Growth and characterization of CarbamideButanedioic Aciddoped with Rubidium Chloride Single Crystal

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ABSTRACT

Numerous applications for the unique organic nonlinear optical crystals have been proposed, including frequency doubling, optical switching, optical data storage, optical modulation, laser remote sensing, and pharmaceuticals. A slow evaporation growth method was employed to create high-quality carbamidebutanedioic acid crystal doped with rubidium chloride. The PXRD pattern proved the crystalline nature. By using FTIR, the necessary functional groups were confirmed. The mechanical stability of the developing crystal indicates that it is a soft material. The grown crystal's dielectric characteristics were addressed. Due to its excellent optical absorbance, the chemical in question is a good choice for device assembly. For NLO applications, the produced crystal seems to be extraordinarily transparent over the whole visible region.

Keywords:Nonlinear optical;FTIR; PXRD; CarbamideButanedioic Acid; Rubidium chloride.

DOI Number: 10.14704/nq.2022.20.13.NQ88426 **NeuroQuantology2022;20(13): 3463-3472**

1. INTRODUCTION

The wide range of possible uses for the novel organic nonlinear optical crystals, including frequency doubling, optical switching, optical data storage, optical modulation, laser remote sensing, and medicinal applications, has generated a lot of attention [1]. High nonlinear optical (NLO) response is displayed by organic molecules with conjugated materials and acentric crystalline packaging, which is greatly admired in laser-optics technology [2]. As opposed to inorganic materials, organic nonlinear materials have a higher optical threshold for laser power, a larger optical susceptibility, and a faster inherent ultra-test response time [3].One such organic NLO substance, carbamide, has two interchain hydrogen bonds along the a/b axis and four intrachain hydrogen bonds along the c-axis, with six strong intermolecular hydrogen links making up the majority of the material's initial coordination sphere. It is significant to note that its carbonyl group participates in four hydrogen bonds, acting as an acceptor [4,5]. Butanedioic acid can exist as succinic acid in a neutral state or as succinate in an ionised form. It creates extremely potent intra-molecular hydrogen bonds with other molecules when it is ionised [6]. Recently, it was discovered that crystals related to succinic acid are used in the fabrication of high electron mobility transistors [7,8]. Our focus is on researching butanedioic acid crystals with various compositions due to their NLO applications. The current study used a slow evaporation method to create single crystals of carbamidebutanedioic acid with rubidium chloride functioning as the dopant. The goal of the current work was to ascertain how adding RbCl2 to CBA affected the crystal's development as well as its structural, mechanical, thermal, and conductivity characteristics.

2. Experimental Details

2.1 Crystalgrowth

The CBA crystal was prepared at room temperature by slow evaporation of aqueous solution containing equimolar proportion of carbamideand butanedioicacid with 1M Rubidium chloride is added as the dopant. Care was taken to minimize mechanical and thermal vibrations. After 21 days, colorless, bright and transparent CBA crystal doped with $RbCl_2$has been harvested and the photograph of the grown CBA crystals doped with $RbCl_2$ is shown in Fig.1.

