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Research Article

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Effect of L-tartaric acid on various properties of L-proline cadmium chloride crystals

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ABSTRACT

L-proline cadmium chloride (LPCC) crystals doped with L-tartaric acid were grown by solution method. Solubility was measured for the samples at different temperatures from 30 ^oC to 50 ^oC. Single crystal XRD studies have been carried out to identify the crystal structure. Microhardness was measured to find the mechanical strength of the samples. SHG efficiency and laser damage threshold (LDT) values were determined for the samples. Dielectric constant and loss factor of the grown crystals were determined at different frequencies and temperatures. Photoconductivity was measured for the undoped and L-tartaric acid doped LPCC samples by applying various electric fields.

Key words: metal organic crystal**;** doping; solution growth; XRD; SHG; laser damage; hardness; dielectric constant

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INTRODUCITON

Nonlinear Optical (NLO) materials can be classified into organic, inorganic and semiorganic NLO materials. Inorganic NLO materials possess high melting point, high mechanical strength, and high degree of chemical inertness but poor optical nonlinearity [1,2]. 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 [3,4]. To consider the advantages of both organic and inorganic NLO materials, researchers concentrate on semiorganic or metal-organic complexes in which a polarizable organic molecule is stochiometrically bonded to an inorganic host molecule. In the case of metal-organic coordination complexes, the organic ligand is usually more dominant in the NLO effect and the metal compounds have high transparency in the UV region [5,6]. Some of semiorganic NLO materials like L-arginine phosphate, L-histidine tetrafluoroborate, L-cystine hydrochloride, L-arginine hydrochloride etc have been synthesized and crystallized [7-11]. L-proline cadmium chloride is a metal-organic NLO crystal and it can be prepared by mixing L-proline and cadmium chloride in 1:1 molar ratio and it crystallizes in orthorhombic crystal system with the space group $P2_12_12_1$. Various studies of L-proline cadmium chloride (LPCC) have been reported in the literature [12-14]. To improve the physical and chemical properties of LPCC crystals, it is desired to add organic material like L-tartaric acid into LPCC host material. Tartaric acid is well known to the cosmetic and skin care industry. It is an ingredient in a variety of cosmetic and personal care products including facial moisturizers, skin toners, shampoos, hair conditioners, sun protection products and anti-aging treatments and it is used to adjust the pH of the products so it is not too acidic or basic [15]. L-tartaric acid is an isomer of tartaric acid and it is an NLO material and if it is added into LPCC crystal, it is hoped that it could improve the NLO properties. Hence, it is decided to grow and study various properties of L-tartaric acid doped LPCC crystals in this work.

EXPERIMENTAL AND INSTRUMENTATION

Growth of crystals

Undoped L-proline cadmium chloride (LPCC) salt was synthesized by taking L-proline and cadmium chloride monohydrate in the molar ratio of 1:1 and dissolved in double distilled water. The dissolved saturated solution was heated at 50 ^{o}C for the synthesis of LPCC salt. To obtain the L-tartaric acid doped LPCC salt, 10 wt% of L-tartaric acid was added into the solution of L-proline cadmium chloride. Single crystals of undoped and glycine doped LPCC were grown by solution method with slow evaporation technique using the synthesized salts. The saturated solutions of the salts were stirred well and were filtered and taken in beakers for crystallization. After a period of 25-30 days, transparent crystals were harvested. During the growth period, the beakers were covered with perforated polythene papers and they were kept in a vibration free platform. The morphology of L-tartaric acid doped LPCC crystals appears to be different when compared to that of the undoped LPCC crystal. The grown crystals were subjected to various studies for the characterization.

Techniques for characterization

Single crystal X-ray diffraction studies were carried out on the grown L-tartaric acid doped L-proline cadmium chloride by employing an ENRAF Nonius CAD-4 / MACH single crystal X-ray diffractometer, with MoK_{α} radiation (λ=0.71073 Ǻ). Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter. Indentations were made for various loads from 25 g to 100 g. Two or three trials of indentations were carried out and the average diagonal lengths were measured for an indentation time of 10 seconds. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the powdered sample of LAAP using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm [16]. The measurements of dielectric constant and dielectric loss for the grown LAAP single crystal were carried out using an LCR meter (Agilent 4284A) at various frequencies in the range 10^2 - 10^6 Hz and at different temperatures ranging from 30° to 80°C. For the good ohmic contact, opposite faces of the sample crystal were coated with good quality silver paint. Laser damage threshold (LDT) studies were carried out for the samples using a Nd:YAG laser with the wavelength of 1064 nm, 18 ns pulse width. The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200).

