Growth and Characterization of Magnesium Chloride Doped L-Leucinium Oxalate Single Crystal

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Abstract

Magnesium Chloride-doped L-Leucinium oxalate (MCLO) single crystals were grown by slow evaporation technique at room temperature.The optical transmittance study was done to find various linear optical parameters such as band gap, reflectance, refractive index, absorption coefficient, extinction coefficient, optical conductivity. Impedance studies were performed for the grown crystal to understand the electrical properties. Vickers Microhardness study was carried out to find the mechanical properties such as hardness, work hardening coefficient, brittleness index and fracture toughness of the grown MCLO crystal

Keywords:Crystal growth, optical conductivity, impedance, Microhardness,Anti-bacterial Activity.

1. INTRODUCTION

Amino acid complexes are found to be important NLO materials for the development of devices. Many amino acids reveal nonlinear optical properties, owing to the presence of a donor NH_3^+ and an acceptor COO^- as well as the possibility of intermolecular charge transfer [1, 2]. Numerous studies have been recently reported on the characteristics of many amino acid complexes and interesting organic, inorganic and semi organic NLO crystalline samples have been grown and studied by differentauthors [3-5].Anbuchezhiyan et al. have grown the crystal of undoped L-leucinium oxalate and it was characterized by XRD, CHN, FTIR, NMR, NLO, optical and hardness studies [6]. Bhaskaran et al. have carried out thermal, optical and electrical properties of L-leucinium oxalate crystals [7]. In this work,L-leucinium oxalateis considered as the base material and doping of an inorganic material like magnesium Chloride was done to alter various properties of the host crystal. The growth, single crystal XRD, optical, SHG, mechanical, impedance and laser damage threshold (LDT) propertiesand anti-bacterial activities of magnesium Chloride-doped L-leucinium oxalate (MCLO) crystals are explained in this communication.

2. MATERIALS AND METHODS

The AR grade chemicals such as L-leucine, oxalic acid and magnesium Chloride with high purity were purchased. Slow evaporation method of crystal growth has many advantages like low cost, easy to grow, easy to control the rate of evaporation and re-crystallization for improving the quality of crystal and hence in this work, this method was adopted to grow magnesium Chloride-doped L-leucinium oxalate (MCLO) crystal.
The sample was prepared by dissolving L-leucine and oxalic acid in double-distilled water in a 1:1 molar ratio and 1 mole % of magnesium Chloride was added to the solution for doping. Care was taken to consider the solution was a supersaturated solution. Stirring of the solution was done by using a hot-plate magnetic stirrer for about 4 hours and then the solution was filtered using good quality Whatmann filter papers. The filtered solution was taken in a Borosil beaker covered with polythene paper containing holes for slow evaporation. Initially, seed crystals were obtained and these crystals were further purified by re-crystallization process [8]. By placing some good quality seed crystals in the supersaturated solution, bulk, big-sized crystals of MCLO crystals were obtained after the growth period of 28 days. It is observed that the grown MCLO crystal is colourless and transparent.

3. RESULTS AND DISCUSSION

3.1. UV-Vis spectral characterization

In UV-visible spectroscopy, promotion of electrons from lower state to higher energy levels occurs and hence it provides information about the molecule's structure. UV-visible spectrophotometer operates between 190nm and 1100nm and it is used to record the transmittance spectrum of MCLO crystal and the recorded spectrum is shown in figure 1. The spectrum reveals that the grown MCLO crystal's lower cut-off wavelength is 218 nm.

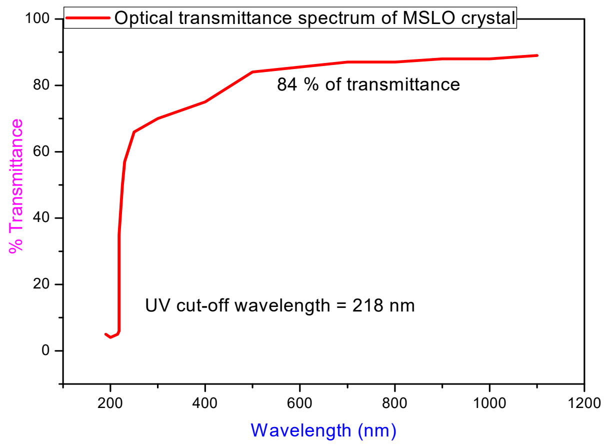

Fig. 1. UV-Vis-NIR transmittance spectrum of MCLO crystal

3.1.1. Band Gap

Using the following relation, the optical band gap (E_g)of the sample was determined.

$$Eg = 1240/\lambda$$

where λ is the wavelength of light in nm. The calculated value of band gap is 5.69 eV and this value is observed to be high. This indicates that MCLO crystal is an insulating material.The purpose of doing UV-Vis spectral study is to find the transmittance, absorption coefficient, optical band gap, extinction coefficient, optical conductivity, complex dielectric constant and linear refractive index and sample's suitability for nonlinear optical (NLO) applications [9].