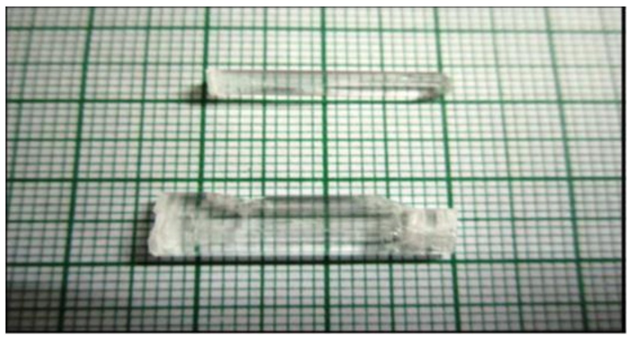

Fig.1PhotographofthegrownCBAdopedwith $RbCl_2$crystals

2.2 Characterization Technique

Powder XRD pattern of the grown CBA doped with $RbCl_2$crystal have been recorded using Reich seifertdiffractometer with Kα radiation (λ = 1.5418 Å).Energy Dispersive X-ray analysis were carried out using a Bruker EDS spectrometer in conjunction with the SEM.FT-IR spectra of CBA have been recorded using Bruker IFS 66 V Spectrometer in the range 4000-100 cm^{-1}.The FTIR spectrum was recorded using a Perkin-Elmer FTIR spectrometer using KBr pellet technique, recorded in the range of 400-4000 cm^{-1}.UV-vis spectrum was recorded in the range of 190-1200 nmusing Lambda 35 Spectrometer. Thermal analysis was carried out simultaneously employing Perkin Elmer thermogravimetric and differential analyser (Mode: PYRIS DIAMOND) in nitrogen atmosphere heated from 10 to 700 with a heating rate of 100ºC to understand thermal behavior.Dielectric study of the grown crystal was carried out at different frequencies with different temperatures using HIOKI 3532 LCRHITESTER. Microhardness analysis was carried out using vicker'smicrohardnessindentor. Q-Swiched High Energy Nd:YAG Laser (QUANTA RAY MODEL) HG-4B-High efficiency instrument was used to carry out for the recording of SHG measurement.

2. Results and Discussion

3.1 PowderX-raydiffractionanalysis

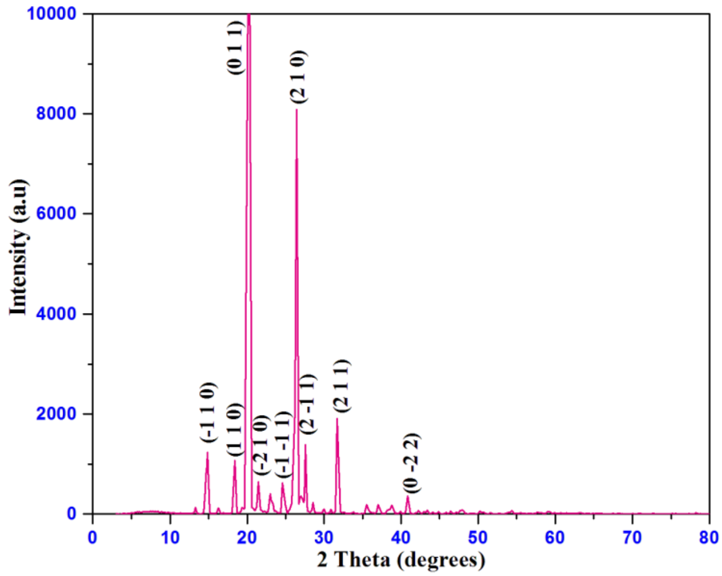

Fig.2PowderXRDspectrumofCBAcrystalsdopedwithRbCl$_2$

X-raypowder diffraction was used for the identification of the synthesized crystal. The Powder XRD spectrum of the grown CBA crystals doped with $RbCl_2$ is shown in Fig.2.The synthesized grown crystal were scanned overtherangeof10 - 70° at scan rateof2°/min at roomtemperature.The sharp peaks depict the crystalline nature of the grown crystals. The data obtained show that the grown crystal belongs to orthorhombic system with lattice parameters a=b=20.2067, c=14.4637, andα= β=γ=90°.

3.2 Energy Dispersive X-Ray Analysis

Fig.3 is describing the EDX spectrum of the grown crystal. The spectrum evidences the purity of the grown crystal composed of Rubidium chloride which can be seen in Figure 3.

