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Research Article

Growth and Characterization of a Nonlinear Optical Crystal: Bis-L-Alanine Barium Chloride

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Abstract

The search for new conversion materials for various device applications has lead to discovery of many organic, inorganic and semi organic NLO materials and they have potential applications in Second Harmonic Generation(SHG), optical storage , optical communication , photonics , electro–optic modulation , optical parametric amplifiers , optical image processing etc., A nonlinear optical material Bis-L-Alanine Barium chloride single crystal was grown from aqueous solution by slow solvent evaporation technique. The unit cell parameters and the crystalline nature of the grown crystal were observed by powder XRD analysis. The functional groups of Bis- L-Alanine Barium chloride crystal was detected by FTIR spectral analysis. The transmittance and absorption of the crystal was studied by UV – VIS spectral studies. The surface features of the grown crystal at different magnifications were analyzed using scanning electron microscope. The mechanical properties of the grown crystal were studied using Vicker's micro hardness measurement. The second harmonic generation test has been confirmed by Kurtz powder test.

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Keywords: NLO materials, optical communication, Powder XRD, Scanning electron microscope.

Introduction

Nonlinear optical (NLO) crystal for the UV-visible region is extremely important for laser spectroscopy and laser processing. Hence, it is important to search for new NLO material, which possesses large NLO co-efficient, shorter cut off wavelength, transparency in the UV region and higher laser damage threshold [1-3].Purely inorganic NLO materials have excellent mechanical and thermal properitis but possess relatively modest optical nonlinearity because of the lack of extended π – electron delocalization [4-5].Hence it may be useful to prepare semi- organic crystals which combine the positive aspects of organic and inorganic materials resulting in useful NLO properities. In semi-organic materials, the organic ligand is ionically bonded with inorganics. These crystals have higher mechanical strength, chemical stability, large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [6-7]Amino acids have been selected as model compounds since they comprise a series of compounds whose physical properties, including their crystallography, are well defined; moreover, they are structurally related to pharmaceutical compounds such as antibiotics, peptides and proteins [8].L-Alanine is the simplest amino acid having SHG efficiency one third of the well known KDP, but the knowledge of studying its properties is very important since L-Alanine can be considered as the fundamental building blocks of more complex amino acids [9].In the field of nonlinear optical crystal growth, amino acids are playing a vital role. Semiorganic NLO crystals are expected to possess the advantages of both inorganic and organic materials. L-Alanine mixed semi organic material will be of special interest as a fundamental building block to NLO properties [10]. While the structures of most amino acids are well defined, the structures of the derivatives of the protein amino acids with inorganic components are not [11].The aim of this work is to grow semi organic NLO single crystal of Bis- L-Alanine Barium Chloride by slow evaporation process and the various characterizations namely powder XRD analysis, FTIR, and UV-visible absorption spectrum of electromagnetic radiation of the grown crystals, surface morphology, hardness and SHG test are reported.

Experimental Procedure

Single crystals of Bis-L-Alanine Barium Chloride were grown by solution method with slow solvent evaporation technique at room temperature (30˚C)by high purity L-Alanine and Barium Chloride in the ratio of 2:1 with pH 5.6 .In accordance with the solubility data, saturated solution of the twice re-crystallized salt of L-ABaCl$_2$ was prepared by dissolving the salt in de-ionized water by continuous stirring of the solution using a magnetic stirrer and the saturated solution was filtered using 4 micro Whatmann filter paper. Then filtered solution was taken in a beaker and covered by a perforated cover for controlled evaporation. The seed crystals of Bis-L-ABaCl$_2$ were obtained by spontaneous nucleation. The super saturation of the solution was found by observing the first crystal formed at the bottom of the solvent. The seed crystals of Bis-L-ABaCl$_2$ were placed in the super saturated solution and the solution was allowed to evaporate the solvent slowly into atmosphere. A typical single crystal with size 3 x 1.5 cm^2 was obtained after 3 weeks as in Fig.1.

