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Optical, Mechanical and Spectroscopic Studies of L-Alanine Cadmium Bromide (LACB) Single Crystals

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ABSTRACT

L-Alanine Cadmium Bromide (LACB) is a semi organic NLO crystal. There are many techniques to grow crystal at room temperature. In the present research work, the crystal has been grown by slow evaporation technique. Fourier transform infrared spectroscopic analysis was carried out to confirm the presence of different functional groups in the synthesized crystal. The powder X-ray diffraction study was used to observe the lattice parameters of the grown crystal. This XRD study shows that the grown crystal has orthorhombic in nature. The stability of LACB crystal has been strengthened by using Vicker's micro hardness study. This test divulged that the hardening of the crystal increases with increase in load. From UV-Vis-NIR spectrum, the optical nature of the grown crystal was carried out. The grown crystal has lower cut off wavelength at 203 nm in this transmission spectrum.

Keywords: LACB, Microhardness, FTIR, Powder x-ray diffraction, Photoluminescence, Optical spectrum

INTRODUCTION

Nature has provided the mankind with many astounding things, one among which is natural crystals. Fascinating colors, smooth surfaces with scintillating reflections of light, definite and varied shapes with sharp edges and deep transparency of some perfect crystals, altogether have aroused the aesthetic sense of the early man who used them as ornaments. Parallel with the growth of other sciences, through time, grew the curiosity of mankind to understand, more quantitatively the properties of crystals. The utility of crystals has been extended from the bounds of ornaments to several useful device applications such as optical, electrical and optoelectronic devices. The fantasy of their external beauty was understood more thoroughly through the laws of mathematics, physics and chemistry.

Processing the details of the crystal such as its structure and properties can be done with the help of modern methods of X-ray diffraction and spectroscopic techniques. External shapes, planes and colors were corrected with the internal atomic content and their arrangements in unequivocal terms. This leads to the study of "crystal growth and its characterization".

Semi organic non-linear optical crystals which are formed by the combination of organic materials (good non-linear optical properties and poor mechanical strength) and inorganic materials (good mechanical behavior and less properties of non-linear optics) have good NLO applications.

Crystal growth from solution technique is a familiar process which occurs well below the melting point of the solid, thus minimizing the risk of thermal decomposition and giving low strain and dislocation content. Crystal growth from aqueous solution is a well-developed flexible and easy-to-realize technique provided that a suitable solvent is available. In semi organic materials, an ionic bond is formed between the inorganic host and organic ligand. This property shows that the semi organic crystals have good mechanical and chemical nature. In the recent years, an intense effect has been focused on the design and development of materials with large NLO property.

Studies of non-linear second order optical processes in solids remain significant to the field of non-linear optics and to further advances in telecommunication technologies. Materials which show large non-linear optical properties are considerable interest for optical and electro optical applications. The second harmonic generation (SHG) process is nothing but the induced oscillating polarization has a component of double the input frequency, and part of the propagated light is frequency doubled.

In view of the requirements of apparatus, the slow evaporation method is similar to the slow cooling method. In slow evaporation method, the temperature is maintained constant and provision is made for evaporation with solvents. It is usually enough to allow the vapour to come freely into the atmosphere. The growth conditions for this technique is the maintenance of temperature to about ± 0.005ºC and the rates of evaporation of a few mm^3/h. The main advantage of this method is that the crystals grow at a constant temperature. In the present research work, L-Alanine Cadmium Bromide (LACB) was grown using slow evaporation technique at room temperature.

Semi organic materials possess better thermal stability property of inorganic materials and higher nonlinear coefficient property of organic materials [1-5]. Semi organic crystals of L-Alanine Cadmium Bromide (LACB) are potential candidates for NLO and electro optic processes. The L-Alanine Cadmium Bromide (LACB) crystals are widely known for their application in long wave X-ray spectrometers. L-Alanine Cadmium Bromide (LACB) crystals are also used as substrates for deposition of thin films of organic nonlinear materials. It can be synthesized by reacting L-Alanine with Cadmium Bromide (LACB) in stoichiometric ratio. It shares the properties of both organic and inorganic constituents. The present investigation was undertaken to study the characteristics such as vibrational and UV-Vis-NIR spectral analysis, microhardness, X-ray diffraction and photoluminescence studies.

