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Research Article

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Studies on structural, mechanical, NLO and electrical properties of L-valine cadmium chloride crystals grown with different concentrations of cadmium chloride

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ABSTRACT

Singe crystals L-valine cadmium chloride by varying the concentration of cadmium chloride were grown by solution method with slow evaporation technique. Single crystal X-ray diffraction technique reveals that the grown single crystals are crystallizing in the monoclinic structure. Kurtz powder technique was used to test the nonlinear optical (NLO) activity of the samples. A Vickers hardness tester was used to test the mechanical strength of the grown crystals. Dielectric parameters like dielectric constant, dielectric loss and AC conductivity were determined for the grown crystals of different concentration of cadmium chloride added L-valine cadmium chloride and the obtained results are discussed.

Key words: Amino acid complex; single crystal; solution growth; XRD; hardness; dielectric constant; SHG; conductivity

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INTRODUCTION

Amino acids are the interesting materials for NLO application as they contain proton donor carboxyl acid (COOH) group and the proton acceptor amino (NH_2) group. Especially some amino acids like L-arginine, L-lysine, L-alanine and γ-glycine are showing NLO activity because they have a donor NH_2 group and acceptor COOH group with a possibility of charge transfer. Crystals of amino acids and their complexes are found to be the promising second order nonlinear optical materials [1-3]. Crystals of pure amino acids are the organic crystals that exhibit higher second order nonlinear coefficient, but poor in thermal and mechanical behavior. If amino acids are mixed with inorganic materials, semi-organic materials are formed and these materials have good thermal and mechanical properties with high nonlinear optical coefficient like L–histidine chloride monohydrate, L-alanine cadmium chloride and L-alanine hydrogen chloride etc.[4-6]. Among the various amino acids, L-valine ($C_5H_{11}O_2N$) is the one of the simplest aliphatic amino acids and it has aliphatic non-polar side chain and has both a primary amino group and a primary carboxyl group. The carboxylate acid group donates its proton to the amino group. So in solid state, amino acid exists as zwitterions, which create hydrogen bonds, in the form of N–H+ –O–C, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures and it is the prerequisite for an effective SHG crystal [7-9]. Maadeswaran et al reported various studies of pure L-valine cadmium chloride crystals [10]. With the aim of finding new crystals with better NLO efficiency, L–valine cadmium chloride (LVCC) crystals were grown with different concentration of $CdCl_2$. The samples considered in this work are $LV(CC)_{0.25}$ (for 0.25 mole $CdCl_2$), $LV(CC)_{0.50}$ (for 0.50 mole $CdCl_2$), $LV(CC)_{0.75}$ (for 0.75 mole $CdCl_2$) and LVCC (for 1 mole $CdCl_2$) and the grown crystals were characterized by studies like structural, mechanical, NLO and dielectric studies.

EXPERIMENTAL SECTION

Analytical reagent (AR) grade chemicals of L-valine and cadmium chloride ($CdCl_2$) were obtained from Merck India Ltd. Double distilled water was used as the solvent for the growth of L–valine cadmium chloride (LVCC) single crystals. LVCC was synthesized by reaction between L-valine ($C_5H_{11}NO_2$) and cadmium chloride and they were taken in the different molar ratios such as 1:0.25 for $LV(CC)_{0.25}$, 1:0.50 for $LV(CC)_{0.50}$, 1:0.75 for $LV(CC)_{0.75}$ and 1:1for LVCC. The calculated amounts of reactants were dissolved in double distilled water and the solution was continuously stirred for an hour maintaining the temperature of 40 ºC. After the condition of saturation was achieved, 0.1 N of HCl was added to the solutions to adjust the pH ~4.5 to 5. The prepared saturated solutions were taken in different growth vessels and the slow evaporation technique was followed to obtain the sample crystals. The growth period was about 30 days and the harvested crystals were observed to be transparent, colourless and non-hygroscopic. It is noticed that the morphology of the LVCC crystals is different when they are grown with different concentrations of cadmium chloride.

RESULTS AND DISCUSSION

3.1 XRD studies

The grown single crystals of LVCC were subjected to single crystal X-ray diffractometer with MoK_α radiation of wavelength λ = 0.717 Å to find the crystal structure. The obtained XRD data for LVCC crystal are a = 10.285 (2) Å, b = 5.622 (3) Å, c = 12.546(2) Å, α = 90°, β = 95.76°, γ = 90° V = 721.78(3) $(Å)^3$. The single crystal XRD data were taken for the samples and it is noticed that the values of lattice parameters for the grown samples are found to be almost the same and the structure is not altered when the concentration of cadmium chloride is changed in the LVCC crystals. The crystal structure for the samples is found to be monoclinic and the space group is observed to be $P2_1$. This implies that the crystal systems are non-centrosymmetric which is the primary requirement for a material to be having the second order NLO activity.

