International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.5, pp 2483-2488, 2014-2015

Growth and characterization of ULMA single crystals doped with zinc chloride

B. Sivasankari[1] and P. Selvarajan[2]*

[1]Department of Physics, Kalasalingam University, Krishnankoil 626 190, India
[2]Department of Physics, Aditanar College of Arts and Science, Tiruchendur 628 216, India

Abstract: Single crystals of zinc chloride-doped urea L-malic acid (ULMA) were grown by slow evaporation technique. Many interesting results on several properties of zinc chloride impurity added ULMA single crystals have been observed and studied. Zinc chloride doping on the growth, optical, structural and hardness properties of ULMA crystals has been investigated. The functional groups were found by FTIR analysis. Powder X-ray diffraction studies confirm the diffraction planes of the grown crystals. Single crystal XRD studies reveal the unit cell parameters. The UV-visible spectrum shows the cut-off wavelength at 225 nm. The NLO property of the grown crystals was confirmed by SHG studies.
Keywords: Single crystal; solution growth; NLO; doping; SHG; FTIR; XRD.

1. Introduction

Crystalline salts of amino acid complexes have attracted considerable interest among researchers due to its wide range of applications [1,2]. Urea L-malic acid (ULMA) is one such material and few reports are available on ULMA crystal in the literature. ULMA crystal crystallizes in the monoclinic system with space group $P2_1$. The reported lattice parameters are a= 9.033(8) Å, b= 6.935(5) Å, c= 6.801(6) Å, and $\alpha=\gamma=90°$, $\beta=$ 94.67(0)° at 295 K [3-5]. ULMA crystal has a wide transmission range in the visible region and could be used as a nonlinear optical (NLO) material [6, 7]. Microelectronics needs low dielectric constant (ε_r) materials and ULMA crystal has low values of dielectric constant, and hence it can be used to reduce the RC delay, reduce power consumption, and reduce cross talk. It is reported that doped NLO materials have more advantages than undoped materials [8-12]. Urea L-malic acid (ULMA) crystal is an organic material, and if an inorganic material like zinc chloride is used as the dopant, it is expected that the physical and chemical properties of the host crystal namely, urea L-malic acid may be altered and NLO properties of ULMA crystal may be improved, and hence in the present investigation, zinc chloride-doped urea L-malic acid (ULMA) single crystals were grown by slow evaporation technique. The grown crystals were characterized by FTIR, single crystal XRD and powder XRD studies, UV transmission, hardness and SHG studies. The results obtained from various studies of zinc chloride-doped ULMA crystals are here reported and discussed.

2. Experimental Studies

2.1. Crystal growth and morphology

High-purity chemicals with deionized water were used to grow crystals by slow evaporation technique. Urea and L-malic acid were taken in 1:1 molar ratio, and zinc chloride was added in three different weight percentages of 5 wt%, 10 wt%, and 15 wt% to the solutions of urea L-malic acid. Uniform stirring was maintained and the temperature and volume were also kept constant as 307 K and 100 ml for all crystals to grow. Nuclei started to appear in the saturated solution after 21 days and crystals of size 10 x 3 x 12 mm^3, 9 x 3.5 x 16 mm^3 and 18 x 8 x 19 mm^3 have been observed after the growth period of 23 days. From these grown crystals, defect-free crystals were selected and used for the studies. Figure 1 shows the as-grown crystals of ULMA doped with different weight percentages of Zinc chloride. In our study, crystallization indicates that dopant addition of different weight percentages of zinc chloride to ULMA crystals found not to affect the prismatic faces of pure ULMA crystal. As reported in literature [5, 6], pure ULMA crystal has prismatic and platy habit. The supersaturation and stirring may be also found to affect the crystal habit.