MATERIALS AND METHODS

Synthesis and growth technique

The making of L-Alanine Cadmium Bromide ($Cd[C_3H_7NO_2]Br_2$) was obtained by reacting L-Alanine ($C_3H_7NO_2$) and Cadmium bromide ($CdBr_2$) in the stoichiometric ratio 1:1. The solvent used in this reaction is water.

The reaction scheme is $C_3H_7NO_2 + CdBr_2 \rightarrow Cd[C_3H_7NO_2]Br_2$

The beginners used in this reaction were taken as highly purified materials. The making and developing process of crystal were initiated in the aqueous solution where the consecutive recrystallization process was carried out to increase the purification of the making crystal. The range of temperature of the solubility of the crystal is measured gravimetrically between 30ºC and 50ºC. The salt is added continually in 100 ml deionized water. The saturation stage was reached. The gravimetric analysis method is used to indicate the amount of salt present in the saturated solution. The constant temperature was selected and the temperature of the prepared solution was kept at this preserved one. A motorized magnetic stirrer was used as prolonged stirrer and it ensures homogeneous temperature and concentration in every part of the volume of the solution.

The above procedure is repeated by raising the temperature of the solvent in steps of 5ºC and in each case, the amount of salt present is measured. The solubility curve obtained is shown in Figure 1 and the curve shows that LACB has a positive solubility-temperature gradient.

Firstly, the desired amount of cadmium bromide was soluble in deionized water and to this solution, L-Alanine was added. The agitation of the prepared solution was continuously carried out for 8 h using magnetic stirring device. After the beginning materials have fully dissolved, the solution was filtered. In this method, the prepared solution was permitted to evaporate at room temperature. From this solution, optically good quality crystal is obtained. The transparent grown crystals are depicted in Figures 2a and 2b. The Table 1 describes the growth details of L-Alanine Cadmium Bromide (LACB) crystal.

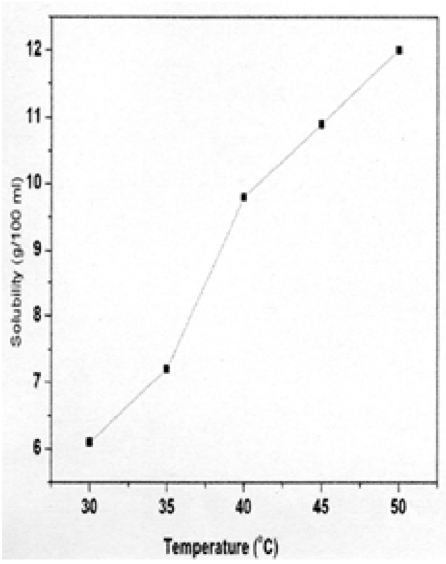
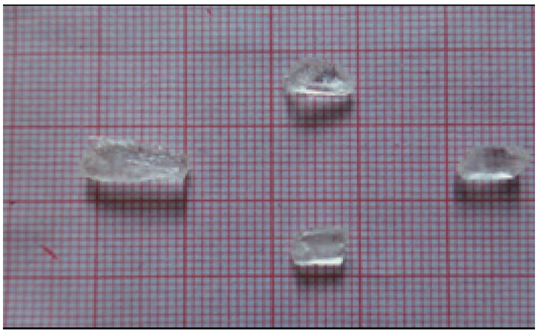
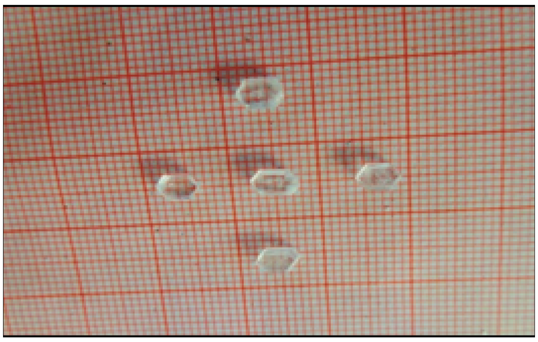


