Growth, spectral, hardness and dielectric studies of lithium formate monohydrate crystals

G.Emerson Robin[1], U.Sankar[2], T.Chithambarathanu[1], P.Selvarajan[3]

[1]Physics Research Centre, S.T.Hindu College, Nagercoil, India.

[2]Department of Physics, Sri KGS Arts College, Srivaikundam, India.

[3]Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, India.

Abstract

Most of the organic nonlinear optical (NLO) crystals are soft in nature, have low thermal stability, low hardness, low chemical stability and difficult to polish. To overcome these problems, a new class of organic-inorganic hybrid compounds known as semiorganic materials are considered by many researchers. A semiorganic NLO crystal has higher mechanical strength and chemical stability compared to an organic crystal. In this work, a semiorganic crystal viz. lithium formate monohydrate crystal was grown and characterized. Commercially available lithium formate monohydrate was purchased and used for the growth of crystals by slow evaporation. The harvested crystals were characterized by solubility studies, XRD studies, SHG studies, microhardness studies, LDT studies, measurement of density and melting point and dielectric studies and the results are presented and discussed.

Key words: Semiorganci crystal; single crystal; solution growth; NLO material; Charactrization; XRD; LDT; hardness; dielectric constant

1.Introduction

Nonlinear optical (NLO) crystals have the potential applications in the fields such as telecommunication, optical computing, optical information process, frequency conversion and optical data storage etc. Inorganic NLO materials possess high melting point, high mechanical strength, and high degree of chemical inertness but poor optical nonlinearity. Organic NLO materials have low melting point, low mechanical strength, high degree of delocalization due to their weak Van der Waal's and hydrogen bondings and also they have the flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high laser damage threshold values [1-4]. To consider the advantages of both organic and inorganic NLO materials, researchers concentrate on semiorganic complexes such as L-arginine phosphate, L-histidine tetrafluoroborate, L-cystine hydrochloride, L-arginine hydrochloride and the lithium compounds lithium iodate, lithium niobate and lithium tantalate etc [5-11]. Lithium formate is a semiorganic material which crystallizes in orthorhombic system and it is a non-centrosymmetric crystal [12,13]. In this work, lithium formate monohydrate crystals were grown using commercially available lithium formate monohydrate by slow evaporation method. The grown crystals of lithium formate monohydrate were subjected to various characterization techniques like X-ray diffraction (XRD) technique, Kurtz powder technique, hardness test, second harmonic generation (SHG) test, measurement of laser damage threshold (LDT), measurement of melting point and density and dielectric test etc.

2.Experimental methods

2.1 Solubility and growth

The sample used in this work is lithium formate monohydrate which is purchased commercially. The purity of the sample was further improved by re-crystallization process. Solubility study was carried out using a constant temperature bath (CTB) by gravimetrical method. The salt of the prepared sample was added step by step to 20 ml of double distilled

water in an air-tight container kept in the CTB and the stirring was continued till a small precipitate was formed at 30 ^{o}C. Then, 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of the samples water was determined. The same procedure was followed to find solubility of sample at other temperatures using the constant temperature bath. Figure 1 shows the solubility curve for lithium formate monohydrate crystal. From the graph, it is observed that the solubility of the sample in water increases with temperature, exhibiting a high solubility gradient and it has positive temperature coefficient. The figure 1 has three regions viz. supersaturated region above the curve, saturated region along the curve and undersaturated region below the curve and the solubility data will be useful to prepare saturated and supersaturated solutions at any temperature in the range 30-60 ^{o}C. In accordance with solubility data, saturated solution was prepared using double distilled water as the solvent and the single crystals of lithium formate monohydrate were grown by solution method with slow evaporation technique. The saturated solution was stirred well and was filtered and taken in a beaker for crystallization. After a period of 30-35 days, transparent crystals were harvested. During the growth period, the beaker was covered with perforated polythene paper and the growth vessel was kept in a vibration free platform.