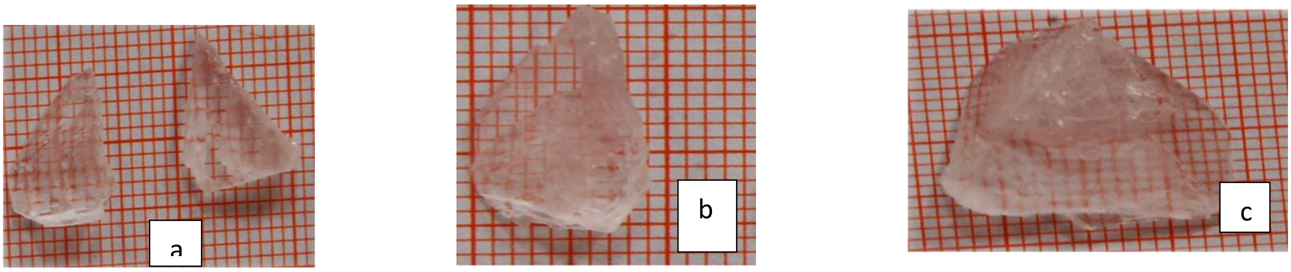

Fig.1:Photographs showing ULMA crystals doped with (a) 5 wt%, (b) 10 wt% and (c) 15 wt% of zinc chloride

2.2. Characterization Techniques

To analyse the presence of functional groups, Fourier Transform Infrared spectrum (FTIR) was recorded using a Shimadzu spectrophotometer with KBr pellet technique in the range of 4000 to 400 cm^{-1}. Single crystal X-ray diffraction data have been collected using Enraf Nonius CAD-4 Diffractometer with graphite monochromated Mo K_{α} radiation. Powder XRD pattern was recorded by employing a powder X-raydiffractometer (PANalytical multipurpose diffractometer) with nickel-filtered Cu K_{α}radiation (λ = 1.54056 Å). The UV- visible-IR transmission spectrum was recorded on a SHIMADZU UV-240 IPC spectrophotometer in the range of 190–1100 nm. Single crystals of zinc chloride-doped ULMA of thickness of 2 mm were used for this study. Vickers hardness measurements were carried out using a microhardness tester fitted with a diamond indenter for various loads ranging from 25 to 200 g. Several trials of measurements were made on the prominent (010) face, and the average diagonal length was calculated for indentation of 5 s. Preliminary experiment was undertaken to observe secondorder nonlinear optical response, and the grown crystals were subjected to Kurtz powder test to find the nonlinear optical property [13] of laser using the first harmonics output of 1064 nm with pulse energy of 4.6 mJ. KDP was used for calibrating the SHG intensity.

3. Results and Discussion

3.1. FTIR Analysis

FTIR spectrum of the grown 5 wt% of zinc chloride-doped ULMA crystal is shown in Figure 2. By the interpretation of FTIR spectra, it is possible to show that certain functional groups are present in the material. Intense band in the range of 3786.10–3157.04 cm^{-1} is due to stretching vibration from amino groups. An intense band in the range of 1885.03–1638.53 cm^{-1} is due to carbonyl stretching vibration. The addition of zinc chloride to ULMA crystals can make a small change in the hydrogen bonding in the crystals. The functional groups of the sample were identified using the FTIR spectrum. The packing of ULMA in crystalline state is very peculiar due to hydrogen bonds as studied by E.de Matos Gomes et al. [7,14].

3.2. Single X-Ray diffraction studies

X-ray diffraction (XRD) was used for the identification of the crystal. The grown zinc chloride-doped ULMA single crystals were subjected to single crystal XRD studies. The obtained values of cell parameters for 5 wt% of zinc chloride-doped ULMA crystal are a = 9.029(1) Å, b = 6.925(1) Å, c = 6.805(2) Å, $\alpha = \gamma$ =90.00(0)^0, β =94.62(2)°, V = 424.11 (Å)^3 and for 10 wt% of zinc chloride-doped ULMA crystal are a = 9.064 (2) Å, b = 6.834(5) Å, c = 6.928(4) Å, $\alpha = \gamma$ =90.00(0)^0, β =95.61(1)°, V =427.08 (Å)^3 and for ULMA crystal and for 15 wt% of zinc chloride-doped ULMA crystal, a = 9.017(6) Å, b = 6.913(5) Å, c = 6.837(2) Å, $\alpha = \gamma$ =90.00(0)^0, β =94.89(2)°, V = 424.63 (Å)^3. It is observed from the results that the grown zinc chloride-doped ULMA single crystals crystallize in the monoclinic system and a small variation is noticed in the values of the lattice parameters of doped ULMA crystals as compared to those of undoped ULMA crystal as reported in the literature [3, 4].