Figure 1: Solubility curve of LACB crystals



(a)



(b)

Figure 2: Photograph of grown LACB crystal

Table 1: Growth details of L-Alanine Cadmium Bromide (LACB) crystal

Method of growth	Slow evaporation technique
Solvent used	Deionized water
Molar ratio	1:1
Grown Temperature	Room temperature
Grown Period	7 days

Characterization

L-Alanine Cadmium Bromide (LACB) is a semi organic NLO crystal. Using slow evaporation technique, it was completely grown from aqueous solution at room temperature. The characterization of grown crystals was studied using powder X-ray diffraction analysis. The structure of the grown crystal was confirmed by the above analysis. The various functional groups present in the title compound were indicated by using FTIR spectral analysis. The hardness of a material depends not only on the properties of materials under test but also largely on the conditions of measurements. Using Vicker's test, the mechanical strength of the grown crystal was analyzed. The optical studies were made by UV-Visible analysis. The material quality was studied by photoluminescence.

RESULTS AND DISCUSSION

Powder x-ray diffraction analysis

The powder XRD spectrum of the grown crystal was recorded using BrukerD8 diffractometer instrument attached to a digital computer along with graphical assembly in which CuKα radiation is the source (λ=1.546Å). The range of 2θ from 10° to 90° was studied by employing continuous scan mode.

From the sharp and well defined Bragg's peaks at specific 2θ angles of the X-ray powder diffraction pattern of the grown LACB crystal shown in Figure 3, the crystalline behavior and purity of the crystal are studied. In the recorded powder XRD pattern of the grown crystal, the maximum intensity was observed. That is, the intensity peak was maximum at 19000 and is recorded as 20°. From the observations of XRD analysis, the synthesized crystal belongs to orthorhombic system. The unit cell parameter observed from the XRD analysis is reported in the Table 2.

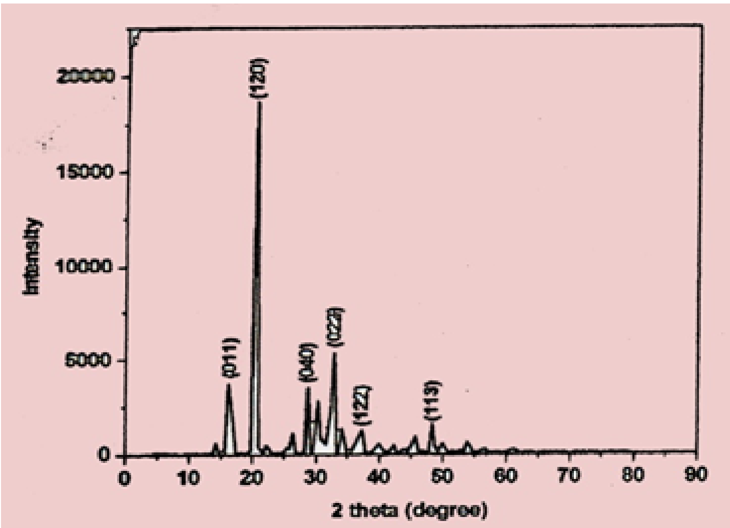


Figure 3: Powder XRD patterns of LACB crystals

Table 2: Lattice parameters of LACB crystal

Parameters	LACB crystal
a (Å)	5.771
b (Å)	6.014
c (Å)	12.298
Cell Volume $(Å)^3$	426.8

FTIR spectral analysis

Fourier transform infrared spectrum of LACB crystal was measured by using Perkin Elmer FTIR spectrometer with KBr pellet technique in region of wavelength from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 1 cm^{-1} at room temperature. This spectral analysis was used to understand the bonding nature of the grown compound. The Figure 4 shows the recorded FTIR spectrum of LACB crystal.