3.1.2. Absorption Coefficient

The absorption coefficient (α) is estimated using the expression $\alpha = [2.303 \log (1/T)] / t$ where T is the transmittance in decimal points and t is the thickness of the crystal. The variation of absorption coefficient with wavelength for MCLO crystal is presented in the figure 2.

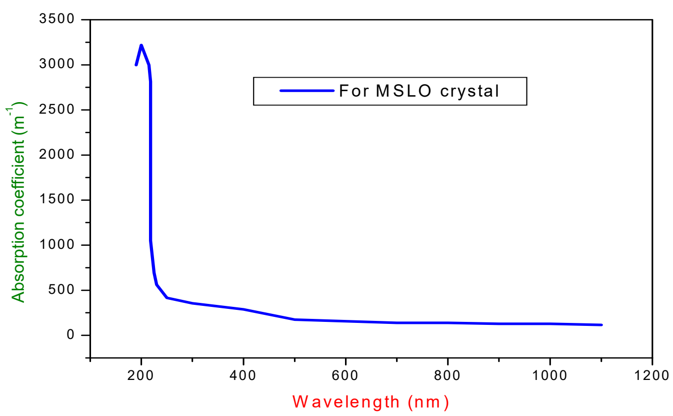

Fig. 2. Plot of absorption coefficient versus wavelength of MCLO crystal

Tauc's relation is given by

$$\alpha = \frac{A\,(h\nu - Eg)^{1/2}}{h\nu}$$

where E_g is optical band gap of the crystal, h is the Planck's constant, ν is frequency and A is a constant[10]. The plot of variation of $(\alpha h\nu)^2$versus photon energy hν is presented in figure 3. The optical band gap was evaluated by the extrapolation of the linear part to the X-axis and the value is found to be 5.70 eV and this value indicates that MCLO crystal is a dielectric material.

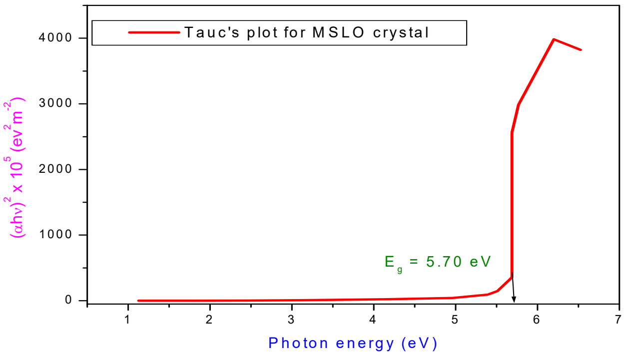

Fig.3: Tauc's plot for MCLO crystal

3.1.3. Extinction Coefficient

The extinction coefficient is the amount of light energy lost per unit thickness in a given medium due to scattering and absorption. The extinction coefficient of the grown crystal of MCLO was calculated using the relation $K = \frac{\alpha\lambda}{4\pi}$ where α is the linear absorption coefficient and λ is the wavelength of the light. Variation of extinction coefficient with wavelength is shown in the figure 4. From the figure, it is observed that the extinction coefficient is high at fundamental absorption in the UV region. In the wavelength region 500-1000 nm, the extinction coefficient increases slightly with increase of wavelength. From the result, it is found that, the extinction coefficient of MCLO crystal is very low. It shows the grown Crystal is a good optical material with very low energy loss.

