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Growth, crystalline perfection, optical, thermal, laser damage threshold and electrical characterization of melaminium levulinate monohydrate single crystal

N. Sivakumar [a], N. Kanagathara [b], G. Bhagavannarayana [c], S. Kalainathan [d], G. Anbalagan [e,*]

[a] Department of Physics, Saveetha School of Engineering, Saveetha University, Chennai 600077, India
[b] Vel Tech Dr. RR Dr. SR Technical University, Avadi, Chennai 600062, India
[c] Materials Characterization Division, National Physical Laboratory, New Delhi 110012, India
[d] Department of Physics, VIT University, Vellore 632014, India
[e] Department of Physics, Presidency College, Chennai 600077, India

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ABSTRACT

Equimolar amounts of melamine and levulinic acid results an organic crystal of melaminium levulinate monohydrate (MLM) at room temperature. MLM belongs to a monoclinic crystal structure having $P2_1/c$ space group which was confirmed by single crystal X-ray diffraction study. Functional groups present in the MLM crystal were identified by FT-IR spectral study. HRXRD study dictates the quality of MLM crystal. UV–visble spectrum of MLM reveals the lower cut-off wavelength of 293 nm with 55% optical transparency and optical band gap was found to be 4.20 eV for the prominent plane (1 0 −1). Refractive indices for the three axes of MLM crystal were found to be n_x=2.6, n_y=2.4 and n_z=2.2 respectively. Further the thermal stability and melting point of MLM crystal were investigated by TG/DTA study. Dielectric permittivity tensor components were estimated for the planes (1 0 −1), (0 1 0) and (1 1 1) respectively. The thermal conductivity of the crystal by Wiedemann–Franz law was found to be 5.99×10^{-11} W/mK at 70 °C. LDT value (2.84 GW/cm^2) of MLM was estimated for laser optical device applications.

1. Introduction

The growth of single crystals with self assembled hydrogen bonds in the molecular structure is of great interest in crystal engineering [1,2]. Currently, much attention is given to hybrid organic–inorganic crystals because of their large hyperpolarizability and high laser damage resistance compared to inorganic materials [3,4]. Melamine, an organic base is a trimer of cynamide having a skeleton of 1,3,5-triazine. The complexes of melamine are results in π–π aromatic ring stacking with self-assembled hydrogen bonded molecular networks [5,6]. Melamine and their complexes are widely used industrial chemicals in the manufacture of dyes, plastics, fertilizers, textiles and its polymers play an important role in technological applications [7,8]. In polymers like epoxy resins, cellulose or flax fibers, melamine acts as a flame retardant agent. Due to the presence of amino groups, melamine derivatives develop well defined self-organized super lattices through donor and acceptor hydrogen bonds. [9]. Sangeetha et al. [10] reported growth and optical, dielectric characterization of melaminium bis (trifluoroacetate) trihydrate single crystal. Combination of various organic and inorganic acids with melamine forms an interesting hydrogen bond system. Because of its versatility, this melamine is taken as the subject of interest. Levulinic acid is a well known example of a very attractive chemical from biomass. Due to the presence of two reactive functional groups, i.e. a ketonic and a carboxylic group, levulinic acid is one of the most bio-based multipurpose molecules [11]. Its functionalized carbon structure is widely used as a chemical intermediate in the manufacture of fuel extenders, biodegradable polymers, herbicides, antibiotics and flavors [12,13]. SooChoi et al. [14] reported the melaminium levulinate monohydrate crystal structure with the chemical formula ($C_3H_7N_6^+ \cdot C_5H_7O_3^- \cdot H_2O$). The results of the reported structure reveal the monoclinic system of MLM crystal with $Z=4$ and lattice cell parameters are a=10. 538 Å, b=16. 214 Å, c=7. 198 Å and space group $P2_1/c$. Co-crystal of melamine and levulinic acid was stabilized through self-assembled hydrogen bond networks. Four N–H…O and two N–H…N hydrogen bonds link two melaminium molecules in which two pairs of each N–H…O bond connect the two H-atoms belong to two amine groups of melamine cations through O-atom of single levulinate [14].