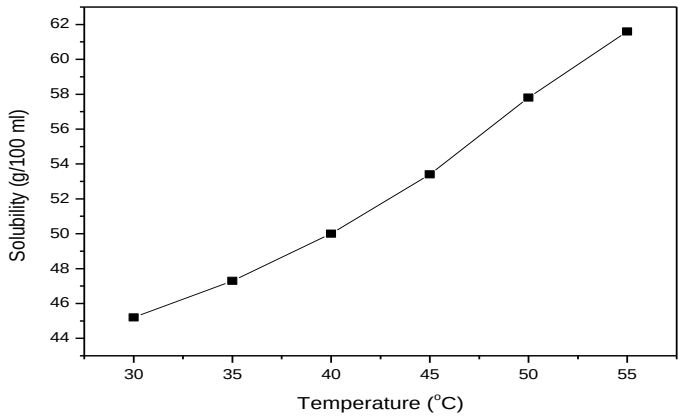

Fig.1: Variation of solubility with temperature for lithium formate monohydrate sample

3.Results and discussion

3.1 X-ray diffraction (XRD) studies

The structure of the grown crystals was identified by using a single-crystal X-ray diffractometer (Model: ENRAF NONIUS CAD-4, MoK_α (λ = 0.71069 Å) and the lattice parameters were obtained. The obtained data from single crystal XRD studies are given in the table 1. From the data, it is observed that lithium formate monohydrate crystal belongs to orthorhombic crystal system. The obtained data are found to be in good agreement with the reported data [12].

Table 1: Crystallographic data for lithium formate monohydrate crystal

Diffractometer	ENRAF NONIUS CAD-4
Radiation, wavelength	MoK_α, 0.71069 Å
Refinement method	Full matrix Least square method
Chemical formula	$CHLiO_2 . H_2O$
Molecular weight	69.97 g/mol
Crystal color	Colorless, transparent
Temperature	293(2) K
Symmetry	Orthorhombic
Space group	$Pbn2_1$
a	4.848 (2) Å
b	6.502 (3) Å
c	9.958(4) Å
α	90°
β	90°
γ	90°
Volume	333.88 (2) $Å^3$
Z	4

3.2 Measurement of density of crystals

Floatation method was used to find the density of crystals. Liquids like xylene and carbon tetrachloride were used to find the density by floatation method. A specific gravity bottle of known weight (w_1) is taken. After mixing the liquids xylene and bromoform in a suitable proportion in the specific gravity bottle, a small piece of the crystal was immersed in the liquid mixture. When the sample had attained a state of mechanical equilibrium, the density

of the crystal was equal to the density of liquid mixture. The density was calculated using the relation $(w_3 - w_1) / (w_2 - w_1)$ where w_1 is the weight of the empty specific gravity bottle, w_2 is the weight of the specific gravity bottle with full of water and w_3 is the weight of specific gravity bottle full of the mixture of xylene and carbon tetrachloride. The density of the grown lithium formate monohydrate crystal was found to be 1.402 g/cc. The density was also calculated from the crystallographic data using the relation $\rho = (M.Z)/(N.V)$ where M is the molecular weight of the material used, Z is the number of molecules per unit cell, N is Avogadro's number and V is the volume of the unit cell and it was found to be 1.391 g/cc.

3.3 Measurement of melting point

The melting point of crystal is measured using a melting point apparatus and the melting point apparatus was purchased commercially (make: TEMPO). A sensitive thermometer is used to measure the melting point of the sample. The apparatus can be used to measure the melting point of crystals upto a maximum of 300 ^{o}C. The grown crystal was kept very close to the tip of the thermometer and the temperature of the crystal is controlled using a voltage controller arrangement. The decompsition or melting point of the sample is observed using a lens and lamp arrangement which is fitted with the apparatus. The melting point or decomposition point of the grown lithium formate monohydrate crystal was found to be 95 ^{o}C.