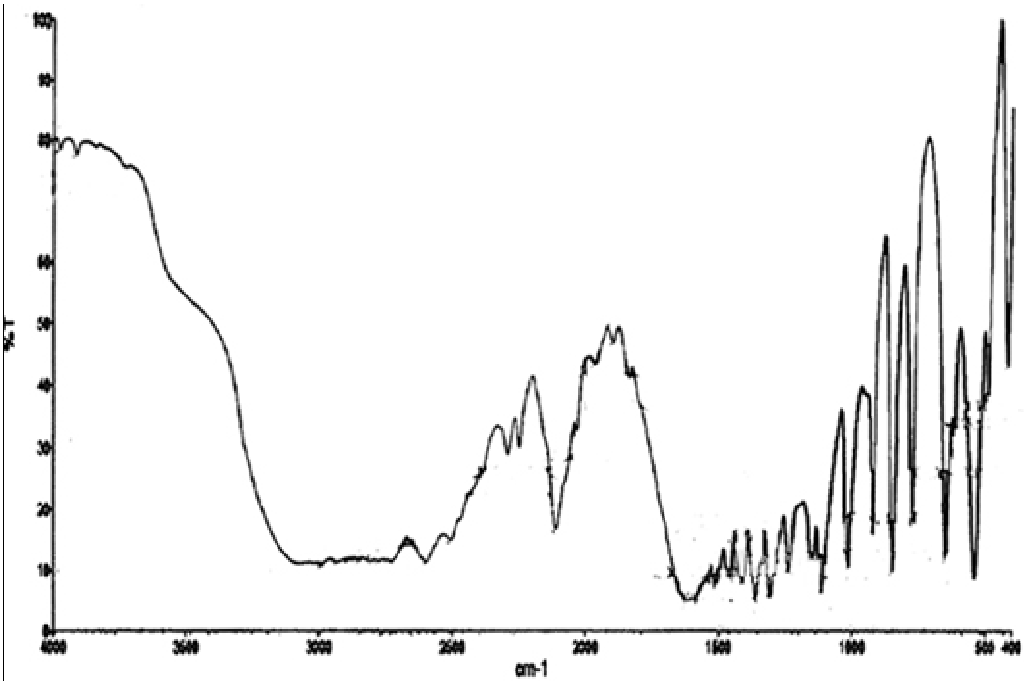


Figure 4: FTIR spectrum of LACB crystal

From the observations of recorded infrared spectrum, the bands along with their vibrational assignments give information regarding the structured study of the grown crystal. A broad band which is observed at 2110.71 cm^{-1} is due to the presence of NH_3^+ torsional oscillation. The peaks observed at 1621.68 cm^{-1} and 1505.44 cm^{-1} are assigned to NH_3^+ asymmetric stretching and NH_3^+ symmetric stretching respectively. This band was shifted to higher wave number region when compared to that of the free ligand. This shift may be due to the formation of bonds in pure and L-alanine mixed CB molecule. The bands at 1360.56 cm^{-1} and 1454.61 cm^{-1} show the presence of CH_2 wagging and CH deformation respectively. The vibrational lines observed at 1412.11 cm^{-1} and 1235.70 cm^{-1} are attributed to COO^- symmetric stretching vibrational mode. The infrared peaks observed at 918.98 cm^{-1} and 849.33 cm^{-1} have been allotted to C-C-N symmetric stretching vibration. The rocking and scissoring vibrations of COO^- are observed at 538.84 cm^{-1} and 648.70 cm^{-1} respectively. The infrared peaks at 772.54 cm^{-1} and 648 cm^{-1} indicates the presence of O-C-O deformation and C-Br stretching respectively. The vibrational assignments of the grown crystals and L-Alanine are compared and the observed shifts may be allotted to the formation of NH_3^+ and COO^- groups. The results are tabulated and given in the Table 3.

Table 3: Assignments of vibrational frequencies of LACB crystal

S. No.	Vibrational Wave number (cm^{-1})	Vibrational Assignments
1.	2110.71	NH_3^+ torsion
2.	1621.68	NH_3^+ asymmetric stretching
3.	1505.44	NH_3^+ symmetric stretching
4.	1454.61	CH deformation
5.	1412.11	COO^- symmetric stretching
6.	1360.56	CH_2 wagging
7.	1235.70	COO^- symmetric stretching
8.	1014.17	C–N stretching
9.	918.93	C–C–N symmetric stretching
10.	849.33	C–C–N symmetric stretching
11.	772.54	O–C–O deformation
12.	648.70	COO^- scissoring
13.	538.84	COO^- rocking
14.	648.00	C–Br stretching

Micro hardness analysis

The micro hardness analysis is one of the relevant methods to find the mechanical characteristics of the materials having a specific correlation with their hardness. Hardness of a material may be termed as a measure of the resistance against lattice destruction or the resistance offered to permanent deformation or damage [6,7].