3.2 NLO studies

The nonlinear optical (NLO) property of the different concentration of $CdCl_2$ mixed LVCC crystals were confirmed by Kurtz powder technique. The determination of SHG efficiency of the crystal using powder technique was done by Kurtz and Perry [11]. Microcrystalline material of KDP was used as a comparison with the samples for the SHG experiment. The grown crystals were ground to powder and packed between two transparent glass slides. The first harmonic output of 1064 nm from Nd:YAG laser was made to fall normally on the prepared crystal with pulse width of 8 ns, 10 Hz pulse rate and 6.5 mJ energy per pulse. The emission of green radiation from the crystals confirms the existence of second harmonic generation in the crystal. The output power from the different concentration of $CdCl_2$ mixed LVCC crystals were compared to that of KDP crystal and the results are presented in Table 1.

Table 1: SHG efficiency values of different concentration of $CdCl_2$ mixed LVCC single crystals

Sample name	SHG efficiency (compared with KDP)
$LVCC_{0.25}$	1.32
$LVCC_{0.50}$	1.61
$LVCC_{0.75}$	2.06
LVVC	2.57

3.3 Microhardness studies

All the grown crystals were polished and subjected to indentation using Vickers microhardness tester fitted with a diamond indenter. Measurements were taken by varying the applied loads from 25 to 100 g (in steps of 25 g) with a dwell time of 30 seconds. Cracks were developed at higher loads (120 g); therefore the maximum applied load was restricted to 100 g. The crack formation is due to the release of internal stress generated locally by indentation. The Vickers hardness number (H_v) was determined using the average length of the diagonals by using the relation

$$H_v = 1.854\ P / d^2,$$

where d and P is an average length of diagonals in mm and applied load in kg respectively. The plot of variation of Vickers hardness number (H_v) with applied load of different concentration of $CdCl_2$ mixed LVCC crystals are shown in Figure 1. From the plot, it is noted that the hardness number (H_v) of the crystal linearly increases with increasing of load. This indicates the reverse indentation size effect (RISE). Also the hardness value increases with increasing concentration of $CdCl_2$ except LVCC crystal. Using the Meyer's law $P = A\ d^n$ (where A is the constant and n is the Meyer's index or work hardening coefficient) [12,13], the work hardening coefficients are found to be 1.627, 1.683, 1.734 and 1.892 respectively for $LVCC_{0.25}$, $LVCC_{0.50}$, $LVCC_{0.75}$ and LVCC crystals respectively.

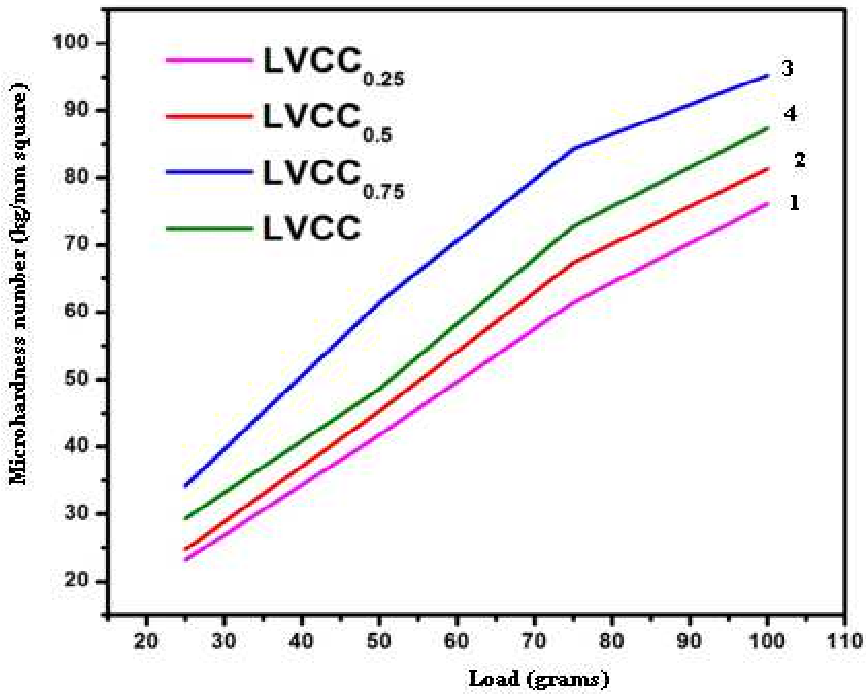

Figure 1:Dependence of hardness on load for various concentration of cadmium chloride mixed LVCC crystals