3.4 Measurement of hardness, yield strength and stiffness constant

Hardness is an important solid state property and plays a vital role in device fabrication. Hardness, yield strength and stiffness constant are some of the mechanical constants and these properties can be determined by carrying out microhardness studies. Microhardness property was measured using a Vickers microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished lithium formate monohydrate crystal was placed on the

platform of Vickers microhardness tester and the loads of different magnitudes were applied in a fixed interval of time. The indentation time was kept 10 s for all the loads. Vickers microhardness values have been calculated by using the formula $H_v = 1.8544\ P / d^2$ kg/mm^2 where H_v is the Vickers microhardness number, P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant for the geometrical shape of diamond pyramidal indenter [14]. The variation of Vickers hardness number with a load for the grown crystal is shown in the figure 2. The result shows that the hardness increases with increase in the load and this can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample and it is called as the reverse indentation size effect. Yield strength is the maximum stress that can be developed in a material without causing plastic deformation and it is the stress at which a material exhibits a specified permanent deformation. Stiffness is the rigidity of an object and its complementary concept is flexibility. Stiffness is a measure of the resistance offered by an elastic body to deformation or pliability. Using the microhardness data, the yield strength and stiffness constant have been determined. Yield strength of the material can be found out using the relation, yield strength (σ_y) = (H_v / 3) and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material. The variations of yield strength and stiffness constant with the applied load for lithium formate monohydrate crystal are presented in the figure 3. From the results, it is observed that the yield strength and stiffness constant are increasing with increase in the applied load. As the values of yield strength and stiffness constant are high, the resistance of plastic to bending and tightness of bonding between neighboring atoms will be high and the lithium

formate monohydrate crystal has the strong binding between the ions and hence the lithium formate monohydrate crystals could be used for device fabrication.

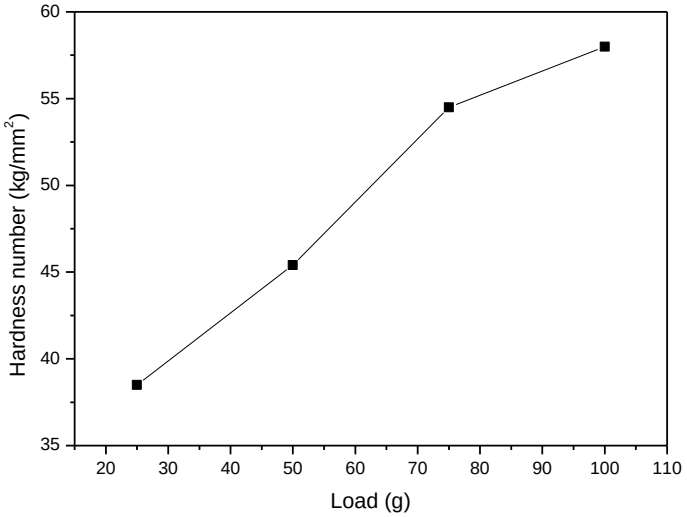

Fig.2:Load dependent hardness for lithium formate monohydrate crystal

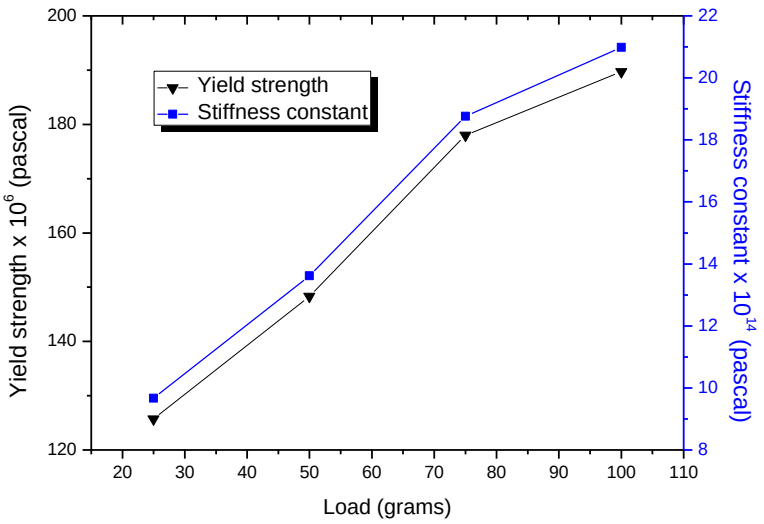

Fig.3: Variations of yield strength and stiffness constant for lithium formate crystal