Using shimadzu HMV-2 micro hardness tester, the values of micro hardness was calculated from 25 g to 100 g load in the present investigation. These values are used to determine the surface hardness of the developed LACB crystal. One of the significant factors to measure the hardness values is the selection of the polished crystal which is transparent and free from cracks. In this reliable method, the indentation marks were made on the crystal surface at room temperature. The loads are applied with 25, 50 and 100 g. For all the loads, the time of indentation is kept constant. If the load value increases from 25 g to 100 g, the values of micro hardness was also found to increase and at the higher loads, the cracks occurred. The Figure 5 shows a graph which has been plotted between H_V and applied load P. The Table 4 gives the micro hardness values of LACB crystals.

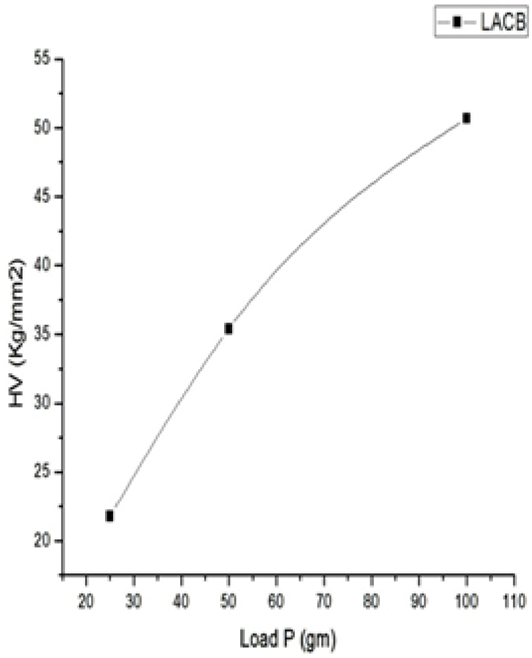


Figure 5: Load vs. hardness for LACB crystal

Table 4: Micro hardness values of LACB crystals

S. No.	Load (gm)	H_v (kg/mm^2)
1.	25	21.8
2.	50	35.4
3.	100	50.7

From the relation, H_v=1.8544 P/d^2 (kg/mm^2), the value of hardness number of the grown crystal was measured. In this relation H_V refers the Vickers hardness number (kg/mm^2), P denotes the applied load (kg) and d indicates the average diagonal length of the indentation on the crystal surface (mm). The plotted graph between H_V and P shows that the hardness value increases with the increasing steps of the applied load. The graphical interpretation shows that the hardness value increased up to 100 g and at this 100 g, the observed value of maximum hardness was 51 kg/mm^2.

Photoluminescence analysis

The photoluminescence study is carried out using spectrafluorometer (Varian cary eclipse). The photoluminescence is an important property to characterize the optical nature of the crystal. The peak positions and the intensities observed in the photoluminescence spectrum are directly related to the defects in the material. The luminescence spectra of LACB crystal is observed by the emission wavelength 300-600 nm. The Figure 6 showed the recorded photoluminescence spectrum of LACB crystal where B is the intensity (a.u.) and λ is the wavelength (nm). The photoluminescence spectrum of LACB crystal is obtained in which the emission wavelength is 360 nm.