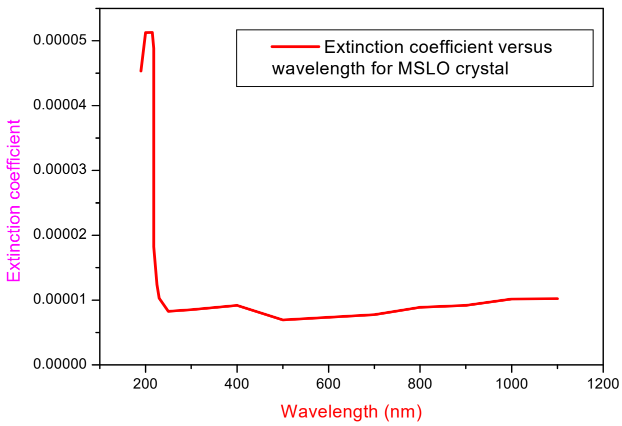

Fig.4: Plot of extinction coefficient versus wavelength for MCLO crystal

3.1.4. Reflectance

Reflectance is the amount of light energy reflected from the crystal. The expression for reflectance (R) is given below.

$$R = 1 \pm \frac{\sqrt{1 - \exp(-\alpha t) + \exp(\alpha t)}}{1 + \exp(-\alpha t)}$$

Where α is absorption coefficient and t thickness of the sample [11, 12]. The variation of reflectance with wavelength is depicted in the figure 5. The result indicates that the reflectance of the sample is low.

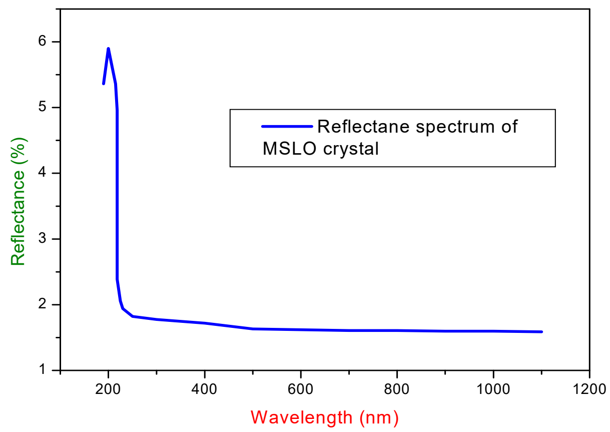

Fig.5: Reflectance spectrum of MCLO crystal

3.1.5. Linear refractive index

The linear refractive index is the ratio of speed of light in vacuum or free space to the speed of light in the medium and it is determined using the following expression.

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

Where R is the reflectance in decimal point. The plot of linear refractive index with photon energy for MCLO crystal is presented in the figure 6. In the high wavelength region, the refractive index is observed to be increasing with increase of photon energy and it is very high near the fundamental absorption region.

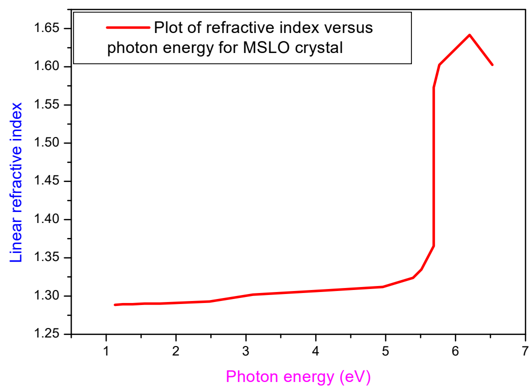

Fig.6: Variation of refractive index with photon energy for MCLO crystal

3.1.6. Optical conductivity

The optical conductivity of the grown crystal was determined using the following relation.

$$\sigma_{OP} = \varepsilon_0 \, c \, n \, \alpha$$

where c is the velocity of light in free space, α is the linear absorption coefficient, ε_o is the permittivity of free space or vacuum and n is the refractive index. As per the relation above, optical conductivity is directly proportional to absorption coefficient and hence a straight line plot is obtained in the figure 7. It is seen that optical conductivity increases as the absorption coefficient increases. The value of optical conductivity of the sample can also be calculated in Gaussian units by using the following relation

$$\sigma_{OP} = \frac{1}{4\pi\varepsilon_0} \varepsilon_0 \, c \, n \, \alpha$$

$$\sigma_{OP} = 9\times10^9 \, \varepsilon_0 \, c \, n \, \alpha$$

The above equations have been used [13] to determine the value of optical conductivity. It is shown in the figure 8.

