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Structural, Thermal, Impedance, FTIR and EDAX Studies of Lithium Formate Monohydrate Crystals Grown by Solution Method

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Abstract-- 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 structural, thermal, impedance, SHG studies, EDAX, FTIR studies and the results are presented here.

Key words: Lithium formate; single crystal; solution growth; NLO material; Impedance, TG/DTA; EDAX

1. INTRODUCTION

Nonlinear optical (NLO) materials play a major role in laser technology, optical communication, optical computing, optical data processing, photonics etc. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials and the stringent problems in connection with their processability, adaptability and interfacing with other materials are encountered. The additional requirements are intrinsically related to the fabrication of nonlinear integrated devices, which besides efficiently performing the expected nonlinear operation, must be miniaturized, compact, reliable and with precisely reproducible characteristics in large-scale production and long term operation [1-3]. Nonlinear optical materials are classified into organic, inorganic and semiorganic crystals. Semiorganic crystals have the advantages of both organic and inorganic NLO materials and many researchers have concentrated 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, zinc tristhiourea sulphate and lithium tantalate etc [4-10]. Lithium formate is a semiorganic NLO material which is a suitable crystal for generating visible laser light [11, 12]. This paper deals with the growth and various studies of lithium formate monohydrate crystals. The aim of this paper is to present the results of XRD, FTIR, impedance, EDAX and thermal studies.

2. GROWTH OF LITHIUM FORMATE CRYSTALS

In accordance with solubility data [13], the saturated solution was prepared using the double distilled water as the solvent and the single crystals of lithium formate monohydrate were grown by solution method with slow evaporation technique. 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 constant temperature bath to maintain the temperature of the solution constant.

3. RESULTS AND DISCUSSION

3.1 STRUCTURAL AND FTIR CHARACTERIZATION

Single crystal XRD studies were carried out using a single-crystal X-ray diffractometer (Model: ENRAF NONIUS CAD-4, MoKα (λ = 0.71069 Å) and the lattice parameters were obtained. The unit cell constants of lithium formate monohydrate crystal are a= 4.848 (2) Å, b= 6.502 (3) Å, c= 9.958(4) Å, α=β=γ= 90°. The results show that the lithium formate monohydrate crystals crystallize in orthorhombic structure. Fourier Transform Infrared (FTIR) spectroscopy is an excellent technique used to identify the functional groups, internal structure of the molecules and nature of the chemical bonds of the compounds. The infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 to 1500 cm^{-1} and all frequencies below 1500 cm^{-1} are considered to be the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule. The functional group region tends to include motions, generally stretching vibrations, which are more localized and characteristic of the typical functional groups, found in organic molecules. In the present work, the Fourier Transform Infrared (FTIR) spectra of the grown crystals were obtained using an FTIR spectrometer (Model: SHIMADZU FTIR 8400S) by KBr pellet technique in the region 4000-400 cm^{-1} (Fig.1). The broad band around 3450-3000 cm^{-1} corresponds to OH stretching mode and 1598 cm^{-1} is attributed to bending mode of water molecule. The spectral assignments for the FTIR spectrum are given in the table 1.

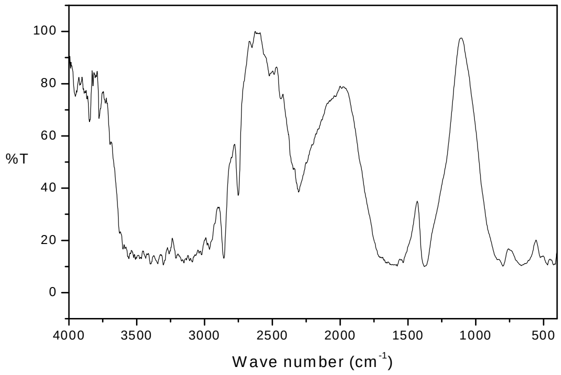

Fig.1: FTIR spectrum of lithium formate crystal

TABLE 1: FTIR SPECTRAL ASSIGNMENTS OF LITHIUM FORMATE MONOHYDRATE

WAVE NUMBER (CM^{-1})	ASSIGNMENTS
3550-3000	OH STRETCHING
2857	CH STRETCHING
2522	CH STRETCHING
1598	OH BENDING
1375	CH SYMMETRIC BENDING
803	M-O BOND
663	LIBERATIONAL MODES OF WATER MOLECULE
424	LIBERATIONAL MODES OF WATER MOLECULE

3.2 IMPEDANCE ANALYSIS

Electrical impedance describes a measure of opposition to alternating current and it extends the concept of resistance to AC circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. The impedance may be represented by its magnitude and phase in the form of a complex number representation which is more powerful for circuit analysis. Impedance analyser analyzes the a.c. response of a system to a sinusoidal perturbation and subsequent calculation of the impedance is a function of frequency of the perturbation. The frequency dependent properties of a material are often represented as complex impedance *Z** and which is related as $Z^*(\omega) = Z' - jZ''$ where Z' and Z'' are the real and imaginary components of impedance. The complex impedance of the electrode/insulator/electrode capacitor can be demonstrated as the sum of the single RC circuit with parallel combination. In this work, the measurements on impedance of the grown lithium formate crystals were carried out using an impedance analyser (Model: IM 6 ZAHNER/Germany-Electrochemical Workstation) to find the impedance, bulk resistance, grain boundary resistance, DC conductivity and relaxation time of the samples.