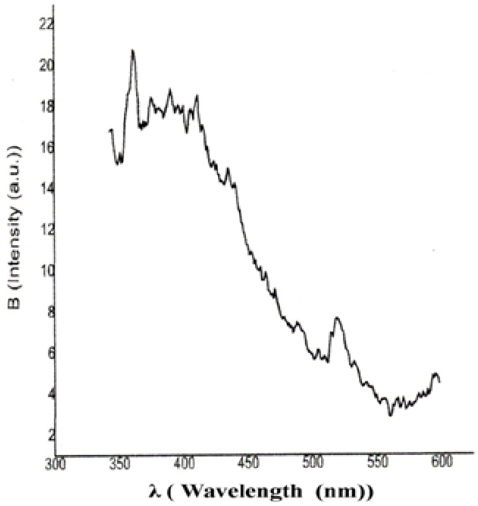


Figure 6: Photoluminescence of LACB crystal

Suppose when the doping level increases, the near band edge emission peak will become broader. This will be suggested that an increase of defect levels within the forbidden energy gap. Also, there will be reducing of photoluminescence intensity due to the increase in the doping level. The reason for this is the photo excited electrons are preferentially transferred to the trap centers as induced by the doping material.

UV-Vis-NIR spectral analysis

The UV-Vis-NIR spectral transmittance was carried out using Varian Cary 5000 spectrometer in the range from 200 nm to 1000 nm. The Figure 7 shows the UV-Vis-NIR spectrum of LACB crystal. There is no absorption band in the wavelength range from 350 nm-1000 nm. This indicates the presence of transparency in the UV spectral region. From the observed spectrum, it ensures that the grown crystals have good transmittance (around 85%) and the observed lower cut off wavelength is 203 nm. This large transmittance behavior of the grown crystal in the entire visible region enables it to be a good candidate for NLO application. It is one of the desired properties of non-linear optical crystal. Also the shift of lower cut off wavelength is due to the mixing of L-alanine with cadmium bromide and hence it is desirable for optoelectronic application.

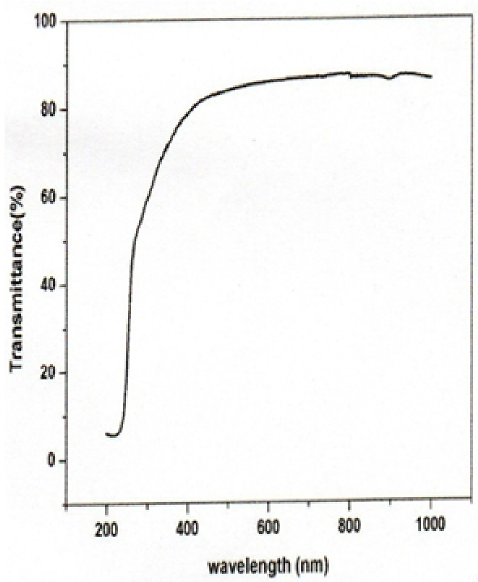


Figure 7: Optical transmittance spectrum of LACB crystal

CONCLUSION

In the present research work, good optical quality single crystals of LACB have been grown by slow evaporation technique at room temperature. X-ray diffraction technique is used to determine the lattice parameters and this analysis shows that the crystal has orthorhombic in nature. The functional groups and amino groups present in the grown crystal have been confirmed by FTIR spectral analysis. The good optical transmittance in the entire visible region makes the crystal a good candidate for optoelectronic applications. From the Vicker's micro hardness test, the maximum hardness value is observed at 51 kg/mm^2 and it shows it has good mechanical strength. The photoluminescence spectrum of LACB crystal is obtained in which the emission wavelength is 360 nm. Because of all these properties, LACB could be a promising material for NLO applications.

REFERENCES

[1] Min-hua, J. and Fang, Q., *Adv Mater*, **1999**. 11: p. 1065-1154.

[2] Ramajothi, J., Dhanuskodi, S. and Nagarajan. K., *Cryst Res Technol*, **2004**. 39: p. 414-420.

[3] Ariponnammal, S., et al., *Cryst Res Technol*, **2005**. 40: p. 786-788.

[4] Rosker, M.J., et al., *Pure Appl Opt*, **1996**. 5: p. 667-680.

[5] Selvaraju, K., *Opt Commun,* **2007**. 269: p. 230-234.

[6] Lal, B., Bamzai, K.K. and Kotru, P.N., *Mater Chem Phys*, **2003**. 78: p. 202-207.

[7] Mott, B.W., Micro Indentation Hardness Testing, Butterworth, London, **1956**.