3.4 Dielectric Studies

The dielectric characteristics of the material are important to know the transport phenomena and the lattice dynamics in the crystal. It also gives the information about the nature of atoms, ions, bonding and their polarization mechanism in the material[14,15]. The dielectric properties like dielectric constant, dielectric loss and the AC conductivity of the LVCC crystals were determined to an accuracy of ± 2% using an LCR meter (Agilent 4284A) with four different frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) at various temperature ranging from 40 – 100 °C. In order to ensure good electrical contact between the crystal and the electrodes, the sample was coated with graphite and the crystal sample is introduced between the electrodes. The measurements were taken while cooling the sample. Figures 2-5 show the variation of dielectric constant with frequencies at different temperatures. Dielectric constant increases with increase in temperature. At low frequencies, the dielectric constant is found to be high and then it decreases with increasing of frequency. Also the present study indicates that the dielectric constant do not vary systematically with the concentrations of $CdCl_2$ which may be attributed to the creation of additional dipoles oriented in random directions. The high dielectric constant at low frequency is due to the presence of polarization viz. pace charge polarization. From the figure it is evident that, for LVCC crystal, the values of ε_r become almost constant in the high frequency regions and this is the normal dielectric behavior. For a normal dielectric material, the dielectric constant decreases with increasing frequency and reaches a constant value depending on the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field. Moreover increasing concentration of $CdCl_2$ decreases the values of ε_r . The materials having low dielectric constant will have less number of dipoles per unit volumes. As a result , it will have minimum losses as compared to the materials having high dielectric constant. Therefore the grown crystals may be used for high speed electro-optic modulation. Variations of dielectric loss factor with temperature at different frequencies for the samples are shown in the figures 6-9 and from the results, it is observed the dielectric loss factor increases with increase of temperature and decreases with increase of frequency. This indicates the normal behavior of dielectric materials. When the concentration of cadmium chloride in LVCC crystals is varied, the loss factor is observed to be not varying systematically.

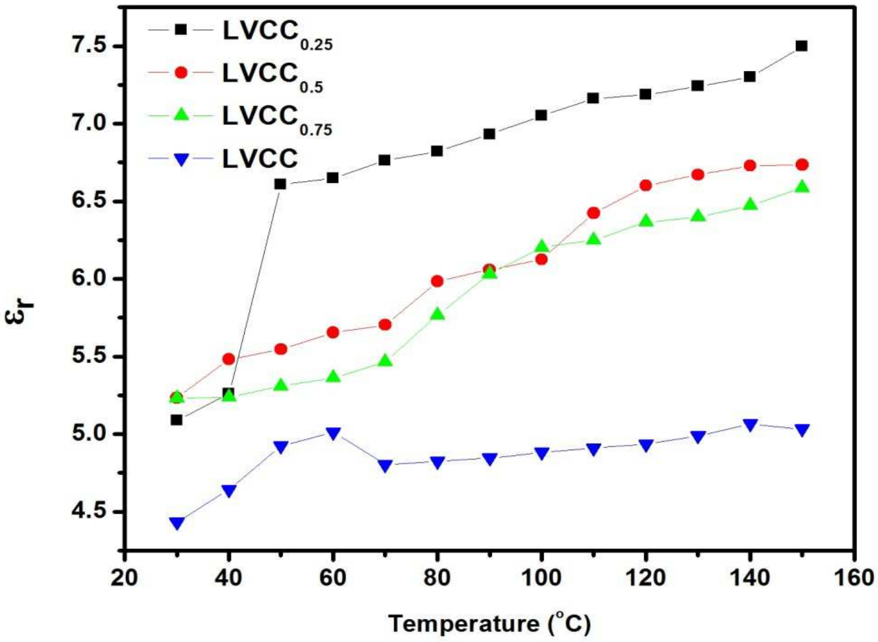

Figure 2: Variation of dielectric constant with temperature for different concentration $CdCl_2$ mixed LVCC crystals at frequency of 1 kHz

