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Investigation on growth and characteristics of undoped and Mn doped glycinium oxalate single crystals

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Abstract

This work aims at investigating the undoped Glycinium Oxalate (GO) and Manganese doped Glycinium Oxalate (Mn:GO) single crystals that were prepared via slow evaporation method. The single crystals grown were characterized for its structural, vibrational, optical, topographical, electrical and mechanical properties. Single and Powder X-ray diffraction suggests that the grown crystals are crystallized in the monoclinic structure. The functional groups and the effect of moisture on the undoped and doped GO crystals can be analyzed with the help of FTIR spectrum. The undoped and doped GO single crystal shows low absorption in the entire visible and IR region, which is suitable for optical device applications. The emission of green light with the use of Nd:YAG laser ($\lambda = 1064$ nm) confirmed the second harmonic generation properties of the grown crystals. Dielectric measurements were carried to the wide range of frequency (50 Hz–5 MHz) at different temperatures. The determined Vickers hardness number and work hardening coefficient of the grown crystals ascertains the soft nature of the crystal.

Keywords: Slow evaporation method; NLO material; Microhardness; Dielectric studies

1. Introduction

L-arginine oxalate, L-alaninium oxalate and glycinium oxalate are the types of amino oxalate crystals [1–3,5,6]. Unlike other amino acid, glycine is the simplest and has no asymmetric carbon atom and is optically inactive. Since the glycine molecule can exist in zwitter ionic form, it is capable of forming compounds with charged (anionic and cationic) and uncharged chemical compounds. Thus a large variety of glycine coordinated compounds can be formed. The carboxylic acid group of glycine donates its proton to the amino group to form a salt of the structure CH_3COO^- NH_3^+. Thus in solid state, glycine exists as dipolar ion in which carboxyl group is present as carboxylate ion. Due to this dipolar nature, glycine has promising physical properties, which make them ideal candidates for NLO applications [4]. When glycine mixes with the oxalic acid, it can be useful for new applications in materials science [3,6]. Motivated by the applications of the glycinium oxalate single crystal, it is noted from the literature that the crystal structure of glycinium oxalate reported by M. Subha Nandhini et al. crystallized as centro-symmetric space group [5]. The same centro-symmetric form was explored in Mn:GO single crystals. Normally crystals of non-centrosymmetric space group exhibit NLO phenomena. But undoped and

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Mn doped GO exhibits positive Second Harmonic Generation (SHG) property in the centro-symmetric space group due to the possible surface effects or local non-centrosymmetric caused by defects [7,8].

In this paper, we have successfully synthesized undoped and Mn doped glycinium oxalate via slow evaporation method. Moreover, structural (single crystal XRD, FTIR and EDX), optical (UV, fluorescence and NLO), electrical and mechanical studies have also been investigated.

2. Experimental

2.1. Synthesis and growth aspects

The solubility of undoped and Mn doped GO was determined in the temperature range of 35–50 °C. It was done by dissolving the undoped and Mn doped GO solute in deionized water at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same process was repeated and the solubility curves for different temperatures were drawn. Fig. 1(A) shows the solubility curve for undoped and Mn doped GO at different temperatures. It is observed from the curve that the solubility is slightly increased for Mn doped GO as compared to the undoped GO. The solubility is found to increase with increase in temperature.

Glycine ($C_2H_5NO_2$), oxalic acid ($H_2C_2O_4$) and manganese diacetate anhydrous ($C_4H_6O_4Mn$) were purchased from an analytical grade of merck brand. All the chemicals were used as received without further purification. In order to synthesize GO crystal, 7.5 g of GO and 9 g of oxalic acid (1:1) was dissolved individually in 50 mL of deionized water under stirring. The oxalic acid solution was added drop-wise to the glycine solution. The combined solution was stirred continuously for 240 min at 45 °C to evaporate the excess of solvent present and also to attain undiversified mixture. After that, the solution was brought back to room temperature by cooling down to attain the quick supersaturated state. The resulting solution was filtered and allowed to evaporate at room temperature. Optically good quality of crystals was harvested over a period of 7 days. The solution was crystallized several times in order to increase the purity of the crystal.

The chemical reaction of the synthesis is as follows:

$$NH_2{-}CH_2{-}COOH + HOOC{-}COOH \rightarrow HOOC{-}CH_2{-}NH_3^+ \cdot COOH{-}COO^- \quad (1)$$

The same procedure was repeated to prepare Mn:GO crystal using 0.34 g (2%) of manganese diacetate anhydrous ($Mn(CH_3COO)_2$). The photograph of as grown undoped and Mn doped GO single crystal is shown in Fig. 1(B). A possible schematic formation of the undoped GO and Mn:GO is shown in Fig. 1(C).

Single crystal X-Ray Diffraction (SXRD) studies were carried out by using the BRUKER axs diffractometer with MoK_α radiation ($\lambda = 0.71069$ Å). The reflection planes of the grown crystals were identified by the Powder X-Ray Diffraction pattern (PXRD) of the powdered sample by using PHILIPS 'X'Pert Pro Radiation CuKα X-ray diffractometer in the range of 10–70° with a scan speed of 1°/min and analysed by using "powder X" refinement software. The surface morphology was examined by the HITACHI S-3400N SEM instrument. The molecular structure was confirmed by the FTIR (SHIMADZU-8400S) Spectrophotometer in the middle IR region from 4000 to 400 cm^{-1}. The chemical composition was investigated by the EDS analysis. The optical spectra were recorded by using the Lambda 35 UV-Vis-NIR spectrophotometer in the range from 190 to 1100 nm. The nonlinear optical studies were characterized by Q-switched Nd:YAG laser (1064 nm, 10 ns, 450 mJ). The excitation spectra were recorded using LS45 Spectrofluorometer. The dielectric properties were characterized by the HIOKI 3532-50 LCR HITESTER. The mechanical properties were carried out using the Shimadzu HMV-2 Vicker's indentation tester.

3. Results and discussion

The structural properties of undoped and Mn doped GO single crystals has been studied by single crystal X-ray diffraction studies. From single crystal XRD, it is observed that both the compound crystallizes in the monoclinic system with a space group $P2_1/c$, which is a centro-symmetric system. The crystallographic data are tabulated in Table 1 and these parameters are in good agreement with the previously reported GO single crystal [5,6,9]. The Mn dopant on GO does not change the original crystal system of glycinium oxalate. As compared to undoped GO crystal, slight change in the lattice parameter and cell volume of Mn

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