RESULTS AND DISCUSSION

Solubility studies

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 L-tartaric acid doped LPCC crystals. 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 30-50 ^{o}C and these data will also be useful to carry out the nucleation kinetic studies.

XRD studies

The grown crystals were subjected to single crystal XRD studies using a single X-ray diffractometer (Bruker-Nonius MACH3/CAD4) and the lattice constants were obtained. The grown undoped and L-tartaric acid doped LPCC crystals are subjected to single crystal XRD studies to identify the crystal structure. The obtained values of cell parameters for undoped LPCC crystal are a = 9.951(2) Å, b = 13.465(3) Å, c = 7.265(2) Å, $\alpha = \beta = \gamma = 90^{o}$ and those for 10 wt% of L-tartaric acid doped LPCC crystal are a = 9.984 (3) Å, b = 13.459 (2) Å, c = 7.286 (3) Å, $\alpha = \beta = \gamma = 90^{o}$ It is observed from the results that the both undoped and L-tartaric acid doped LPCC crystals crystallize in the orthorhombic system and a small variation is noticed in the values of the lattice parameters of doped LPCC crystals as compared to those of undoped LPCC crystal as reported in the literature [17].

SHG studies

Kurtz and Perry powder method is an important tool for measuring the second harmonic generation (SHG) efficiency. A laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. SHG is confirmed by emission of green light from the sample (λ= 532 nm) when the fundamental wavelength (1064 nm) from Nd:YAG laser is used. The input laser energy incident on the sample was

0.68 J. The output laser energy values from the undoped LPCC and L-tartaric acid doped LPCC samples are observed to be are 16.42 mJ and 18.57 mJ respectively and for the reference sample (KDP), it is 8.8 mJ. The relative SHG efficiency for undoped and L-tartaric acid doped LPCC samples are found to be 1.87 and 2.11 respectively and hence when LPCC crystal is doped with L-tartaric acid, the value of SHG efficiency increases.

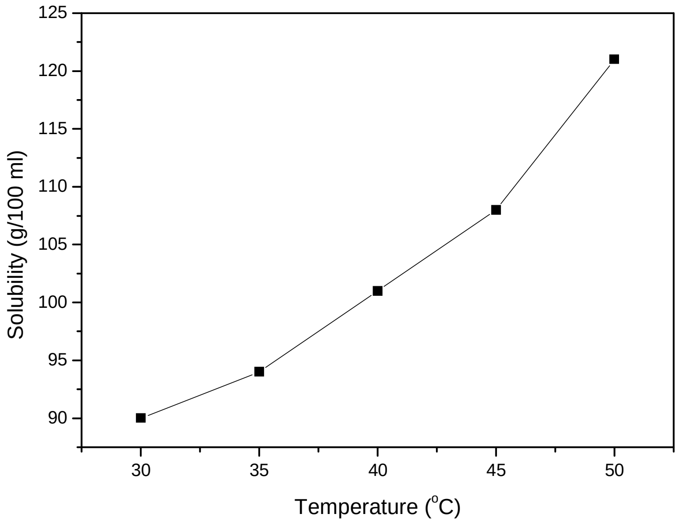

Fig.1: Solubility curve of L-tartaric acid doped L-proline cadmium chloride sample

Microhardness studies

The mechanical studies of the samples were made by Vickers hardness measurement at room temperature. Crystals, free from cracks, with flat and smooth surfaces were chosen for the static indentation tests. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 25 to100 g for a period of 10 s using Vickers diamond indenter attached to an incident ray research microscope. The Vickers hardness (H_v) number at different loads were calculated using the following relation H_v= 1.8544 P/d^2 where, 'P' is the applied load in kilogram and 'd' is the average diagonal length of the indentation marks in millimetre. The variation of hardness number with the applied load is plotted in the figure 2. The undoped and L-tartaric acid doped LPCC crystals show the reverse indentation size effect (RISE), in which the hardness value increases with the increasing load. When LPCC crystal is doped with L-tartaric acid, it is observed that the hardness increases and this increase in the hardness value of L-tartaric acid doped LPCC crystal could be due to the incorporation of the dopant in the lattice of LPCC crystal. The presence of L-tartaric acid in the interstitial positions of LPCC crystal may increase the strength of crystal bindings and hence hardness is observed to be increased.