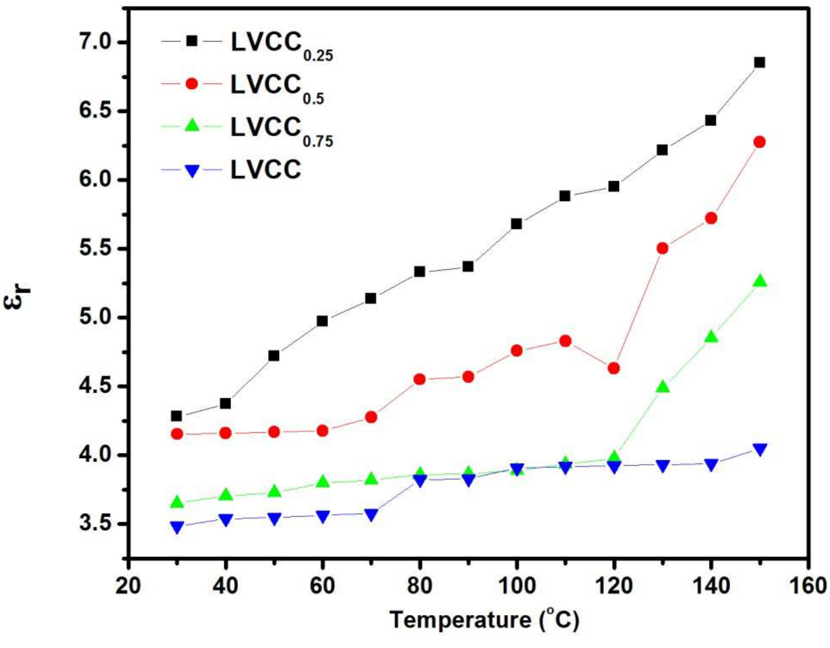

Figure 3: Variation of dielectric constant with temperature for different concentration $CdCl_2$ mixed LVCC crystals at 10 kHz

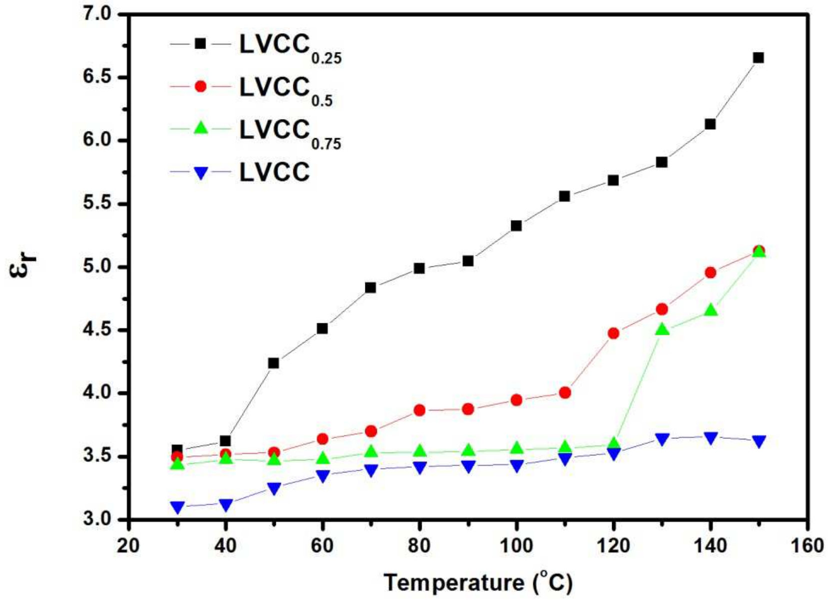

Figure 4: Variation of dielectric constant with temperature for different concentration $CdCl_2$ mixed LVCC crystals at 100 kHz