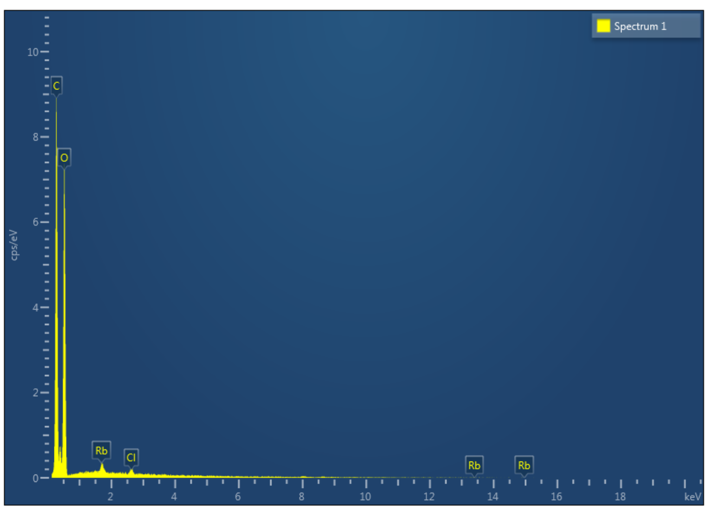

Fig 3 EDX spectrum of the grown crystal

3.3Scanning Electron Microscope

The sample obtained via electron sample interactions is used to determine the quality of the crystal surface morphology and to determine the chemical composition. Figure 4 displays a SEM image of the surface of CBA doped with RbCl2 crystal. Even though there are some inclusions, such as micro crystals, on the surface of the formed crystals in Figure 4, the surface appears smooth and free of fissures. These changes took place during its growth and had an impact on the growth parameters.

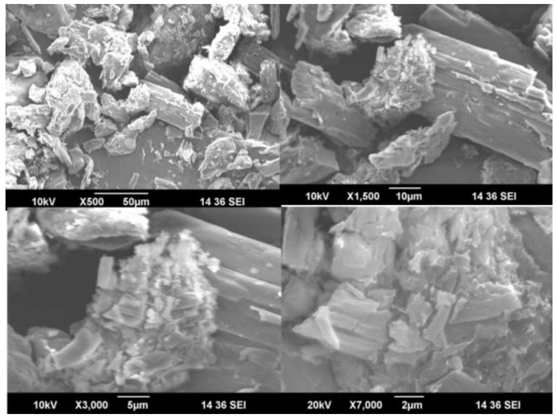

Fig 4 SEM Analysis

3. 4. FTIRAnalysis

The observed FTIR spectrum of the grown crystalisshowninFig.5and Table 1 gives the band assignments of CBA crystal doped with $RbCl_2$. Usually O-H stretching band is characterized by broad bandsappearing near about 3400-3500 cm^{-1}[12] and it has beenobserved as a very strong band at 3340 cm^{-1}in IR. O-H bendingvibration is observed in IR at 1410cm^{-1}.Red shifting of this band depicts the level of intermolecular N-H…O hydrogen bonds are the most abundant hydrogenbonds and their effect can be observedin IR spectrum by broadness and strength of bendingand in stretchingregion. Most conspicuous change in adduct spectra occurs in N-Hstretching frequency region. Asymmetric and symmetric stretchingvibration occurred at 3436 and 3237 cm^{-1}in urea [13] are observedas a strong intensity band at 3480 and 3237 cm^{-1}respectively. This asymmetricstretching is shiftedfrom the expected region due to red shifting of N-H stretchingmode,providing a strong evidence for the existence of strongN-H…O intermolecular hydrogen bonding.The narrow bands at 2935 and 2870 cm^{-1} are associated with C-H stretching vibration. Stewart [14] assigned 1603 cm^{-1}band to NH_2bending mode in urea which is observed at 1410 cm^{-1}as a very strong band in IR.

