the plane. In order to find the increase in strength that accompanies plastic deformation of the grown crystal, Work hardening coefficient (n) was calculated using the Meyer's relation $P = ad^n$, where P is the applied load, d is the diagonal length of the indentation and a is the constant for the given material. Fig.7 shows the graph showing the relationship between logarithmic value of the load P applied on the crystal and the diagonal length d of the indentation. The work hardening coefficient was calculated by taking a slope and it was found to be 8. According to Onitsch [13] n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials, further if $n > 1.6$, then the microhardness H_v increases with the increase of load [14, 15] and vice versa. Since the 'n' value is 8, it is suggested that the grown barium chloride dihydrate crystal is a softer material. Yield strength can be calculated using the relation [16] $\sigma_y = (H_v/3)(0.1)^{n-2}$ from the measurement of microhardness, where σ_y is the yield strength, H_v is the Vicker's microhardness of the material and n is the logarithmic exponent. According to the relation, the yield strength was calculated as 85 MPa for the barium hydrogen phosphite dihydrate crystal and hence the grown barium chloride dihydrate crystal has relatively low mechanical strength.

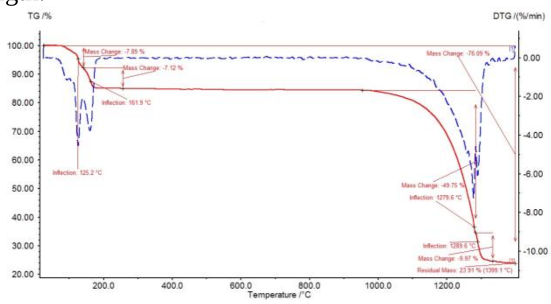

Figure 8: TG/DTA curves of Barium chloride dihydrate crystal

The basic thermal properties of the BCD crystal were revealed by the Thermogravimetric and Differential thermal analysis curves shown in the Fig.8. In the TGA curve, it is ascertained that there is no weight loss till 90 ºC and thereafter 7.89 % mass change is found at 150 ºC, and hence it is confirmed that the material is inclusion of water molecule. At 180 ºC, the remaining 7.12 % mass of water molecules in the barium chloride dihydrate compound gets decomposed completely, which is shown in the DTA curve as an endothermic peak at the corresponding temperatures. There is no further remarkable change found in the TGDTA curve till 960 ºC and from that point it decreases gradually, which indicates the melting point of the title compound. The maximum percent of the compound undergoes dissociation at 1279 ºC as shown in the given thermal curves. Hence from the thermal analysis barium chloride compound lose its very partial mass at about 100 ºC and the remaining at the temperature above 960 ºC.

5. Conclusions

An inorganic barium chloride dihydrate optical single crystal with very high transparency can be grown by slow solvent evaporation technique with the aid of phosphorous acid in an aqueous solution at room temperature. Various characterizations of linear optical, dielectric, thermal and mechanical properties were made on the grown crystals and presented well. The cell parameter and space group analyzed from single crystal X-ray diffraction confirms the grown crystal is barium chloride dihydrate of centrosymmetric system. The crystal has optical transmittance 94% in the visible region, which makes the suitability of the grown crystal for any linear optical device. Dielectric constant is 14.5 at lower frequency and Vicker's microhardness is 255 kg/mm^2. Due to the presence of water molecules in it, this inorganic crystal possesses low mechanical strength. The grown crystal barium chloride dihydrate lose very low percentage of its mass at 150 ºC due to the hydration of that compound and melt at 960 ºC due to the covalent bonding between the alkaline earth metal barium and the electronegative halogen chlorine. From the microhardness studies made on the crystal, yield strength was calculated, which shows that the crystal possesses low mechanical strength.

6. Acknowledgement

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