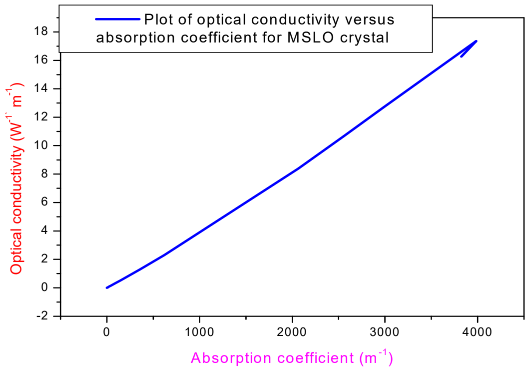

Fig.7: Plot of opticalconductivity (in SI units) versus absorption coefficient for MCLO crystal

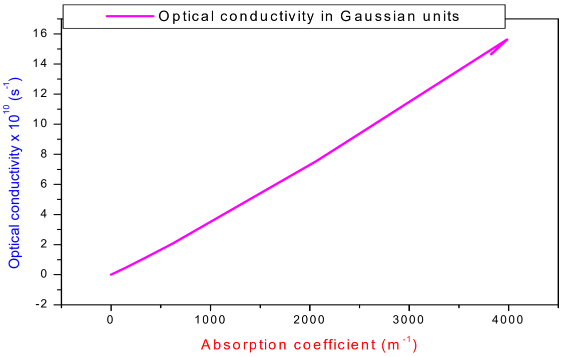

Fig.8: Plot of opticalconductivity (in Gaussian units) versus absorption coefficient for MCLO crystal

3.2. Impedance analysis

Impedance is a parameter opposition to the AC current in a sample. The complex impedance is givenby Z = Z' + jZ" where Z' is the real part of impedance, Z" is the imaginary part of impedance and j is complex parameter. The measurement of impedance provides a lot of information such as grain boundary resistance, bulk resistance, DC conductivity, electrical relaxation phenomena etc. Impedance measurement for MCLO crystal was carried out using an impedance analyser over the frequency range of 1 Hz-10^6 Hz at 30°C and 50°C. The frequency-dependent real part and imaginary part of impedance for MCLO crystal are given in the figures 9 and 10. It is noticed from the figures that,as the frequency increases, both the real and imaginary components of impedance decreases and appears to converge at the higher frequency side. This may be due to the reduction of space charge polarization. Further, as the temperature increases, the impedance values increase and this indicates that the sample has the negative temperature coefficient.

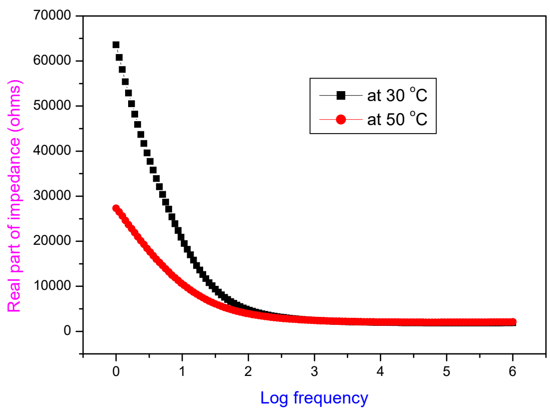

Fig.9: Variation of real part of impedance with frequency at differentTemperatures for MCLO crystal

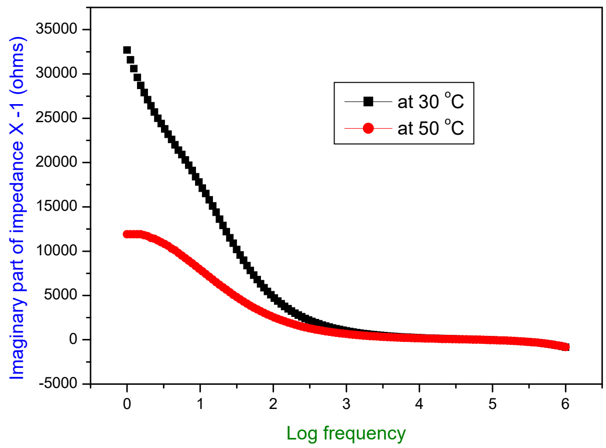

Fig.10: Variation of imaginary part of impedance with frequency at different temperatures for MCLO crystal

The Nyquist plot of the grown MCLO crystal for different temperatures is shown in figure 11. The result reveals the electrical characteristics of MCLO crystal are mostly caused by grain boundary and bulk effects [14, 15].