The variations of real part of impedance (Z') and the imaginary part of impedance (Z'') with frequencies at temperatures 30, 50 and 90 ^{o}C are shown in the figures 2 and 3. From the results, it is observed that the real and imaginary part of impedance decreases with rise in temperature and rise in frequency. The decrease of impedance of the sample with temperature gives an indication of negative temperature coefficient of resistance behavior like that of insulators. The high value of impedance at low frequency indicates low ion mobility in the grown samples and it may result in improving NLO properties of the samples. The peaks in the plots of impedance versus frequency are corresponding to relaxation process and the peak frequency is equal to relaxation frequency. The peak broadening on increasing temperature, suggests the presence of temperature dependent relaxation processes in the samples. Lithium formate monohydrate crystal seems to show the double relaxation processes corresponding to two peaks noticed in the figures 2 and 3. Due to relaxation processes in the sample, it is noticed that there are shifting of peaks to higher frequency side as temperature increases. The obtained values of relaxation frequency for lithium formate crystal are given in the table 2.

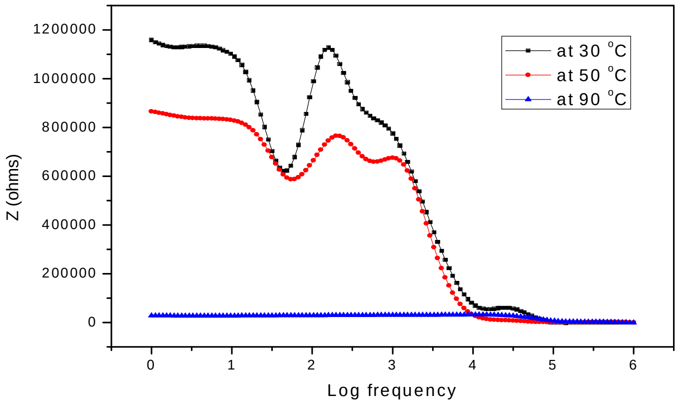

Fig.2: Plots of real part of impedance with frequency for lithium formate monohydrate crystal at different temperatures

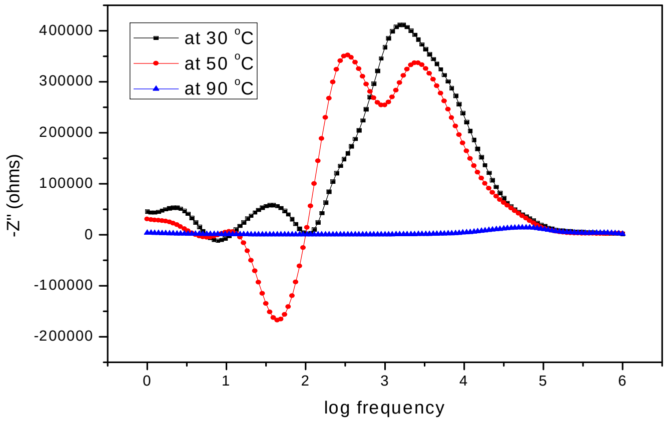

Fig.3: Plots of imaginary part of impedance with frequency for lithium formate monohydrate crystal at different temperatures

Nyquist plots for the grown crystal have been drawn between real part and imaginary part of impedance at different temperatures and they are presented in figure 4. Nyquist plots of the sample show the transport response function characteristically, one semicircular arcs and spikes and these plots reveal the presence of bulk effect, grain boundary effect of the samples. Semicircles at low frequencies are considered due to the grain boundary (blocking core) whereas the semicircles at higher frequencies depict the bulk effect. The bulk effect arises due to the parallel combination of bulk resistance and bulk capacitance of the sample.

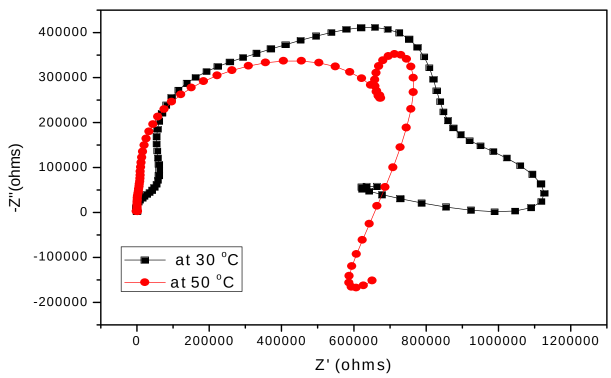

Fig.4: Nyquist's plots for lithium formate monohydrate crystal at different temperatures

The value of bulk resistance at different temperatures has been obtained from the intercept of the semicircular arc on the real axis and the value of grain boundary resistance is obtained from Z' value corresponding to the peak of the semicircle. The obtained values of bulk and grain boundary resistance of the samples are provided in the table 2. The results show that the bulk resistance and grain boundary resistance decrease with increase of temperature.