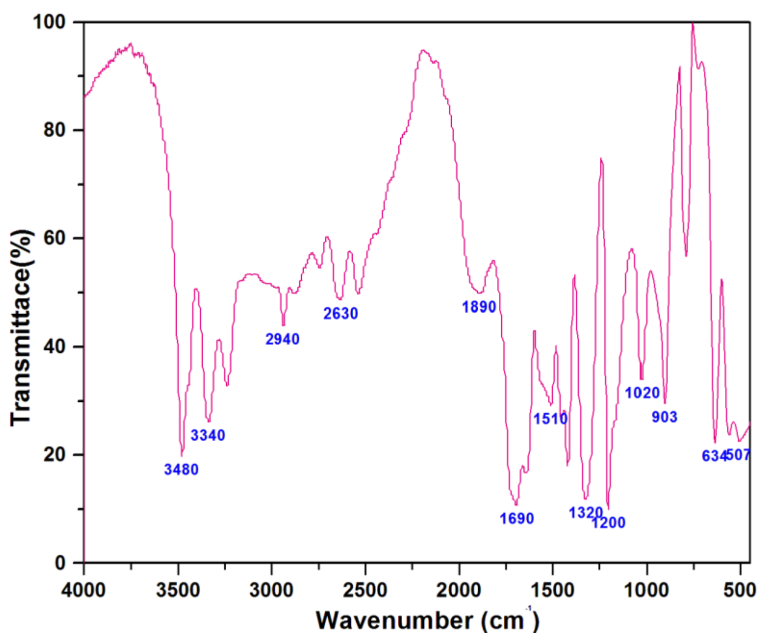

Fig.5FT-IRspectrumofCBAcrystalsdopedwith $RbCl_2$

C=O stretching vibrations in saturated aliphatic aldehydes,ketones and acids have frequencies in range 1740-1700 cm^{-1}. Inamides the frequency is lowered to 1690 cm^{-1}[15] which is dueto the existence of resonance structures. C-O stretching band occursat ~1684 cm^{-1}in urea [13,15] and is observed at 1693 and 1650 cm^{-1}as a strongband in IR.The other contributions are given in Table 1.

Table 1FTIRbandassignmentsofCBA crystal dopedwith $RbCl_2$

Frequency (cm^{-1})	Assignments
3480	$\nu_{as}NH_2$
3340	νO- H
3237	$\nu_{ss}NH_2$
2940	νCH
2870	νCH
1693	νC=O
1650	βOH, δNH2, τCN
1510	τNH, τCN, ν_{as}CO2
1410	τNH, τCN, βO-H
1320	βOH, $\nu_{as}CO_2$
1200	τCN, βOH, ρNH_2, ρNH_2
1020	ρCH_2, ρCH_2, $\omega 2CO_2$
903	νCC, βCC, νC-N
789	ωNH, ωNH_2, τCN, τNH, δCO2
634	τOH, ωCO_2, δCO2
507	$\rho 2CO_2$, ρCO_2, ωCO_2, ρCOO-
506	ωCO_2, ρCH_2, τOH

υ_{SS}- symmetric stretching; υ_{AS}- asymmetric stretching; υ_{IP}- in-plane stretching;υ_{OP}- out of plane stretching; β-in-plane bending; ω- wagging; δ- scissoring; τ-torsion; ρ-rocking;

3.5 UV-Visibleanalysis

Transmittance is an important property of a material being used for NLO applications. The optical absorption spectrum of the grown crystal was recorded in the range of 100-1100nm and the UV-Visible absorption spectrum is shown in figure 6. From the UV absorption spectrum, it was found that there is very low absorbance in the entire visible region. It is due to the direct transition of an electron from a non - bonding 'n' orbital to an anti-bonding 'π*' orbital (n →π*). It is important that for efficient NLO crystal, lower cut-off wavelength should be in the range of 200 to 400 nm [16]. The title compound has excellent optical absorbance with the lower cut-off wavelength at 212 nm makes it as a potential material for device fabrication. For the entirevisible region the grown crystal seems to behighly transparent, which suits for NLOapplications.