3.5 Measurement of SHG efficiency

Second Harmonic Generation (SHG) is a second-order nonlinear optical (NLO) property and it was tested for the grown lithium formate monohydrate crystals using the powder technique of Kurtz and Perry [15] using a pulsed Nd:YAG laser(Model: YG501C, λ=1064 nm). The grown crystals were ground to powder of grain size 150-175 µm and the input laser beam was passed through IR reflector and directed on the powdered sample. Potassium Dihydrogen Phosphate (KDP) was used as the reference sample. The SHG behavior was confirmed by the emission of green light (λ = 532 nm) from the sample. The second harmonic generation signal of 9.85 mJ for lithium formate monohydrate crystal was obtained for an input energy of 0.68 J. But the standard KDP sample gave an SHG signal of 8.80 mJ for the same input energy. Hence, relative SHG efficiency of lithium formate monohydrate crystal is 1.12 times that of the standard KDP sample.

3.6 Measurement of LDT values

Laser damage threshold (LDT) values for the samples were measured using an Nd:YAG laser (1064 nm, 18 ns pulse width). The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). LDT value is determined using the formula $P = E/ \tau \pi r^2$ where E is the energy in mJ, r is radius of the spot in mm and τ is the pulse width. The obtained value of LDT of the grown lithium formate monohydrate crystal is 1.46 GW/cm^2. The laser damage property is nearly 7.3 times higher than other standard NLO material of potassium dihydrogen

phosphate (0.20 $GWcm^{-2}$) and the higher value of LDT could be useful for manufacturing nonlinear optical devices.

3.7 Dielectric properties

The important electrical properties of dielectric materials are dielectric constant and dielectric loss. The dielectric constant in polar materials is rarely a constant, but varies with the frequency of applied field, stress, temperature and other parameters. The capacitance and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor method at a temperature of 30 ^{o}C using an Agilent 4284A LCR meter at different frequencies ranging from 10^2 to 10^6 Hz. Using the values of capacitance without sample and with sample of the capacitor, the dielectric constant is calculated. The dielectric loss factor can be measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency for lithium formate monohydrate crystal are displayed in figure 4. It is observed that the dielectric constant has higher values at lower frequencies and further it decreases with increase in frequency and become independent at higher frequencies. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientation and a space charge polarization which is high relay upon on the frequencies. The space charge polarization is generally active at lower frequencies. It is observed that the dielectric loss decreases with the increasing of frequency. The low value of dielectric loss with high frequency for lithium formate crystal suggests that the sample possess enhanced quality with lesser defects. Lower values of dielectric constant will increase the efficiency of SHG and this is called as the Miller's rule and hence the lower value of dielectric constant at higher frequencies for lithium formate monohydrate crystal is an important parameter for the improvement of SHG coefficient [16].

