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Structural, optical, mechanical and dielectric studies of pure and doped L-Prolinium Trichloroacetate single crystals

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HIGHLIGHTS

- Pure and metal ions doped LPTCA single crystals were grown by slow evaporation solution method.
- Co^{2+} doped crystal exhibit higher hardness than pure and Ni^{2+} doped LPTCA crystals.
- Ni^{2+} doped LPTCA crystal possesses high dielectric constant compared to pure and Co^{2+} doped LPTCA crystals.

GRAPHICAL ABSTRACT

Single crystals of (a) pure LPTCA (b) Ni^{2+} doped LPTCA (c) Co^{2+} doped LPTCA.

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ABSTRACT

In the present work, pure and metal substituted L-Prolinium trichloroacetate (LPTCA) single crystals were grown by slow evaporation method. The grown crystals were subjected to single crystal X-ray diffraction (XRD), powder X-ray diffraction, FTIR, UV–Visible–NIR, hardness, photoluminescence and dielectric studies. The dopant concentration in the crystals was measured by inductively coupled plasma (ICP) analysis. Single crystal X-ray diffraction studies of the pure and metal substituted LPTCA revealed that the grown crystals belong to the trigonal system. Ni^{2+} and Co^{2+} doping slightly altered the lattice parameters of LPTCA without affecting the basic structure of the crystal. FTIR spectral analysis confirms the presence of various functional groups in the grown crystals. The mechanical behavior of pure and doped crystals was analyzed by Vickers's microhardness test. The optical transmittance, dielectric and photoluminescence properties of the pure and doped crystals were analyzed.

Introduction

In recent years there has been considerable interest in the synthesis and growth of single crystals of new materials with large second-order optical nonlinearities, because of their potential applications in various fields including telecommunications, optical computing, optical data storage and optical information processing [1,2]. In the past decades, amino acids and their complexes based semiorganic materials were studied for different applications [3]. In recent years, amino acid group materials were mixed with organic [4] or inorganic salts [5] to enhance their chemical stability, laser damage threshold, thermal and optical properties. Many reports reveal that the mechanical and optical

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properties of the crystals are enhanced by adding small amount of impurities as dopants [6–10]. Further the selection of impurities is playing a vital role in enhancing the properties of the crystals [11]. It has been demonstrated that metal ions, specifically the transition metal ions, are the most versatile in modifying the properties of amino acid based crystals. Transition metal dopants occupy interstitial position in the crystal lattice and exhibited very good optical properties. Metal dopants like Cu (II), Ni(II), Cr(III) and Zn(II) have enhanced the net polarization which in turn modifies the properties amino acid based single crystals [7,12–14]. Therefore, in the present study, we have chosen transition metal ion dopants, Nickel and Cobalt to tune the properties of L-Prolinium Trichloroacetate. Also metal ions doped single crystals are presently getting greater attention due to the rapid development of laser diodes [15,16].

Structural, mechanical and optical properties of L-Prolinium trichloroacetate (LPTCA), one of the semi-organic single crystals, were reported [17–19]. But there are no systematic studies available on the growth of metal ions doped LPTCA single crystals. Therefore in the present work, the effect of Ni^{2+} and Co^{2+} dopants on the growth and properties of the LPTCA single crystals is reported. The crystal system of the grown crystals was confirmed by single crystal and powder X-ray diffraction (XRD) studies. Fourier Transform Infrared (FT-IR), UV–Visible–NIR, photoluminescence, hardness and dielectric studies were carried out to analyze the functional groups, optical, mechanical and electrical properties of the grown crystals.

Synthesis and crystal growth

The commercially available raw materials of L-proline and trichloroacetic acid were used to synthesize LPTCA material. Aqueous solution of LPTCA was prepared by dissolving L-proline and trichloroacetic acid in stoichiometric ratio in deionized water. The pure LPTCA crystals were grown by slow evaporation technique at 25 °C. The reaction mechanism between L proline and trichloroacetic acid in water medium is given below:

$$C_5H_9NO_2 + Cl_3CCOOH \rightarrow C_5H_{10}N^{+}O_2C_2Cl_3O_2^{-}$$

The synthesize of metal ions doped LPTCA was obtained by adding separately dopants of 0.1 mol% concentration of Nickel (II) Sulphate and Cobaltous Chloride hexahydrate to the LPTCA solution. The pure and doped LPTCA single crystals with good optical quality and well defined morphology were harvested after a growth period of 20 days. Generally, the presence of the impurities is found to have a strong influence on the growth rate [20]. Co^{2+} dopants is found to promote the growth rate than that of the dopant Ni^{2+}. Addition of higher amount of Co^{2+} dopants increases the solubility which may lead to decrease in surface energy and hence decrease in the rates of layer displacement that causes increase in the growth rate [20,21]. However in the present case the addition of Ni^{2+} into the crystalline lattice decreases the crystal growth rate and slows down the growth processing. Fig. 1a–c shows the photograph of the harvested pure, Ni^{2+} and Co^{2+} doped LPTCA crystals respectively.

Results and discussion

Single crystal XRD analysis of pure and metal ions doped LPTCA

The lattice parameters of pure, Ni^{2+} and Co^{2+} doped LPTCA single crystals are determined from single crystal X-ray diffraction studies and given in Table 1. It reveals that the lattice parameters of Ni^{2+} and Co^{2+} doped LPTCA crystal have slight deviations compared to the corresponding values of the pure crystal which may be due to the incorporation of dopants in the LPTCA crystal. The results compare well with the reported values [17].

Powder XRD analysis of pure and metal ions doped LPTCA

Powder X-ray diffraction studies of pure and metal ions doped LPTCA crystals were carried out using XPERT-PRO X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation. The samples were scanned for 2θ values from 10°–80° at a rate of 2°/min. Fig. 2 shows the powder XRD pattern of the pure and doped LPTCA. In the XRD pattern, slight shift in peak position towards lower angle side is observed for doped crystals which is due to the incorporation of dopants. The intensity of the peaks (023), (024), (124) and (331) of pure LPTCA crystal, is reduced due to metal ions doping in the LPTCA crystals. The slight change in the lattice parameter of the doped crystals and slight change in the intensity of peaks reveals the incorporation of the these ions in the crystal lattices.

Inductively coupled plasma studies

In order to calculate the exact weight percentage of metal dopants present in the LPTCA crystals, 10 mg of powder of the Ni^{2+} and Co^{2+} doped LPTCA were dissolved in 10 ml of double distilled water and subjected to inductively coupled plasma (ICP) elemental analysis. The weight percentage of the Ni^{2+} and Co^{2+} can be calculated from the equation

$$\text{Weight}(\%) = \frac{\text{ppm}\left(\frac{\text{mg}}{\text{L}}\right) \times \text{Volume in mL} \times \text{dilution factor} \times 10^{-4}}{\text{Weight of samples in grams}}$$

The experimental results are depicted in Table 2. From these results it is concluded that the amount of dopants incorporated into the host crystal lattice is very smaller compared to its original concentration in the solution.

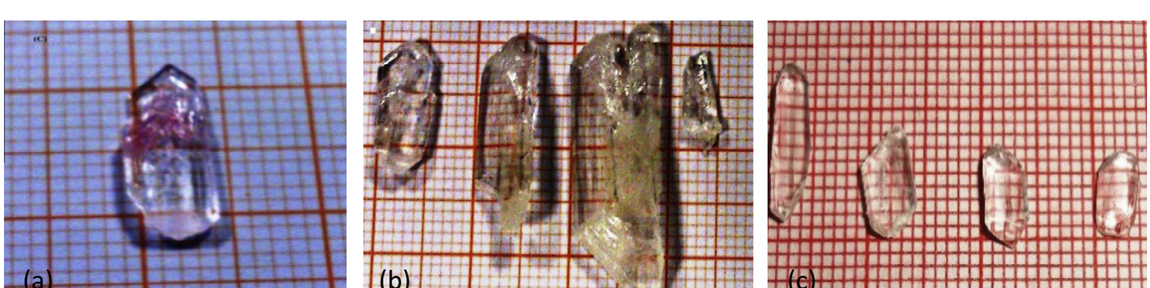

Fig. 1. Grown single crystals of (a) pure LPTCA (b) Ni^{2+} doped LPTCA (c) Co^{2+} doped LPTCA.