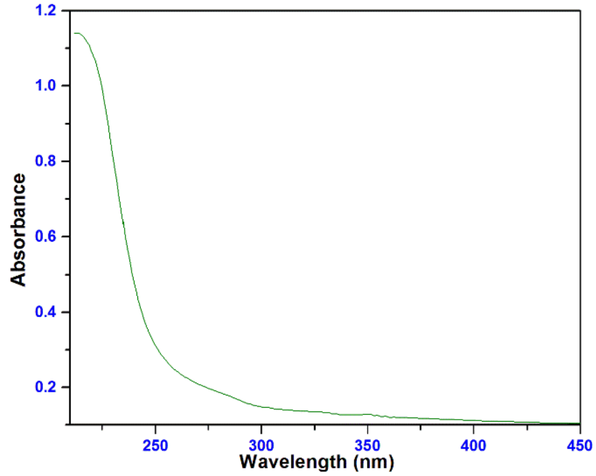

Fig.6UV-visibleabsorption spectrumofCBAcrystalsdopedwith $RbCl_2$.

3.6 Mechanicalstudy

Hardness of the material is a measure of resistance observed by a solid to the movement of dislocations [1]]. Microhardness testing is one of the best methods of understanding the mechanical properties of the materials; such as fracture toughness, yield strength and brittleness index [18,19].. A plot between hardness number and the load is depicted in fig.7 (A) . It clearly infers that the microhardness number increases with increasing load, exhibit the reverse indentation size effect (RISE).Aplotobtainedbetweenlog pandlog d,showninfig.7(B)givesastraightline.

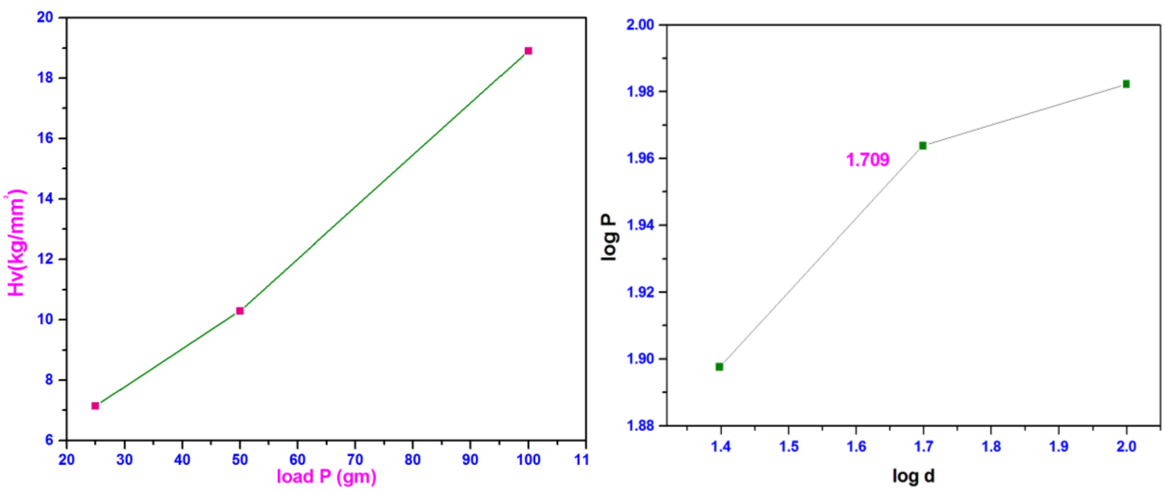

Fig.7(A) PlotofloadversusHardnessand(B) logdagainstlogpforCBAdopedwithRbCl2 crystal

Onitsch pointed out that n lies between 1 to 1.6 for hard materials and it is more than 1.6 for soft materials [20]. The n value for the tittle compound is 1.709which reveals that the grown CBA crystal doped with $RbCl_2$ is soft. Theyieldstrengthisfoundtobe476.2016Mpa.