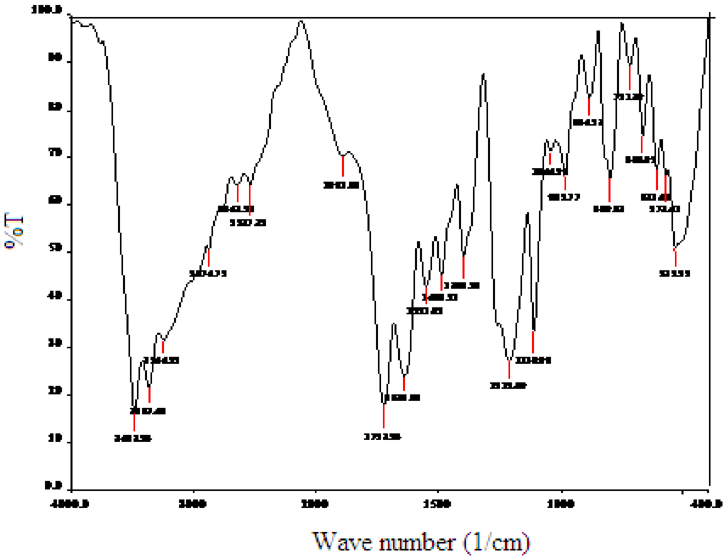

Fig.2: FTIR spectrum of zinc chloride doped ULMA crystal

3.3. Powder X-Ray diffraction studies

Single crystal XRD studies give the values of unit cell parameters of the samples. To confirm the obtained values of unit cell parameters, powder XRD studies were carried out for the samples of this work. Also powder XRD studies will give ideas of direction planes of the crystals. Figure 3 shows the powder XRD spectra of the grown samples, and all the observed reflection peaks were indexed. Using the powder XRD data, the lattice parameters were obtained with the help of UNITCELL software package, and it is found that the lattice parameters obtained from the powder XRD studies are very close to those obtained from single crystal XRD studies. The slight shift of the peaks in powder XRD patterns of the doped samples comparing that of pure ULMA crystal indicates that the dopant has entered into the lattice of the host crystal [15].

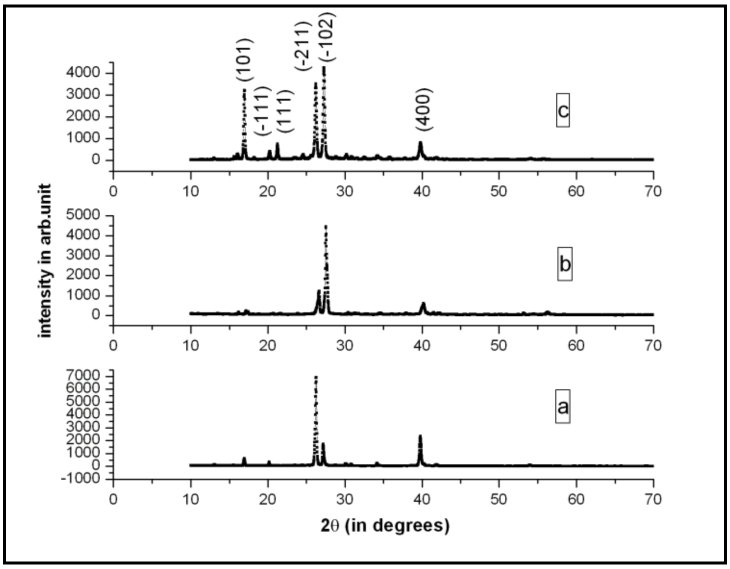

Figure 3: XRD patterns of the grown zinc chloride doped ULMA samples, a) 5 wt% of zinc chloride doped ULMA, b) 10 wt% of zinc chloride doped ULMA, c) 15 wt% of zinc chloride doped ULMA

3.4. Optical Transmission Studies

The UV-visible transmission spectrum of the grown samples was shown in Figure 4. For all optical applications in general and especially for SHG the material considered must be transparent in the wavelength region of interest. All crystals of zinc chloride-doped ULMA can be utilized for second harmonic generation in visible wavelengths since the transparency is good in that range. The transmittance increases in the visible region by 40%, 44%, 52% for the zinc chloride-doped ULMA crystals with doping concentration of 5, 10, 15 wt% respectively. This shows that the zinc chloride as impurity has not destroyed the optical transparency of the crystal, and it is found to suppress the inclusions and improves the quality of ULMA crystal with higher transparency range. The lower cut off wavelength which corresponds to the fundamental absorption occursat 225 nm for different weight percentages of zinc chloride-doped ULMA crystals. The short cut off wavelength facilitates the grown crystals of this work to be potential nonlinear optical materials for second harmonic generation.

