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Crystallization, thermal decomposition and dielectric behavior of a third order NLO material: Iminomethanediaminiumtosylate (IMT)

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Organic nonlinear optical single crystal of iminomethanediaminiumtosylate was successfully grown from aqueous methanolic medium embracing low temperature solution growth technique at room temperature. The essential properties such as structural, thermal and dielectric behavior of the grown crystal have been investigated.

1. Introduction

Thermogravimetricand differential thermal analyses (TG-DTA) are the most widely used analytical technique to determine the thermal stability of materials. In recent years, the applications of TG and DTA to study the materials have gained a panoramic attention among researchers. Thermal decomposition information has been extensively used to predict the lifetime of materials for electrical and telecommunication cables [1]. Iminomethanediaminiumion is relatively simple chemical species, whose structure is related to those of amides and proteins in which there is a considerable interest. The iminomethanediaminiumion also forms a broad family of hydrogen bonded crystals [2]. Thus iminomethanediamine is an interesting molecule in the field of crystal engineering and supramolecular chemistry because of its π-delocalized systems which attributes largest nonlinear responses than covalently bonded molecules and solids [3].Furthermore, protonation of iminomethanediamine enables the resultant material to be an excellent hydrogen bond donar and acceptor. Organic crystals in terms of nonlinear optical properties possess advantage when compared to their inorganic counterparts [4]. The crystal structure of iminomethanediaminiumtosylate (IMT) has been solved and reported as $C_8H_{13}N_3SO_3$ [5].The authors have shown interest to grow the titular material with appreciable size and hence the structural, thermal and dielectric studies have been carried out to exploit the material for application purposes.

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2. Experimental Procedure

2.1 Synthesis and growth of bulk crystal

Iminomethanediaminiumtosylatewas synthesized and crystallized from aqueous methanol solution espousing low temperature solution growth technique. Equimolar ratio of iminomethanediaminehydrochloride and p-toluenesulfonic acid monohydrate under aqueous methanolic medium was stirred continuouslyat room temperature to attain homogeneity. The prepared solution was filtered and resumed isolated. After a span of 16 days, colourless hexagonal crystals of the title material with considerable size wereobtained. The photograph of the as grown IMT crystal is shown in Figure 1. The chemical reaction for the synthesis of IMT crystalline material is given as follows:

$$CH_5N_3.HCl + C_7H_{10}SO_3.\ H_2O \rightarrow C_8H_{13}N_3SO_3 + 2H_2 + HCl$$

Figure 1. As grown IMT crystal

3. Results and discussion

3.1 Single crystal x-ray diffraction study

The single crystal X-ray diffraction study reveals that the IMT crystal crystallizes in monoclinic crystal system with space group $P2_1/c$. The lattice parameters of the grown crystal was detected and revealed to be a = 12.392(15) Å, b = 7.405(9) Å, c = 25.680(3) Å, β = 95.587(3)° and volume, V = 2345.3(5) Å^3.

3.2 Thermal Analysis

The thermal stability of the title compound was examined by thermogravimetric(TG) and differential thermal analyses (DTA). The IMT sample weighing 9.57 mg was analyzed using a STA 409 PL thermal analyzer in the range 40°C – 600°C under nitrogen atmosphere and is shown in Figure 2. The TG curve shows two stage weight loss pattern. A major weight loss starting from 331°C to 395°C with a mass change of 72% is due to the elimination of p-toluenesulfonate anion. The second stage weight loss in the DTA curve starting from 395°C to 554°C with a mass change of 25% is due to the elimination of guanidinium molecule. The endotherm in the DTA curve found associated with the weight loss confirms the absorption of energy for breaking of bonds during decomposition. An endotherm in the DTA curve, found around 230°C before decomposition can be assigned to be the melting point of the IMT crystal. The decomposition process was carried up to 600°C with the removal of material into gaseous products (mixture of CO, CO_2, NO and hydrocarbons). From the thermal analyses, it is evident that the IMT material is thermally stable up to 230°C.