Fig.1 Grown crystal of Bis- L-Alanine Barium Chloride

Characterization Techniques

The grown crystals were characterized using an optical microscope to study the growth kinetics and surface features. Powder X-ray diffraction pattern was recorded using a Siemens D 500 diffractometer with CuKα (λ= 1.5418 Ao) radiation for structural analysis. In order to confirm the presence of functional groups in the crystal lattice, FTIR spectra were recorded by KBr pellet Technique using a Bruker Model IFS66 V spectrometer in the wave length range 400- 4000 cm-1.The optical transmission spectrum was recorded using a UV – visible spectrometer (SHIMADZU-1601) reveals the linear optical property of the Bis-L-ABaCl$_2$ crystal. The surface features of the grown crystal at different magnifications were analyzed using scanning electron microscope. The micro hardness measurements of the grown crystal Bis- L-ABaCl2 were carried out using Leitz Weitzlier Vicker's micro hardness tester. Kurtz powder SHG test was performed in the Bis -L-ABaCl2 crystal.

Results and Discussion

Powder X-ray Diffraction Analysis

The grown crystals have been characterized by single crystal powder X-ray diffractometer with in the 2θ range (20 to 80°). Fig.2 represents the powder X-ray pattern of the grown Bis-L-alanine barium chloride single crystal. The Bis-L-alanine barium chloride was crystallizes in orthorhombic structure and the results are in good agreement with reported literature values. It is clear that sharp and strong peaks confirm the good crystalline nature of the grown samples. The lattice parameter values of Bis-L-alanine barium chloride single crystal (L-ABaCl$_2$) taken from the literature were used for the simulation of hkl values and corresponding d values have been calculated. The calculated cell parameters of L-alanine barium chloride (L-ABaCl$_2$) as a=5.797(7) A0, b=6.050(7) A0 , c=12.387(14) A0 and the volume of the crystal was found to be 435 A03(α = β = γ = 900)

Table 1 Cell parameters of L-Alanine andBis-L-ABaCl$_2$ single crystal

Sample	a(A°)	b(A°)	c(A°)	Volume (A°)
L-Alanine	6.023	12.343	5.784	429.99
Bis-L-ABaCl$_2$	5.799	6.050	12.387	435