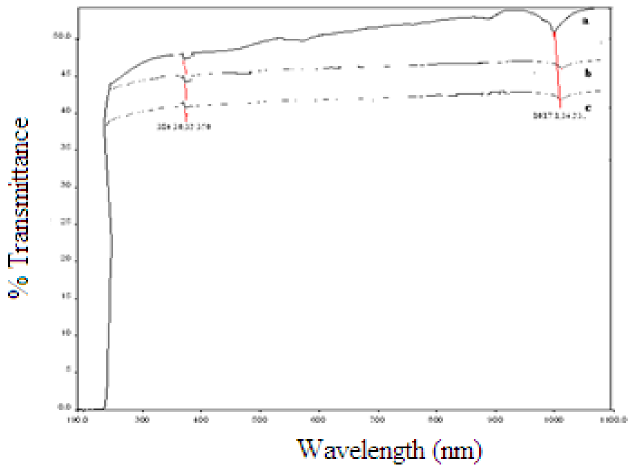

Fig.4: UV-visible spectra for zinc chloride doped ULMA crystals

3.5. Microhardness Studies

Vickers hardness number was evaluated from the relation $H_v = 1.8544\ P/d^2\ kg/mm^2$, where H_v is Vickers hardness number, P is the indenter load in kilograms, and d is the diagonal length of the impression in millimetres [16]. Figure 5 shows the variation of microhardness values with applied load for the samples. Microhardness values found to be increasing with increase of load. For loads above 100 g, cracks developed on the surface of the crystal due to release of internal stress generated locally by indentation. It was observed that microhardness values of zinc chloride-doped ULMA crystals are higher than that of pure ULMA crystal. The results indicate that the mechanical properties of pure ULMA crystal could be increased by doping of zinc chloride as impurity.

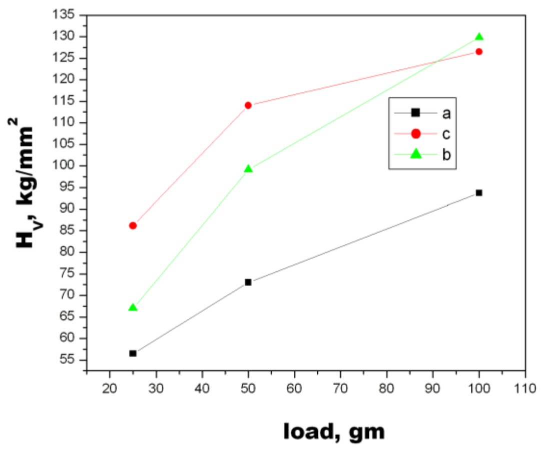

Fig.5: Variation of hardness number with load for (a) ULMA crystal doped with 5 wt% of zinc chloride, (b) ULMA crystal doped with 10 wt% of zinc chloride and (c) ULMA crystal doped with 15 wt% of zinc chloride

3.6. Nonlinear Optical Test

The nonlinear optical test (NLO) was carried out for the samples. The second harmonic generation (SHG) is found to be appreciably increased as 2.5, 2.55, 2.77 times of urea by the addition of 5, 10, 15 wt% of zinc chloride as impurity into ULMA single crystal. The dopant zinc chloride is an inorganic material, and if it is added into the lattice of ULMA, it is possible that the dopant may neutralize the OH group of ULMA, and this might be the cause of the enhanced second harmonic generation (SHG) efficiency. If OH group of ULMA crystal is neutralized by doping zinc chloride, the electron delocalization will be more in the doped samples, and this leads to enhancement of NLO property in the zinc chloride-doped ULMA sample [17].

4. Conclusion

ULMA crystals doped with zinc chloride as dopant were grown and the morphology changes were noted. Grown crystals were characterized by single crystal and powder XRD studies and they confirmed that all the grown crystals belong to monoclinic system. Improvement in the optical transmission percentage and mechanical strength has been observed with ULMA crystal due to zinc chloride as impurity addition. The improved nonlinear optical properties of zinc chloride-doped ULMA crystal proved it as a promising material for nonlinear applications.