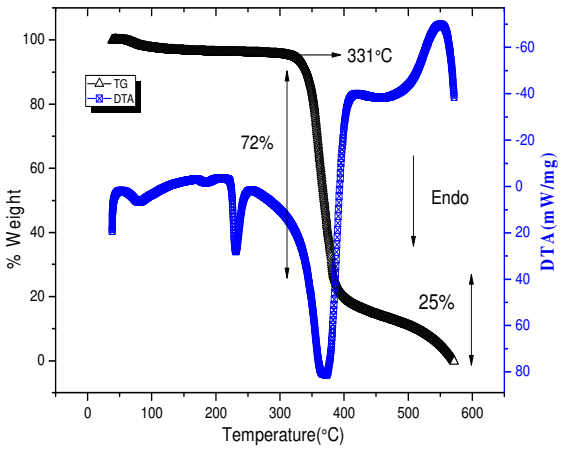

Figure 2.TG-DTA curve of IMT

2.3 Dielectric study

The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature. The four primary contributions to the dielectric constant would be the extrinsic nature of the material, deformation of the ions, electronic and ionic polarizability [6]. The relative dielectric constant and dielectric loss of IMT crystal was determined as a function of frequency ranging from 50 Hz to 5 MHz at temperatures 313 K, 323 K, 333 K and 343 K using a HIOKI 3532–50 LCR HITESTER instrument. The relative dielectric constant ε′ was calculated from the formula,

$$\varepsilon' = \frac{1}{\varepsilon_o}\frac{(Cp.d)}{A}$$

where c_p is the capacitance (F), A is the area of the sample (mm^2), d is the thickness of the sample (mm) and ε_0 is the permittivity of free space. The plot of dielectric constant versus frequency of IMT crystal is shown in Figure 3. The dielectric constant is found to be high at lower frequencies

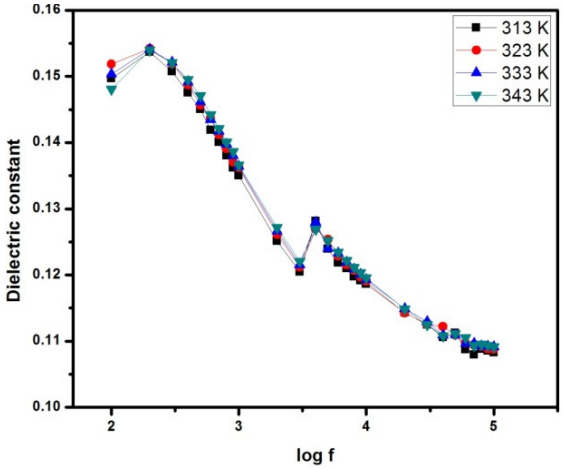

Figure 3. Dielectric constant of IMT

and is knocked to decrease exponentially with enforced frequencies. The decrease in dielectric constant of the compound at high frequencies is typically due to the presence of all four types of polarizations [7]. The low value of dielectric constant at high frequency may be due to the gradual loss of space charge polarization of molecular dipoles. This indicates the low power dissipation. Dielectric loss is the quantity of energy absorbed by a dielectric material. The dielectric loss (tan δ) similar to that of dielectric constant (ε′) firmly depends on frequency of the applied field. The plot of dielectric loss against frequency with respect to temperature is shown in

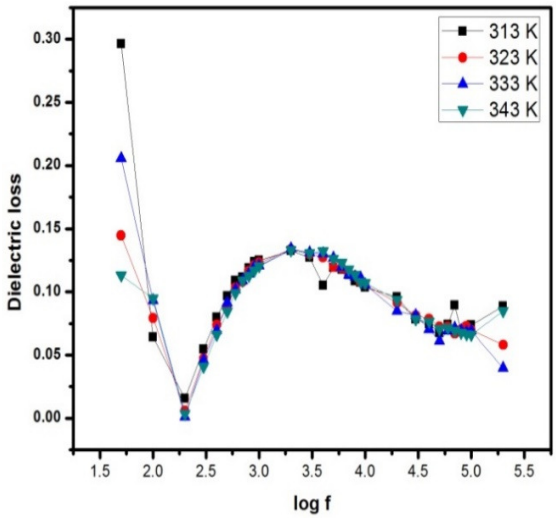

Figure4. Dielectric loss of IMT

Figure 4. The low dielectric loss at high frequencies confirms that the grown crystal is of good quality with fewer defects. This exhibits that the IMT crystal is a promising dielectric material for constructing photonic devices.

Conclusion

Crystallization of iminomethanediaminiumtosylate single crystal was synthesized adopting slow evaporation solution growth technique. The structural, thermal and dielectric behavior of the grown crystal was determined and reported. Based on the properties of IMT crystal it is evident that the grown crystal is a suitable candidate for telecommunication applications.

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