3.7 Dielectricstudy

Dielectric study of the grown crystal was carried out to an accuracy of ±2°C using an LCRZ meter with five different frequencies, viz. 100 Hz,1 KHz, 10 KHz, 100 KHz and 1 MHz at various temperatures ranging from 30°C to 150°C. The variation of dielectric constant on various frequencies at different temperatures is shown in Fig. 8.

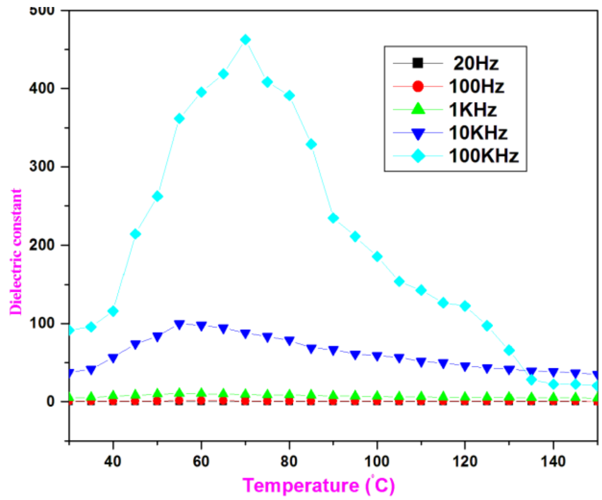

Fig.8Variation of dielectric constant with temperature at different frequencies

The dielectric constant is strong at low frequencies and gradually falls as frequency increases. The local electron displacement caused by the electronic exchange of ions in the direction of the applied field led to polarization[21]. All types of polarisation, including electronic, ionic, orientational, and space charge polarisations, contribute to the high dielectric constant at low frequencies. After a certain point, the space change cannot continue as frequency rises, and the dielectric constant begins to fall. Figure 9 shows how dielectric loss (tanδ) varies with temperature at various frequencies. Graph is similar to dielectric constant graph, as frequency increases dielectric loss gradually decreases. Crystal possesses enhanced optical quality with lesser defects, which is an essential factor for the fabrication of NLO device[22].

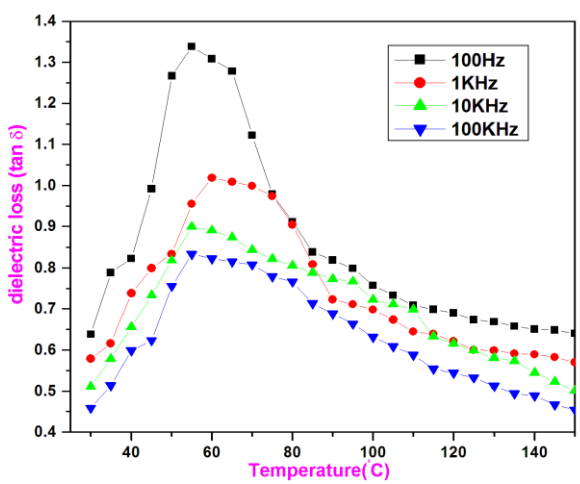

Fig.9VariationofdielectriclosswithtemperatureatdifferentfrequenciesforCBA crystal doped with $RbCl_2$

3.8 ThermalAnalysis

Thermo- gravimetric and Differential Thermogravimetric analysis (DTA) is used to studyvarious stages of decomposition and melting point. CBA crystal doped with $RbCl_2$ was heated in an alumina crucible in nitrogen atmosphere at the flow rate of 20 ^{0}C/min.A careful examination of TGA curve elucidates the occurrence of three stage weight loss pattern and it is also evident that CBA crystal doped with $RbCl_2$is stable up to 160°C as given in Table 10. The first stage weightlossisoccurredbetween160°C–260°Celiminating95%of initialmasswhichisduetotheevaporation of water molecules, ammonia and carbon dioxide. The decomposition process after 260°Cis accompanied with residual masses. The sharp DTA curve indicates that the melting point is at 260°C.