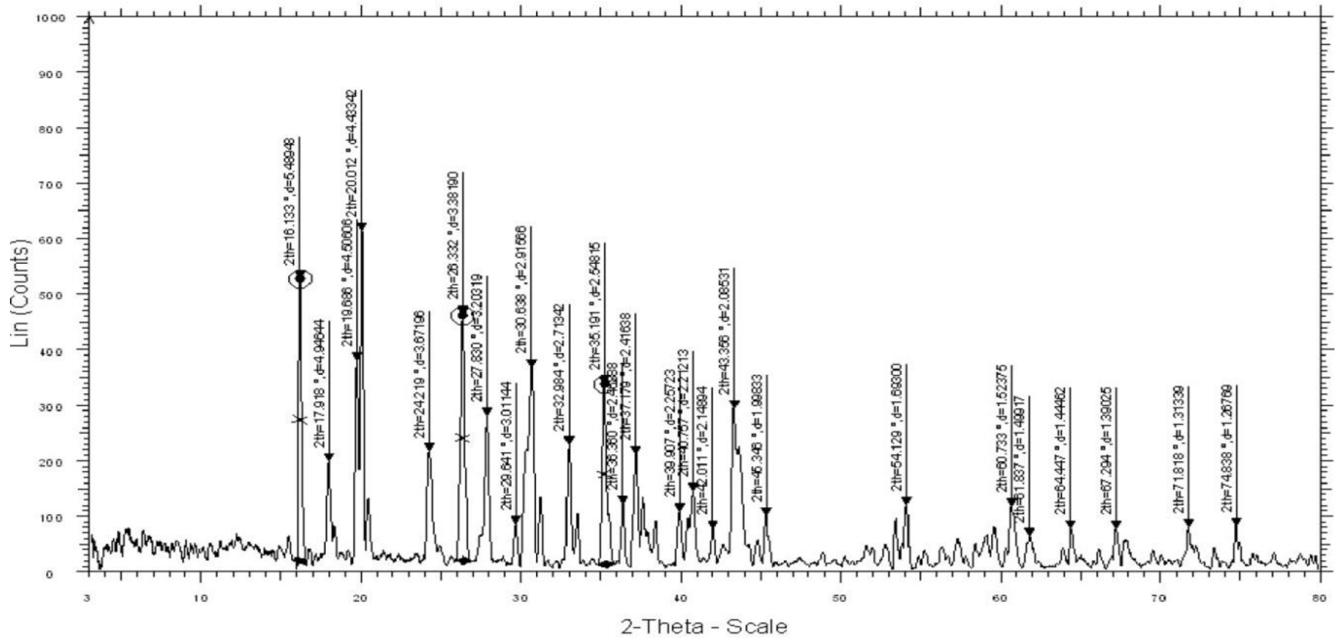

Fig.2 XRD Pattern of Grown crystal of Bis-L-ABaCl$_2$

Fourier Transform Infrared (FT-IR) Analysis

Functional groups presented in the Bis L-alanine barium chloride (Bis L-ABaCl2) crystal were analyzed using Fourier transform infrared (FT-IR) spectroscopy. The spectrum was recorded using the Bruker IFS 66Vmodel FT-IR spectrometer in the wave number range 400–4000cm−1 using the KBr pellet method. The FT-IR absorption spectrum of Bis L-ABaCl$_2$crystal is shown in Fig. 3. The vibration band at 3461cm^{-1} was ascribed to a primary amine free radical with N-H symmetric stretching mode of vibration. The C-O stretch of –COOH seems to have intense peaks at 1013cm^{-1}. The Ba–Cl stretching vibration frequency is assigned to 701 cm^{-1} from FT-IR spectrum. Thus the FT-IR spectrum confirms the formation of Bis-L-alanine barium chloride and its characteristic frequencies are observed as mentioned above.

UV-Visible- NIR Absorption Analysis

The UV – Vis spectrum gives limited information about the structure if the materials, because of the absorption of UV and visible light involve promotion of the electron in σ and π orbital from the ground state to higher energy states [12].Single crystals are mainly used in optical applications, optical transmission range and the transparency. The above mentioned application in the UV-cutoff is very important. The UV–Visible absorption spectra were studied using cut and polished Bis L-ABaCl_2single crystal of 2mm thickness. The recorded spectrum is shown in Fig. 4. The lower UV-cutoff wavelength is around 220 nm. And also, it shows that the crystal has a transmission of 80%. From the UV-Visible spectrum of the material Bis L-ABaCl_2 we find that this material is transparent to all the wavelengths of visible and UV. From this we can conclude that the Bis L-ABaCl_2 crystal may find possible application in second order harmonic generation.

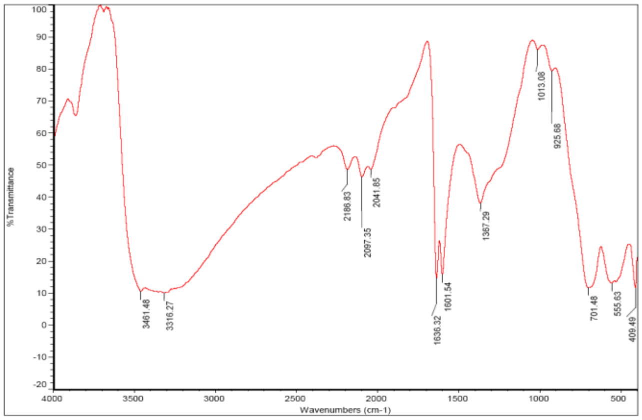

Fig.3 FTIR Spectrum of Grown crystal of Bis- L-ABaCl_2

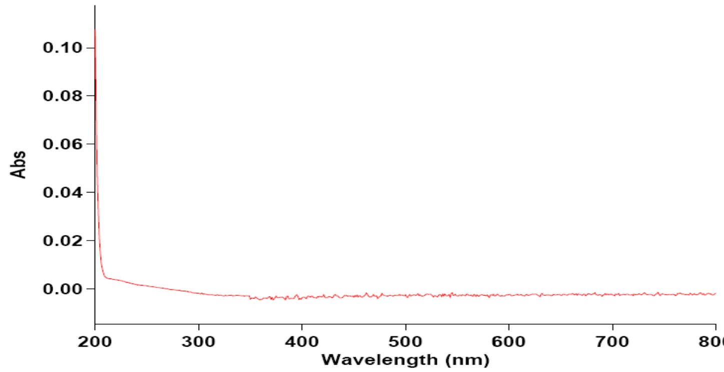

Fig 4 UV- Vis - NIR Spectrum of Bis- L-ABaCl_2

Scanning Electron Microscope (SEM) analysis

In SEM, the surface of solid sample is scanned in a raster pattern with a beam of energetic electrons. The back scattered and secondary electrons produce from the surface by the interaction of primary electron beam with loosely bound electrons of the surface atoms serve as the basis of SEM. When the electron beam scans the specimen surface, there will change in the secondary electron emission according to the surface texture [13].The SEM images of Bis-L-ABaCl_2 are presented in the Figures 5(a) and 5(b).