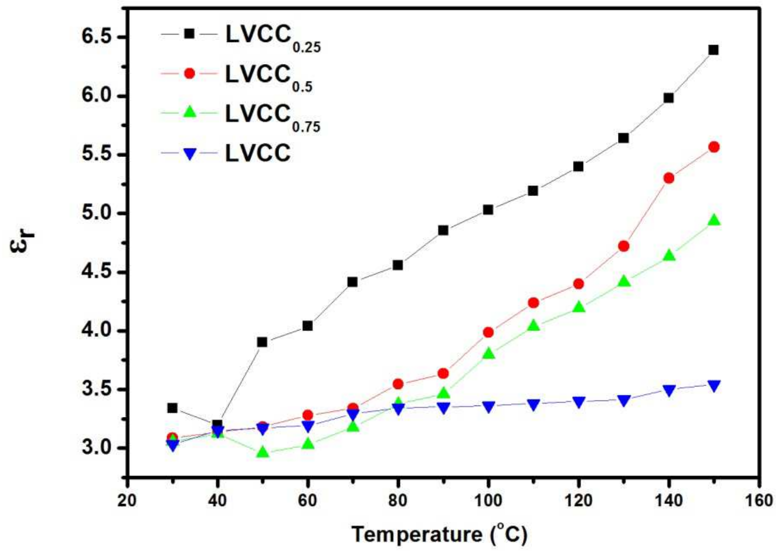

Figure 5: Variation of dielectric constant with temperature for different concentration $CdCl_2$ mixed LVCC crystals at frequency of 1 MHz

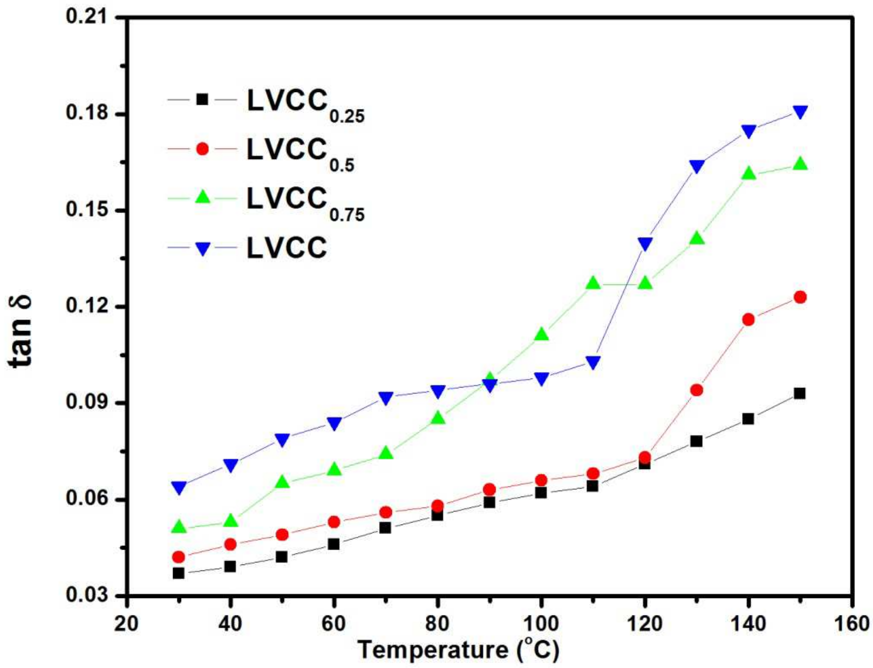

Figure 6: Variation of dielectric loss with temperature at 1kHz for LVCC crystals

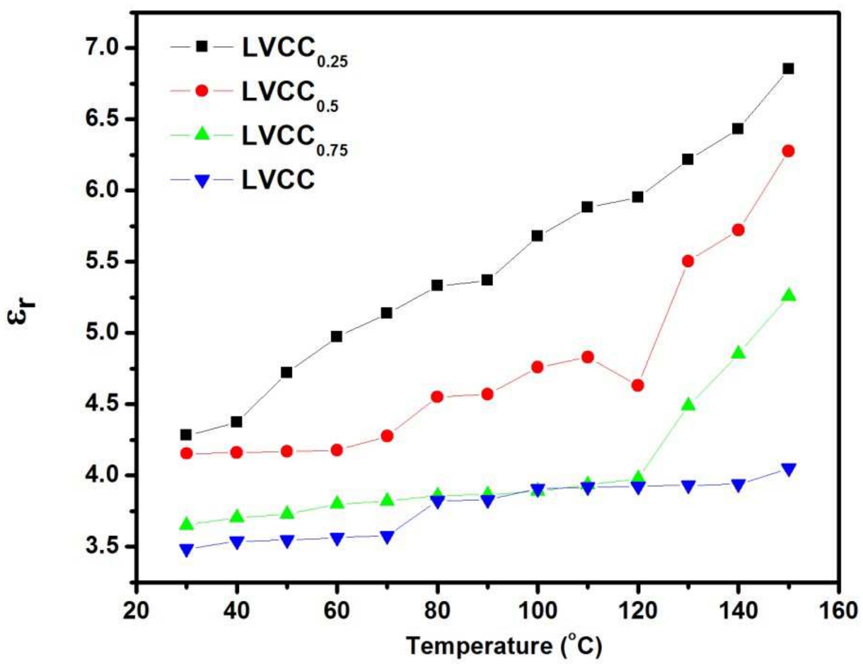

Figure 7: Variation of dielectric loss with temperature at frequency of 10 kHz for LVCC crystals