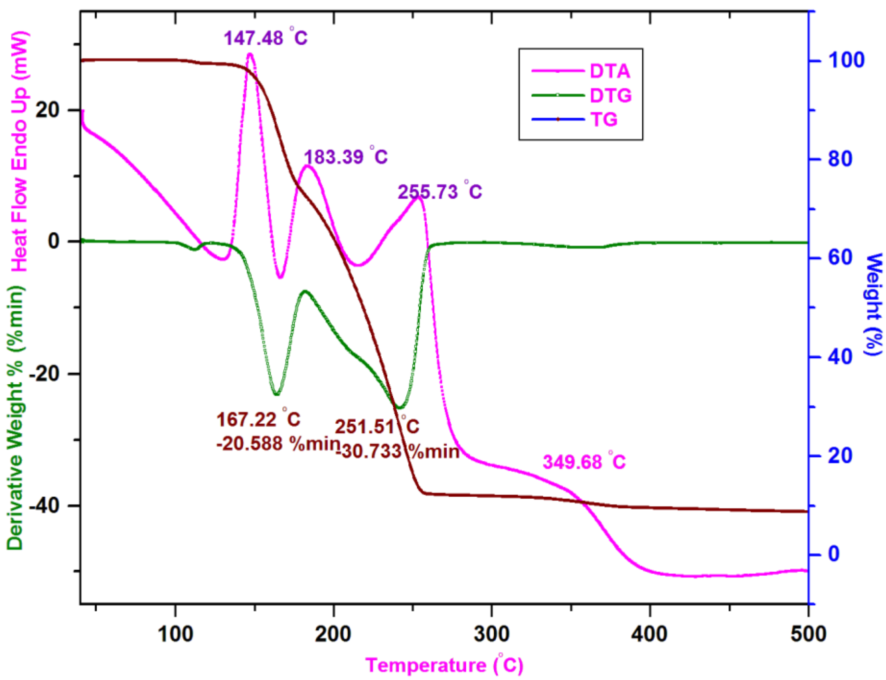

Fig.10TG/DTAspectrumofCBAdopedwith$RbCl_2$ Crystals

3.9 Non linear optical studies

The effectiveness of a nonlinear optical material in transferring energy from a fundamental beam to a second harmonic beam is explored using the Second Harmonic Generation (SHG) efficiency as a key parameter. For initial screening of materials for second harmonic generation, the Kurtz and Perry powder approach is used [23], which also identifies the materials as having a non-centrosymmetric crystal structure. For a 0.69 J input energy, a second harmonic generation signal of 12.02 mJ for CBA crystal was produced. But for the same input energy, the common KDP crystal produced a SHG signal of 17.3 mJ. Thus, it can be seen that the developed single crystal's SHG efficiency is 0.69 times more than that of a typical KDP crystal. This demonstrates how well apt the CBA crystal is for NLO applications.

4 Conclusion

The slow evaporation technique was employed to grow CBA with $RbCl_2$crystal. Using powder XRD studies the crystalline nature of the grown crystal is confirmedand its unit cell parameterswere obtained.. The fundamental vibrations were observed from the FTIR analysis. The linear optical transmittance cut off wavelength was found to be 212 nm. The work hardening coefficient and yield strength for CBA crystal have been estimated. Assignments of the vibrational bands have been done and existence of N-H…O hydrogen bonding in themolecule is shown by lowering of NH2asymmetric stretching in FT IR spectrum. This demonstrates how well apt the CBA crystal is for NLO applications.CBA doped $RbCl_2$ crystals are useful asa good non-linear material and for optoelectronics applicationsdue to low cut off wavelength and are transparent tothe entire visible region, which shows the wide window fornonlinear applications. Observed low dielectric constant andlow dielectric loss suggests that the grown crystals are suitablefor NLO applications in accordance with Miller's rule.

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