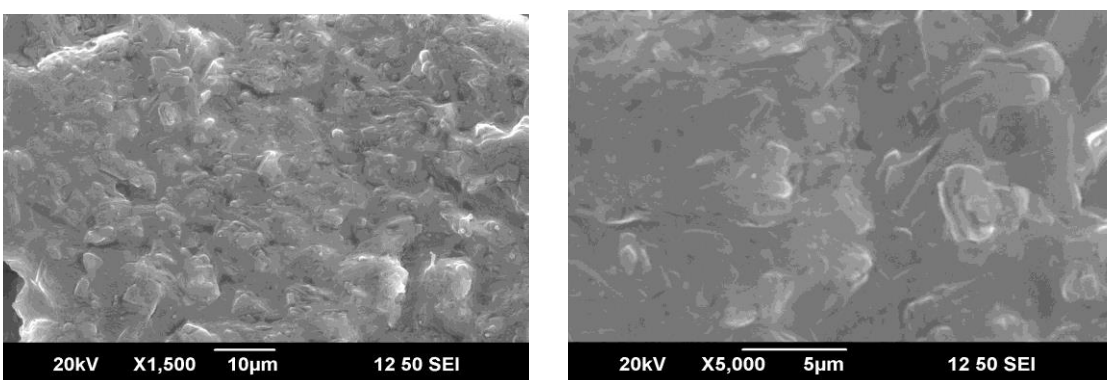

Fig.5 SEM images of Bis- L-ABaCl_2

Micro hardness studies

Micro hardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indentor.The mechanical behavior of the L-ABaCl_2 crystal was analyzed using Vicker's micro hardness test at room temperature. The selected surface of the crystals were lapped,polished.washed and dried. Hardness measurements were taken for applied loads varying from 25 to 100 gm keeping the indentation constant at 10 seconds for all the cases. The Vicker's hardness number (VHN) of the grown crystal were calculated using the relation kg.mm^{-2}, where is VHN, P is the applied load in kg,d is the average diagonal length in mm of the indentation mark.A graph was plotted between hardness values decreases with increase of load.So the brittleness of the crystal for the load is large and crystal may be considered as soft material.

Second Harmonic Generation Test

The second harmonic generation (SHG) test on the Bis-L-ABaCl_2 was performed by Kurtz powder SHG method. The powdered sample of crystal was illuminated using the fundamental beam of 1064 nm from Q- switched Nd:YAG laser. Pulse energy 4 ml/pulse width of 8 ns and repetition rate of 10 Hz were used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm collected a monochromator after separating 1064 nm pump beam with an IR- blocking filter. A photomultiplier tube is used as a detector. It is observed that the measured SHG efficiency of Bis-L-ABaCl_2 crystal was 0.6 times that of potassium dihydrogen phosphate (KDP).

Conclusion

The seed crystals of semi organic Bis-L-Alanine Barium Chloride (Bis L-ABaCl_2) were successfully grown from the slow evaporation technique. The formed crystals are characterized and the following results are obtained. From the powder XRD pattern we infer that the material Bis L-ABa$Cl_2$is crystalline and the system is orthorhombic. Further the FTIR spectrum reveals the presence of functional groups. From the UV-visible absorption spectrum of the material Bis L-ABaCl_2 we find that this material is transparent to all the wavelengths of visible and UV which is the key factor for the fabrication of optoelectronic devices. The surface features of the grown crystal at different magnifications were analyzed using scanning electron microscope. Mechanical property of the grown crystal has been studied by micro hardness test and the crystal is found to be soft in nature. The powder second harmonic generation efficiency measurement shows the grown Bis-L-ABaCl_2 crystal have 0.6 times higher nonlinear optical efficiency that potassium dihydrogen phosphate (KDP).

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