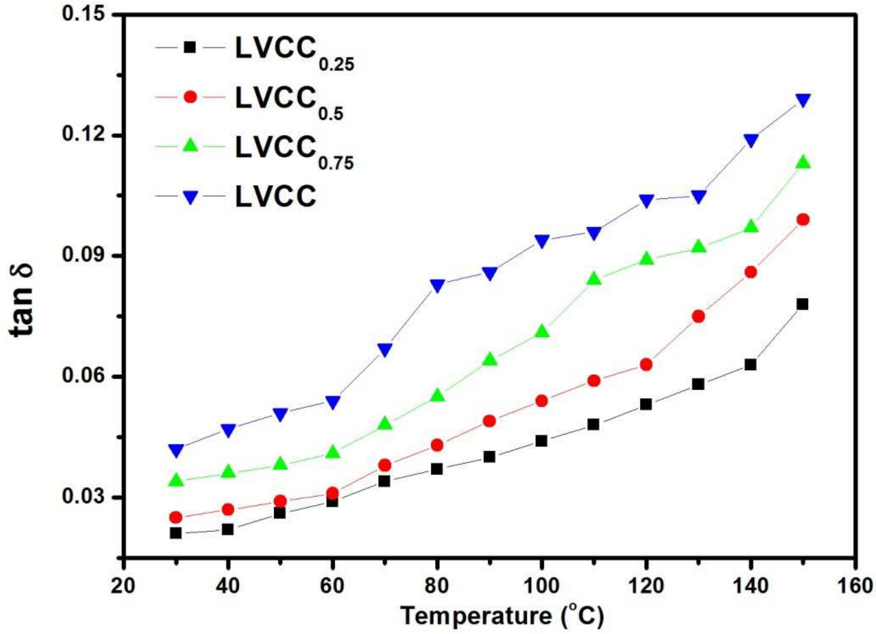

Figure 8: Variation of dielectric loss with temperature at 100 kHz for LVCC crystals

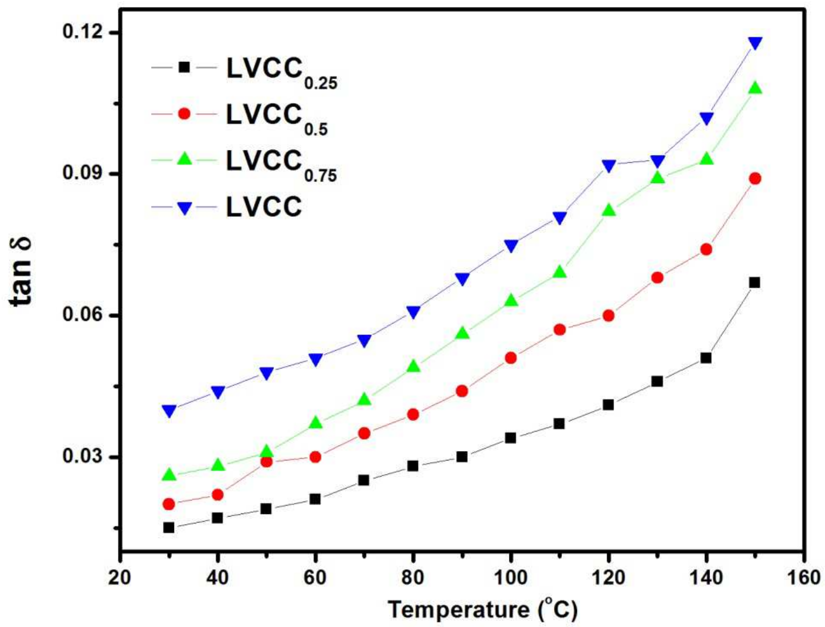

Figure 9: Variation of dielectric loss with temperature at frequency of 1 MHz for LVCC crystals