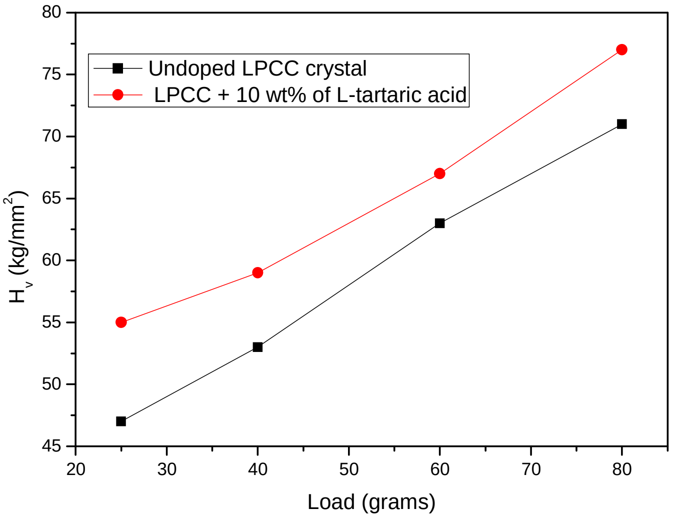

Fig.2: Plots of microhardness number (H_v) with the load for undoped and L-tartaric acid doped LPCC crystals

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, τ is the pulse width, r is radius of the spot in mm. The LDT value is one of the important device related properties of NLO crystals. The obtained values of LDT of the undoped and L-tartaric acid doped LPCC crystals are 0.37 GW/cm^2 and 0.42 GW/cm^2. From the results, it is observed that the value of laser damage threshold gets increased when LPCC crystal is doped with L-tartaric acid.

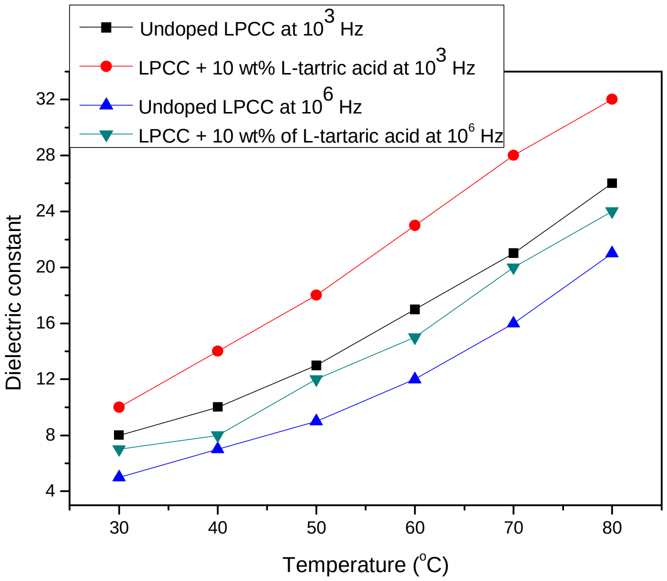

Fig.3: Temperature dependence of dielectric constant for undoped and L-tartaric acid doped LPCC crystals at 10^3 and 10^6 Hz