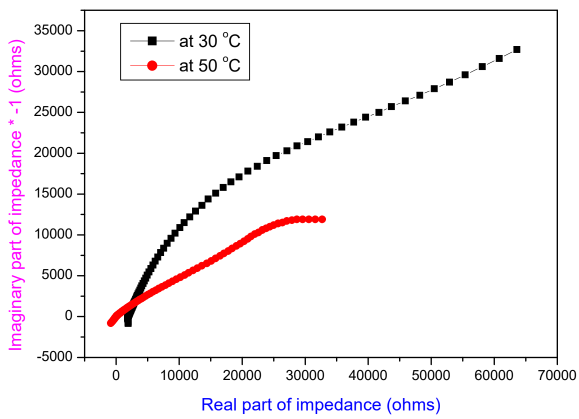

Fig.11: Nyquist plot of the grown MCLO crystal

3.3. Vickers Microhardness study

Microhardness measurement was carried out using a Vickers Microhardness indenter. Vickers hardness test comes under static indentation test method and this method is used to study the Microhardness of the grown crystals. Hardness test provides useful information on the strength and deformation characteristics of material. The most popular and simplest form is the static indentation test wherein the specific geometry is pressed into the surface of a test specimen under a known load. The indenter may be ball or diamond cone or diamond pyramid. Upon removal of the indenter, a permanent impression is retained in the specimen. The hardness is calculated from the area or depth of indentation produced by measuring the cross sectional area or the depth of the indentation. The Vickers hardness number (H_v) or Diamond Pyramid Number (DPN) is estimated using the relation

$$Hv = (1.8554\,P)/d^2$$

Where P is the applied load and d is the average diagonal length of the indented impression and 1.8544 is a constant of a geometrical factor for the diamond pyramid indenter [16]. The variations of average diagonal indentation length (d) with load (P) for the samples are shown in figure 12 and it is seen that the values of d are increasing as the applied load increases and value of d of MCLO crystal is observed to be less compared to that of undoped L-leucinium oxalate crystal.

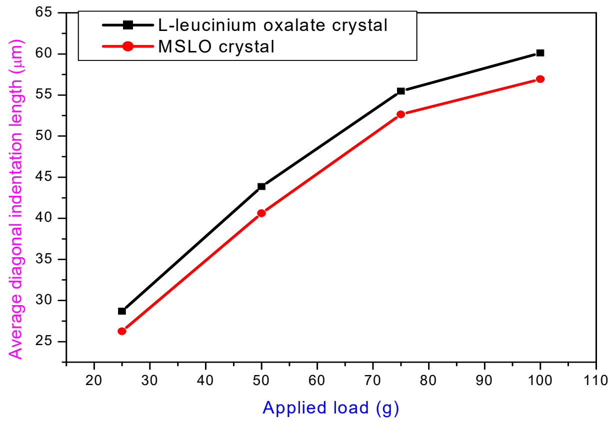

Fig.12: Plots of average diagonal indentation length versus applied load for undoped and magnesium Chloride-doped L-leucinium oxalate (MCLO) crystal

Figure 13 shows the plots of hardness with applied load for both the samples and hardness is observed to be more for MCLO crystal compared to that of undoped L-leucinium oxalate crystal. The observed high hardness value for MCLO crystal is due to presence of magnesium Chloride in the form of ions in the lattice of L-leucinium oxalate crystal.

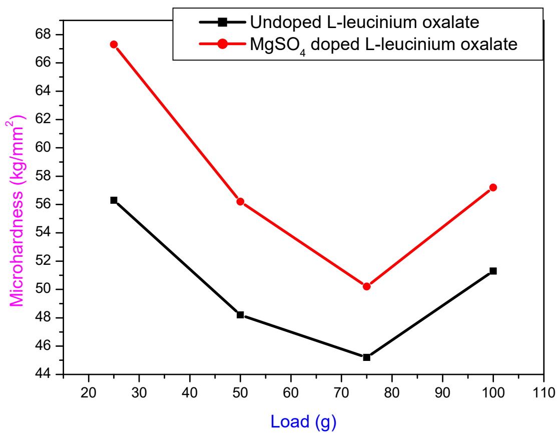

Fig.13: Plots of Microhardness versus applied load for undoped and Magnesium Chloride-doped L-leucinium oxalate (MCLO) crystal

3.3.1. Work hardening coefficient

Meyer gave a relationship between hardness and work hardening capacity of a material and is given by $P = (a \times d^n)$where a and n are constants for a given material. The value of n can be considered as a parameter representing the capacity for work hardening or Meyer's index and it may be determined experimentally by performing the test at various loads. The above relation can be written as $\log P = \log(a) + n \log(d)$ and the slope of the line plotted between log(d) and log(P) gives the value of n. The plots of between log (d) and log (P) for undoped and magnesium Chloride-doped L-leucinium oxalate (MCLO) crystals are presented in the figures 14 and 15. From the figures, the values of work hardening coefficient are found to be 2.236 and 2.517 respectively for undoped and MCLO crystals. As these values are more than 1.6, the grown crystals are confirmed to be soft category of materials [17, 18].