Electrical conductivity is one of the important properties of dielectrics and it is an impurity controlled process in the low temperature region and a defect-controlled process in the high temperature region. AC conductivity (σ_{ac}) of the samples can be determined using the relation $\sigma_{ac} = 2 \pi f \varepsilon_o \varepsilon_r \tan \delta$ where f is the frequency of the a.c. supply, ε_o is the permittivity of free space, ε_r is the dielectric constant and tan δ is the dielectric loss. The variations of AC conductivity with temperature for the different concentration of $CdCl_2$ mixed LVCC crystals are presented in the figures 10-13. The values of σ_{ac} increase with both frequency and temperature for the samples. When the temperature of the crystal is increased there is a possibility of weakening of the hydrogen bond. This results in an enhanced conduction in these materials. Since the AC conductivity is directly proportional to dielectric constant, frequency and loss factor, it is observed to be increasing with increase of frequency and temperature.

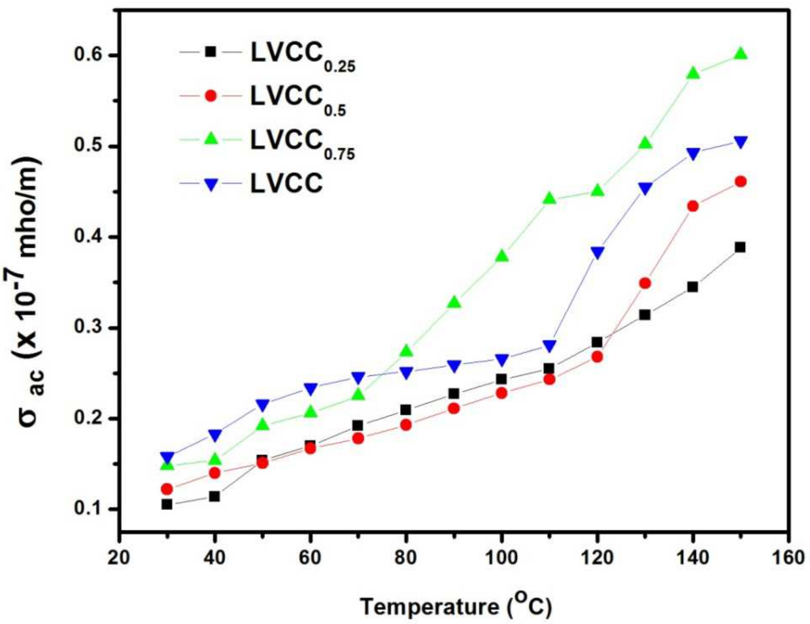

Figure 10: Variation of AC conductivity with temperature at the frequency of 1 kHz for LVCC crystals

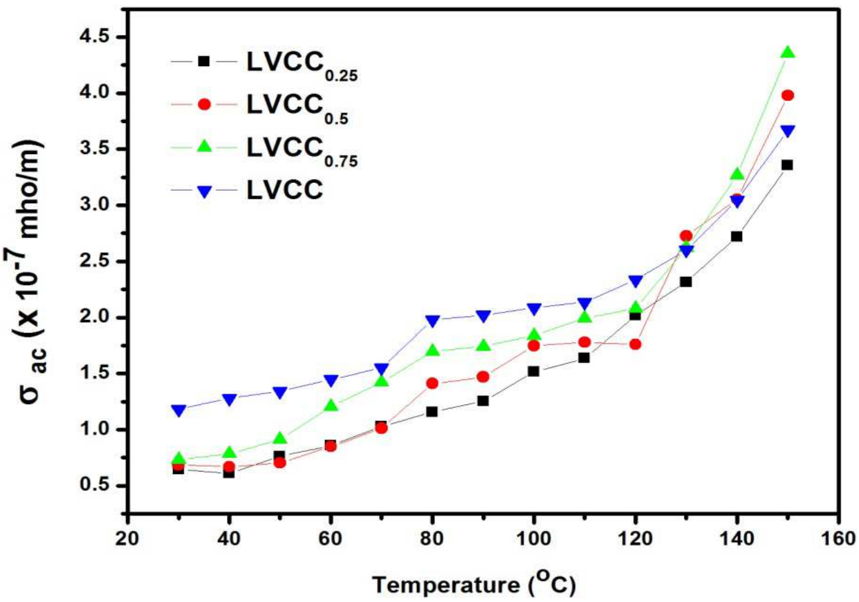

Figure 11: Variation of AC conductivity with temperature at the frequency of 10 kHz for LVCC crystals