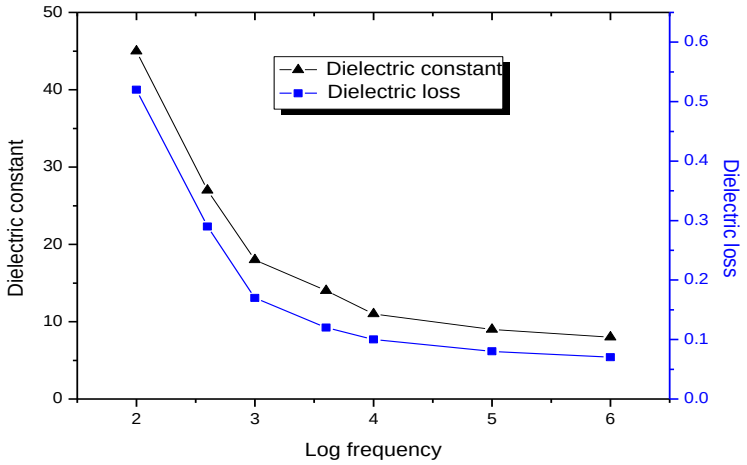

Fig.4: Variations of dielectric constant and dielectric loss with frequency for lithium formate monohydrate crystal at room temperature (30 ^{o}C)

4. Conclusion

Using the commercially available lithium formate monohydrate salt, single crystals were grown by slow evaporation technique at room temperature. The solubility of lithium formate monohydrate crystal is observed to be increasing with increase in temperature and hence it has positive temperature coefficient of solubility. The crystal structure of lithium formate monohydrate crystal is found to be orthorhombic. SHG efficiency of the sample is found to be 1.12 times that of KDP sample. Vickers microhardness studies were carried out for the grown lithium formate monohydrate crystal to determine values of hardness, yield strength and stiffness constant. The LDT value of the grown sample was found to be 1.46 GW/cm^2 and the density was found to be 1.40 g/cc. The low values of dielectric constant and loss factor, high values of SHG and LDT of lithium formate monohydrate crystal ascertain that the grown crystal could be a potential nonlinear optical material for laser applications.

Acknowledgement

The authors are thankful to the management of KGS Arts College, Srivaikundam, S.T. Hindu College, Nagercoil and Aditanar College of Arts and Science, Tiruchendur for the encouragement given to us to carry out the research work. The authors are grateful to the research staff members of St.Joseph's College, Trichy, STIC, Cochin University, Cresent

Engineering College, Chennai, VIT, Vellore, S.T. Hindu College, Nagercoil for taking the research data for our samples.

References

1. K.R. Choudhury, S. Mukhopadhyay, Chin, Opt. Lett.1 (2003)132.
2. K. J. Arun, S. Jayalakshmi , J. Min. Mater. Charact. Eng. 8 (2009) 635.
3. G. Madurambal, M. Mariyappan , S. Monojumdar , J. Therm. Anal. Calorim. 100 (2010)763.
4. S. B Monaco, L. E. Davis, S. P. Velsko, F. T. Wang, D. Eimerl, A Zalkin, J. Crystal Growth 85 (1987) 252.
5. L. N. Rashkovich, B.Y. Shekunov, J Crystal Growth 112(1991) 183.
6. M.D. Aggarwal, J. Choi , W.S.Wang, K. Bhat, R.B. Lal, A.D.Shields, J Crystal Growth (204) 1999179.
7. D.Rajan Babu, D.Jayaraman, R.Mohankumar, R.Jayavel, J. Crystal Growth 245(2002)121.
8. R. Ittyachan, P. Sagayaraj, J. Crystal Growth 249 (2003) 557.
9. U. Chatterjee, A.M. Rudra, G.C. Bhar, Appl. Phys. B 61 (1995) 489.
10. F. Laeri, R. Jungen, G. Angelow, U. Vietze, T. Engel, M. Wuïrtz, D. Hilgenberg, Appl. Phys. B 61 (1995) 351.
11. V. Gopalan, M.C. Gupta, Appl. Phys. Lett. 68 (1996) 888.
12. J. K. Mohana Rao, M. A. Viswamitra, Ferroelectrics 2(1971)209.
13. D. Joseph Daniel, P. Ramasamy, Optical Materials 36 (2014) 971.
14. A.S.J. Lucia Rose, P. Selvarajan, S. Perumal, Spectrochimica Acta Part A 81 (2011) 270.
15. S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
16. U. Von Hundelshausen, Phys. Lett. A 34 (1971) 405.