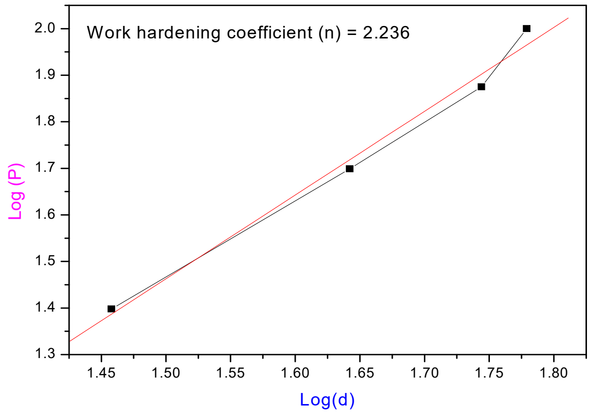

Fig.14: Plot between log (d) and log (P) for undoped L-leucinium oxalate crystal

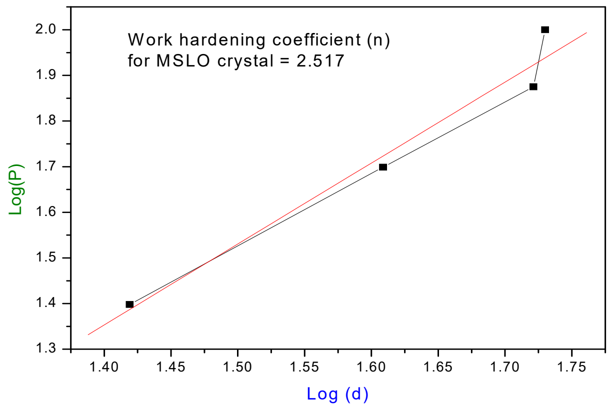

Fig.15: Plot between log (d) and log (P) for MCLO crystal

The values ofhardness, yield strength and stiffness constant are given in Table 1.

Table 1: Values of hardness, yield strength, and stiffness constant for MCLO crystal

Applied Load (g)	**Hardness (kg/mm^2)**	**Yield strength 10^6 (pascal)**	**Stiffness constant (pascal)**
10	55.10	2.422459	1.91276E+15
20	101.9	4.480010	5.60984E+15
30	137.0	6.023174	9.41687E+15
50	195.3	8.586320	17.5136E+15
70	220.6	9.698629	21.6748E+15
80	205.4	9.030364	19.1292E+15
100	187.2	8.230205	16.2623E+15

4. Conclusion

Magnesium Chloride-doped L-leucinium oxalate (MCLO) single crystals were grown by slow evaporation technique at room temperature (30 ºC). The optical transmittance study was done to find various linear optical parameters such as band gap, reflectance, refractive index, absorption coefficient, extinction coefficient, optical conductivity. The spectrum reveals that the grown MCLO crystal's lower cut-off wavelength is 218 nm. The calculated value of band gap is 5.69 eV and this value is observed to be high. The extinction coefficient increases slightly with increase of wavelength. The reflectance of the sample is low. The refractive index is observed to be increasing with increase of photon energy. Impedance studies were performed for the grown sample to understand the electrical properties. It is found that, as the frequency increases, both the real and imaginary components of impedance decreases and appears to converge at the higher frequency side. Further, as the temperature increases, the impedance values increase and this indicates that the sample has the negative temperature coefficient. Vickers Microhardness study was carried out to find the mechanical properties such as hardness, work hardening coefficient of the grown MCLO crystal. It is seen that the values of average diagonal indentation length (d) are increasing as the applied load increases and value of d of MCLO crystal is observed to be less compared to that of undoped L-leucinium oxalate crystal. Hardness is observed to be more for MCLO crystal. The value of work hardening coefficient is found to be 2.236.

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