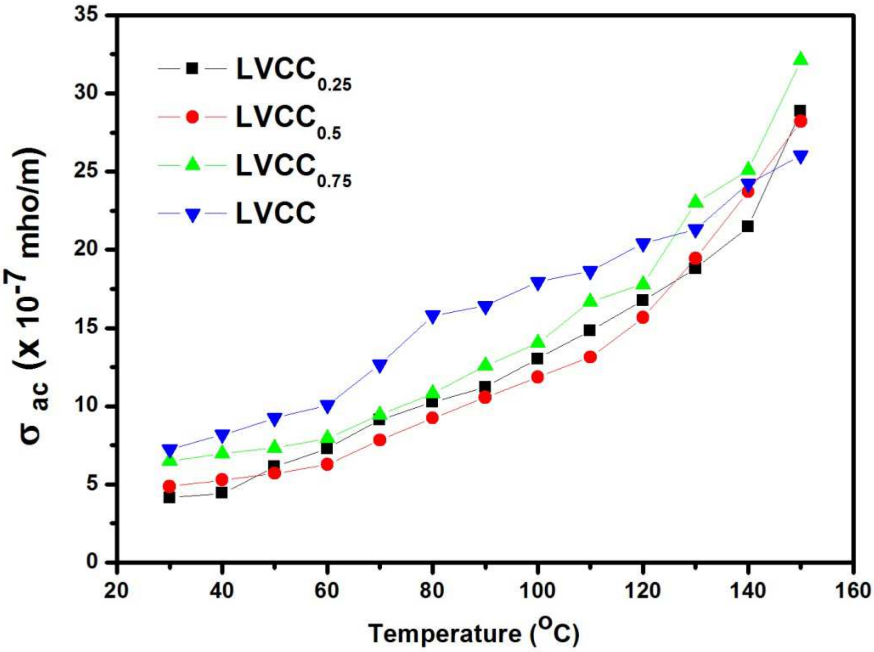

Figure 12: Variation of AC conductivity with temperature at the frequency of 100 kHz for LVCC crystals

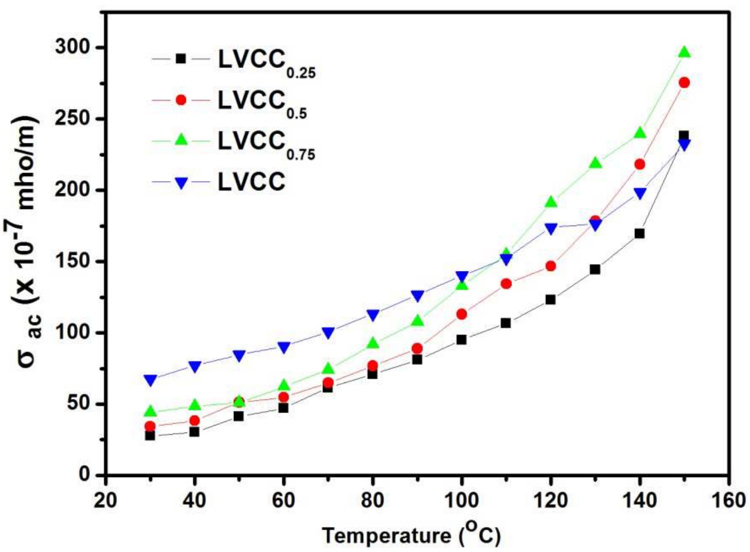

Figure 13: Variation of AC conductivity with temperature at the frequency of 1 MHz for LVCC crystals

CONCLUSION

Slow evaporation technique was used to grow the different concentration of cadmium chloride added L-valine cadmium chloride crystals. When L-valine is mixed with $CdCl_2$ in different concentrations, the morphology of the crystals is appeared to be different. The obtained crystals were subjected to XRD studies and the crystal structure of the samples is identified to be monoclinic. SHG efficiency of the grown crystals was measured in comparison with

KDP and the samples are identified to be good second harmonic generators. The dielectric constant and dielectric loss factor were measured using an LCR meter at different temperatures and frequencies and it is observed that these parameters are found to be increasing with increase of temperature and decreasing with increase of frequency. AC conductivity values were determined using the data of dielectric constant and loss factor and these values are observed to be increasing with increase of temperature and frequency. The mechanical parameters such as microhardness number and work hardening coefficient were determined and the grown crystals are found to be mechanically stable.

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