Acknowledgement

The supports extended in the research by Indian Institute of Technology (Chennai), Crescent Engineering College (Chennai), Cochin University (Cochin) and St.Joseph's College (Trichy) are gratefully acknowledged. Also the authors are thankful to the management of Aditanar College of Arts and Science, Tiruchendur and the management of Kalasalingam University, Krishnankoil for the encouragement given to us to carry out the research work.

References

1. A. S. J. Lucia Rose, P. Selvarajan, and S. Perumal, (2011): Growth,structural, spectral, mechanical, thermal and dielectric characterization of phosphoric acid admixtured L-alanine (PLA) single crystals. SpectrochemicaActa A., 81: 270–275.
2. S. A. Martin BrittoDhas, G. Bhagavannarayanaand S. Natarajan, (2008): Growth and characterization of a new potential NLO material from the amino acid family l-prolinium picrate. Journal of Crystal Growth., 310(15): 3535–3539.
3. V. K. Dixit, S. Vanishri, H. L. Bhat et al., (2003):Crystal growth andcharacterization of a new nonlinear optical material: urea L-Malic acid. Journal of Crystal Growth., 253(1–4): 460–466.
4. S. Moitra and T. Kar, (2008): Studies on the crystal growth and characterization of urea l-malic acid single crystals grown from different solvents. Materials Letters.,62(10):1609–1612.
5. L. Zhu, J. Zhang, D. Chen et al., (2006): Characteristics of an organic nonlinear optical material urea L-malic acid. Materials Letters.,60 (13):1740–1743.
6. A. Deepthy, S. Vanishri, et al., D. Ambika et al., (2008):Photo acoustic investigations on thermal anisotropy in urea l-malic acid singlecrystals. Materials Research Bulletin.,43 (7): 1641–1648.
7. E. de Matos Gomes, V. Venkataramanan, E. Nogueira et al., (2000): Synthesis, crystal growth and characterization of a new nonlinear optical material—urea L-malic acid. Synthetic Metals.,115 (1): 225–228.
8. P. Selvarajan, J. Glorium Arul Raj, and S. Perumal, (2009): Characterization of pure and urea-doped-glycine single crystals grownby solution method. Journal of Crystal Growth., 311 (15): 3835–3840.
9. C. Krishnan, P. Selvarajan, and S. Pari, (2010): Synthesis, growthand studies of undoped and sodium chloride-doped ZincTris-thiourea Sulphate (ZTS) single crystals. Current AppliedPhysics., 10 (2): 664–669.
10. R. J. Davey, J. W. Mullin, and M. J. L. Whiting, (1982): Habit modication of succinic acid crystals grown from different solvents. Journal of Crystal Growth., 58 (2):304–312.
11. M. SenthilPandian and P. Ramasamy, (2008):Growth and characterization of solution-grown tetra glycine barium chloride (TGBC)single crystals. Journal of Crystal Growth., 310 (10):2563–2568.
12. I. Quasim, A. Firdous, B. Want, et al., (2008): Single crystal growth and characterization of pure and sodium modified copper tartrate. Journal of Crystal Growth., 310 (24): 5357–5363.
13. K. Betzler, H. Hesse, and P. Loose, (1978): Optical second harmonicgeneration in organic crystals: urea and ammonium-malate, .Journal of Molecular Structure.,47:393–396.
14. C. J. Pouchert, Aldrich Library of Infrared Spectra, Aldrich Chemical Company, Milwaukee, USA, 3rd edition, 1981.
15. B.Sivasankari and P. Selvarajan,(2010): Characterization of urea L-malic acid (ULMA) crystals grown in water, acetone andethanol. Journal of Experimental Sciences., 1: 1–3.

16. B. Helina,P. Selvarajan, and A. S. J. Lucia Rose, (2012): Structural,optical, thermal, Mechanical and dielectrical characterizations of γ-glycine crystals grown in strontium chloride solution. PhysicaScripta., 85: 055803–055808.
17. P. V. Dhanaraj, C. K. Mahadevan, G. Bhagavannarayana, P.Ramasamy, and N. P. Rajesh, (2008) : Growth and characterization of KDP crystals with potassium carbonate as additive. Journal of Crystal Growth., 310(24): 5341–5346.

*****