Research Article

Growth and Characterization of Pure and Doped L-Alanine Tartrate Single Crystals

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Single crystals of pure and Lanthanum doped L-Alanine Tartrate were grown by slow evaporation method. The cell parameters were determined using single crystal X-ray diffraction method. To improve the physical properties of the LAT crystal, Lanthanum dopant was added by 2 mol%. ICP studies confirm the presence of Lanthanum in the grown LAT crystal. Transparency range of the crystal was determined using UV-VIS-NIR spectrophotometer. The functional groups of pure and doped LAT crystals were analyzed by FT-IR spectroscopy. Using Vickers microhardness tester, mechanical strength of the material was found. Dielectric studies of pure and doped LAT single crystals were carried out. The doped LAT crystal is found to have efficiency higher than that of pure LAT crystal.

1. Introduction

In recent years organic nonlinear optical (NLO) crystals have attracted much attention for their large nonlinear coefficient, high laser damage threshold [1, 2]. However, most of organic NLO materials have poor mechanical and thermal properties, resulting in the damage of crystal during processing. To avoid this drawback, a new type of NLO material has been grown from organic-inorganic complexes. These semiorganic materials have high optical nonlinearity of a purely organic compound combined with the mechanical and thermal properties of inorganic materials [3]. Amino acids have attracted a wide interest of the researchers, since all the compounds in the class consist of an optically active property. Thus, amino acids have special physical properties which make them an ideal candidate for their NLO applications [4]. Recently, L-Alanine crystals have increased attention for photoinduced nonlinear optical effects and dispersion of the linear and nonlinear optical susceptibilities. Photoinduced nonlinear optical effects of L-Alanine single crystals show that the increasing time of illuminations leads to slight changes in the absorption backgrounds without changes in the spectral features [5]. Dispersion of the linear and nonlinear optical susceptibilities of L-Alanine single crystals was reported [6].

In the present work, a systematic study has been carried out on the growth of pure and Lanthanum doped L-Alanine Tartrate (LAT) crystals. An attempt has been made to improve the physiochemical properties of LAT by adding Lanthanum dopant.

Single crystal X-ray diffraction study has been carried out to confirm the grown pure and doped crystals. ICP studies have been carried out to confirm the presence of Lanthanum in the grown crystal. FT-IR, UV-VIS-NIR, microhardness, dielectric analysis and NLO property were studied for grown pure and doped crystals. The second harmonic generation (SHG) studies had been carried out for the grown pure and doped crystals.

2. Experimental Procedure

Pure LAT crystal was grown by slow evaporation technique using water as a solvent. Analytical grade (AR) L-Alanine and Tartaric acid was taken in equimolar ratio. Saturated solution was prepared, filtered, and allowed to evaporate at room temperature under optimized conditions. Seed crystals were obtained in a period of one month. Good quality crystals were obtained by successively recrystallization method. The same procedure was applied to grow the metal doped crystals

FIGURE 1: Photographs of pure and doped LAT crystals.

TABLE 1: Lattice parameter value for the pure and doped LAT crystals.

Lattice parameters	Pure LAT	La ²⁺ -LAT
<i>a</i> (Å)	5.790 (Å)	5.823 (Å)
<i>b</i> (Å)	6.386 (Å)	6.372 (Å)
<i>c</i> (Å)	12.157 (Å)	12.121 (Å)
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁	P2 ₁
Volume (Å ³)	449.504 (Å ³)	449.70 (Å ³)

by adding 2 mol% of Lanthanum to the LAT solution. Good quality crystals were obtained in a period of three weeks. The incorporation of dopant into the pure solution has improved the growth rate and the quality of the crystals. The grown crystal was further studied by various characterization techniques. The photographs of grown pure and Lanthanum doped crystals are shown in Figure 1.

3. Results and Discussion

3.1. Single Crystal X-Ray Diffraction Studies. Single crystal X-ray diffraction studies of pure and Lanthanum doped LAT crystals were carried out using MESSRS ENRAF NONIUS CAD4-F, single X-ray diffractometer. Both the pure and doped LAT crystals belong to monoclinic crystal system with the space group P2₁. The lattice parameter values of pure and doped crystals were also tabulated.

There is a slight variation in the lattice parameters of doped LAT compared with pure LAT. These variations are due to the incorporation of Lanthanum in the LAT crystal lattice. The lattice parameters of the pure and doped crystals are shown in Table 1.

3.2. ICP Studies. The exact weight percentage of the La²⁺ present in the doped crystal is determined.

10 mg of fine powder of the doped LAT crystal was dissolved in 30 mL of doubled distilled water, and the prepared sample was subjected to ICP analysis. The result shows that

only 0.5% of La²⁺ is present in the sample out of 2% of the dopant. It is seen that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution.

3.3. Fourier Transform-Infrared Spectroscopy (FT-IR). The fine powdered samples of pure and doped LAT crystals are taken for this experiment. The FT-IR spectrum is recorded for the pure and doped LAT single crystals at room temperature in the range of 400–4000 cm⁻¹ by employing BRUKKER IFS 66V FT-IR spectrometer, using KBr pellet method. The FT-IR spectra of pure and doped crystals are shown in Figure 2.