The decrease in grain boundary resistance at elevated temperatures represents the role of grain boundaries in electrical conduction process of the sample and it may be due to the lowering of barrier favoring the increase of mobility of charge carriers that adds to the conduction process [14,15].

TABLE 2: VALUES OF RELAXATION FREQUENCY, BULK RESISTANCE AND GRAIN BOUNDARY RESISTANCE FOR LITHIUM FORMATE MONOHYDRATE CRYSTAL

TEMPERATURE	RELAXATION FREQUENCY	BULK RESISTANCE	GRAIN BOUNDARY RESISTANCE
30 ^oC	950 Hz	0.95 M Ω	0.63 M Ω
50 ^oC	1100 Hz	0.66 M Ω	0.40 M Ω

3.3. MEASUREMENT OF SHG

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 [16] 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.

3.4 THERMAL STUDIES

The thermogravimetric (TG) and differential thermal analyses (DTA) curves were recorded using a thermal analyser (Perkin Elmer TG/DTA instrument). An alumina crucible was used for heating the sample and analyses were carried out in an atmosphere of nitrogen at a heating rate of 10 ^oC/min in the temperature range of 35–720 ^oC. The TG/DTA curves of lithium formate are shown in Fig. 5. In the DTA, there is an endothermic peak at 76.72 ^oC which corresponds to liberation of water molecule from the sample. The second endotherm is observed at 400 ^oC and it represents the decomposition point of the sample. This sample thermally stable upto 75 ^oC and it can be used for low temperature NLO applications.

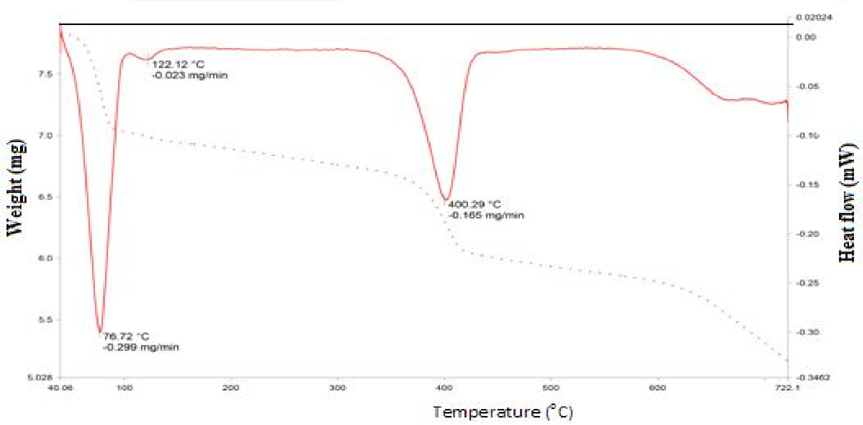

Fig.5: TG/ DTA curves for lithium formate monohydrate crystal

3.5 EDAX STUDIES

The EDAX spectrum was recorded using Jeol 6390 LV model scanning electron microscope and it is shown in the figure 6. From the results it is confirmed that the elements such as carbon and oxygen are presented in lithium formate monohydrate crystal. It is to be mentioned here that hydrogen and lithium cannot be identified from the sample by EDAX method.

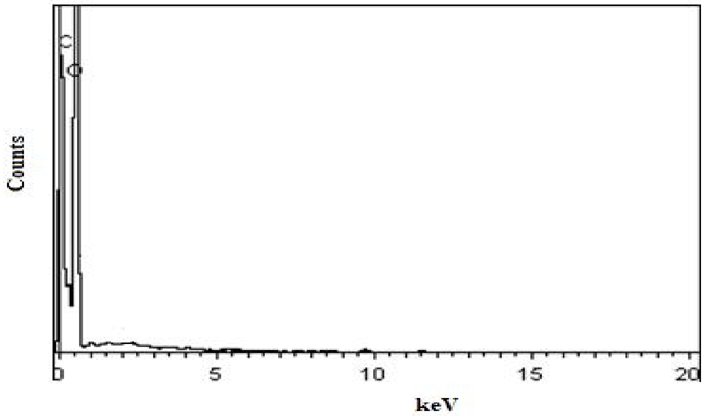

Figure 5: EDAX spectrum of lithium formate monohydrate crystal

4. CONCLUSION

Lithium formate monohydrate crystals were grown by slow evaporation technique. 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. The functional groups of the grown crystal have been identified using FTIR spectrum. The presence of elements in the sample was confirmed by EDAX analysis. The liberation of water molecule and the decomposition point were ascertained by TG/DTA studies. The impedance studies for lithium formate crystals were carried out to find relaxation frequency, bulk resistance and grain boundary resistance.

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