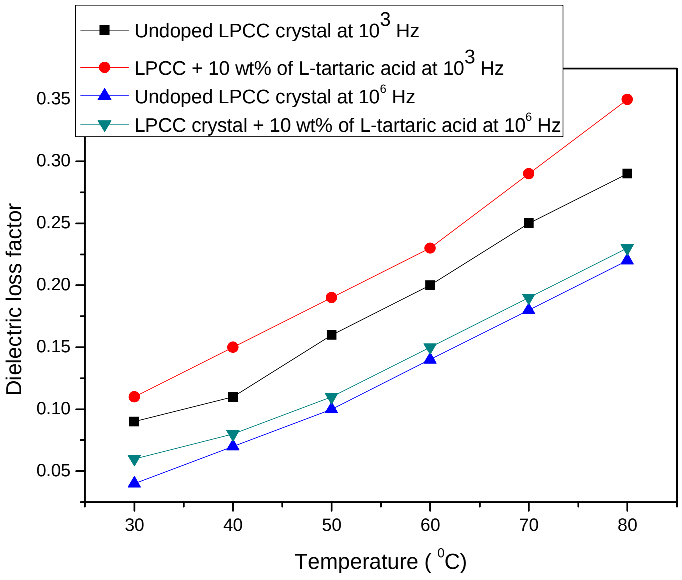

Fig.4: Temperature dependence of dielectric loss factor for undoped and L-tartaric acid doped LPCC crystals at 10^3 and 10^6 Hz

Dielectric constant and dielectric loss

The dielectric constant and the dielectric loss factor are measured at different frequencies for various temperatures using a multi-frequency LCR meter. The temperature dependence of the dielectric constant and loss factor at frequencies 10^3 and 10^6 Hz for undoped and L-tartaric acid doped L-proline cadmium chloride crystals are presented in Figs. 3 and 4. It is observed that the dielectric constant and loss factor have high values at lower frequencies and are low 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 and high temperatures [18]. The dielectric constant and loss factor are found to be increasing with increase in temperature. The low values of dielectric loss of the samples confirm the good quality of dielectric samples. The results show that values of dielectric constant and loss factor of the LPCC crystals are increased when they are doped with L-tartaric acid.

Photoconductivity studies

The photoconductivity studies for the grown crystals were carried out by measuring dark and photo currents at different applied electric fields. The variations of dark and photo currents for undoped and L-tartaric acid doped L-proline cadmium chloride crystals are shown the figure 5. It is noticed that the values of dark current and photo current increase with increase of applied electric field. The LPCC crystal has negative photoconductivity because photo current is less than dark current and the similar behavior is observed for L-tartaric acid doped LPCC crystal. The negative photoconductivity of the samples is due to reduction of charge carriers when light is passed onto the samples.

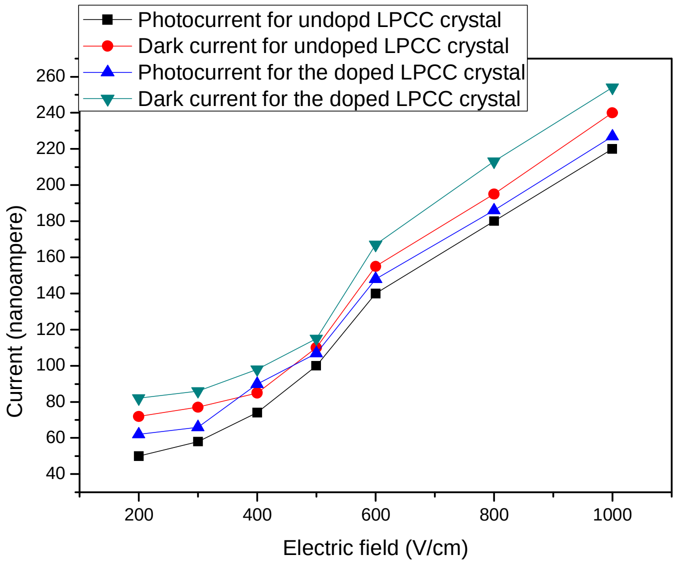

Fig.5: Variations of photocurrent and dark current with the applied field for undoped and L-tartaric acid doped LPCC crystals

CONCLUSION

Undoped and L-tartaric acid doped L-proline cadmium chloride crystals were grown by slow evaporation technique at room temperature. The solubility of the samples have been measured and it increases with increase in temperature. The XRD studies are carried out to find the crystal structure of the grown crystals. The dielectric constant and loss factor were measured for the samples at various frequencies and temperatures and these values are observed to be increasing when LPCC crystals are doped with L-tartaric acid. The hardness L-proline cadmium chloride (LPCC) crystals is observed to be increasing when L-tartaric acid is added as the dopant into LPCC crystal. The SHG efficiency of L-tartaric acid doped LPCC crystal is found to be more when compared to that of undoped LPCC crystal. The photocurrent is observed to be increasing when LPCC crystal is doped with L-tartaric acid.

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