The OH stretching vibrations were observed for both of the pure and metal doped LAT crystals at 3085 cm⁻¹. Both of the pure and doped metal doped compounds show strong absorption at 2601 cm⁻¹ indicating the presence of amine group. The absorption at 2111 cm⁻¹ is due to NH₃⁺ asymmetric deformation and NH₃⁺ hindered rotation. It shows that addition of metal dopant do not show any significant from the pure crystal spectrum.

3.4. UV Analysis. The UV absorption study of the pure and doped LAT crystals was carried out by UV-VIS-NIR spectrophotometer. Figure 3 shows the maximum absorption of pure and doped LAT crystals starts from 203 nm. After this wavelength, absorption abruptly decreases to nearly 2% for pure and 1.5% for doped LAT crystals. The lower cut-off wavelength of pure and doped crystals occurs at 246 nm and 235 nm, respectively. Thus it is clear that both of materials possess very good optical transparency up to 1500 nm. The doped crystal has better transparency window compared to the pure one. This property makes the material suitable for the many potential and nonlinear applications.

3.5. Microhardness Study. Microhardness studies of pure and doped LAT crystals have been carried out using HMV SHI-MADZU microhardness tester, fitted with diamond Vickers pyramidal indenter. The microhardness measurements are carried out on the well-developed face (1 0 0). The static indentations were made at room temperature with a constant

FIGURE 2: The FT-IR spectra of pure and doped crystals.

FIGURE 3: UV-VIS-NIR spectra of pure and doped LAT crystals.

indentation time of 15 seconds for all indentations. Maximum indenter load applied for LAT crystal was 50 g, and above this load microcracks are observed. The plot of variation of Vickers hardness number with applied load for the plane (1 0 0) of pure and doped LAT crystals is shown in Figure 4.

For pure LAT crystal the hardness value increases as load increase up to 45 g. Beyond this load cracks were found to develop. Thus the pure material is mechanically stable up to the load of 45 g. In metal doped LAT crystal the cracks were found when the load value is 50 g. This indicates that the metal dopant in the compound increases the mechanical hardness of the material. By plotting $\log p$ versus $\log d$, the value of the working hardness coefficient n value for pure and doped LAT crystals was found to be 1.38 and 1.27. According to Onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft materials [7]. Hence, it is concluded

that the pure and doped LAT crystals belong to hard material category.

3.6. Dielectric Analysis. The dielectric study of pure and doped LAT single crystals was carried out using the HIOKI 3532-50 LCR HITESTER instrument. The capacitance values for both pure and doped crystals are found for frequencies varying from 50 Hz to 5 MHz at room temperature.

Figure 5 shows the variations of dielectric constant with log frequency for pure and doped LAT crystals. It is observed from the plot that the dielectric constant decreases with increasing frequency and attains a constant value in the high frequency region. At room temperature, the dielectric constant decreases with applied frequency. From the graph it is clearly evident that the La^{2+} doped LAT crystal shows

FIGURE 4: The plot of variation of Vickers hardness number with applied load for the plane (1 0 0) of pure and doped LAT crystals .

FIGURE 5: Dielectric constant with log frequency for pure and doped LAT crystals.

more efficiency than the pure one. Thus the dielectric nature of pure LAT is altered by the presence of La^{2+} metal.

In La^{2+} doped LAT crystal the low dielectric constant with high frequency suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications [8].

3.7. NLO Studies. Nonlinear optical (NLO) property of pure and doped LAT crystals was carried out from Kurtz powder second harmonic generation (SHG) test using the Nd: YAG Q-switched laser beam. The sample of same size was illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ.

The second harmonic signals of 324 mV and 384 mV, respectively, were obtained for pure and doped LAT crystals

with reference to KDP (275 mV). Thus, the SHG efficiency of pure and doped LAT crystals is nearly 1.18 and 1.40 times greater than KDP. The doped LAT crystal is found to have efficiency higher than that of pure LAT. The increase in the SHG efficiency of the doped crystals is due to the presence of metal dopant in the crystal lattice [9]. It is concluded that the doped LAT crystal can be used for desired NLO applications.

4. Conclusion

Single crystals of pure and Lanthanum doped L-Alanine Tartrate (LAT) were grown successfully by slow evaporation technique. Single crystal X-ray diffraction studies were carried out, and the lattice parameters are tabulated. ICP studies confirm the presence of the dopant in the grown crystal. UV-VIS-NIR studies reveal that the pure and doped crystals

possess wide transparency in the entire visible region. FT-IR studies reveal the presence of various functional in the crystal, and vibrational structure of the compound has been elucidated. Hardness of both pure and doped LAT crystals reveals that these crystals are hard materials. The dielectric studies reveal that the dielectric constant decreases with log frequency. NLO studies proved that the Lanthanum dopant has increased the efficiency of pure LAT. Thus it is concluded that the presence of dopant has improved the NLO properties of the grown crystals.

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