* Corresponding author. Tel.: +91 94871 40051.
E-mail address: anbu24663@yahoo.co.in (G. Anbalagan).

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The present research work describes the bulk growth of good quality melaminium levulinate monohydrate (MLM) using the solvent evaporation technique. For the first time, we are reporting the solubility and dielectric properties with TG/DTA studies. In addition to these studies, MLM crystal is subjected to optical and surface laser damage threshold analysis and their details are discussed completely.

2. Experimental details

2.1. Material preparation

The equimolar ratio of melamine and levulinic acid was taken for the synthesis of melamine levulinate monohydrate (MLM). A hot aqueous solution of melamine was prepared at 45 °C and levulinic acid was gently added to this solution. Homogeneous solution was obtained by stirring it for about 7 h. In this reaction a proton is transferred from the electron donor group of levulinic acid to the electron acceptor group of melamine. The resultant product is melaminium levulinate monohydrate (MLM), in which the levulinate anion and melaminium cation result from proton transfer. The resultant solution was kept undisturbed in a dust free atmosphere. Crystalline salt of MLM was obtained after 2 weeks of solvent evaporation. Five times of the crystallized salt were used to prepare the saturated solution at 30 °C. The solution was filtered in a beaker using filter paper (Whatmann) and is allowed for evaporation. Rate of evaporation has been controlled by closing the neck of the beak with polythene sheet having less number of micrometer sized holes. The beaker was then placed in a constant temperature bath having ±0.01 °C accuracy. Optically clear and chemically stable MLM crystal with dimension of $20 \times 20 \times 7$ mm^3 was harvested after 10 days of controlled solvent evaporation at room temperature. The photograph of as-grown crystal with well defined morphology of MLM are shown in Fig. 1.

2.2. Solubility and meta stable zone width

Solubility of the solute molecules present in the solvent will decides the shape, growth and size of the crystals. The materials solubility depends on factors like temperature and impurity which defines the supersaturation and is the driving force for the nucleation. Growth of bulk crystals is mainly influenced by the two key factors, (i) dipole moments between crystal component and the solvent, (ii) heat of crystallization [15]. The synthesized salt of MLM was subjected to solubility study using an equivalent ratio of water-methanol solvent. Solubility study was carried out over the wide range of temperatures from 35 °C to 55 °C insteps of 5 °C using constant temperature bath with Eurotherm controller (of accuracy ±0. 01 °C). Water bath was initially kept at 35 °C and then allowed for continuous stirring for about 1 h to ensure the temperature homogeneity. Fig. 2 reveals the positive solubility gradient of MLM crystal. A trend of this solubility curve is quite enough for the bulk growth of crystals by slow cooling as well as slow evaporation techniques. Supersaturation state is acting as a driving force of crystallization, in which the concentration of solute molecules will be more when compared to that of solubility state at a given temperature. In the supersaturation range called metastable zone, the spontaneous crystallization is not possible. Metastable zone width mainly depends on the presence of impurity, cooling and stirring rates. Hence, in the growth of crystals, controlled crystallization can be achieved. In the present case, we estimated the metastable zone width of MLM in the binary solvent of methanol–water.

Constant temperature water bath was utilized for the nucleation studies of MLM crystal for the temperatures 35, 40, 45, 50 and 55 °C. When the solution reaches supersaturation state, it is allowed to cool slowly by a cryostat unit. At a particular lower temperature, the formation of first crystal nuclei was observed and is called critical nuclei. The difference in temperature between the states of saturation and nucleation determines the value of metastable zonewidth [16]. Fig. 2 shows the metastable zonewidth of MLM solution in which zonewidth decreases as the temperature increases. The large metastable zone width of the crystalline material indicates the fast growth rate and stability of growth solution.

2.3. Characterization

The grown crystal of MLM was subjected to single crystal XRD analysis in order to determine the lattice parameters and morphology

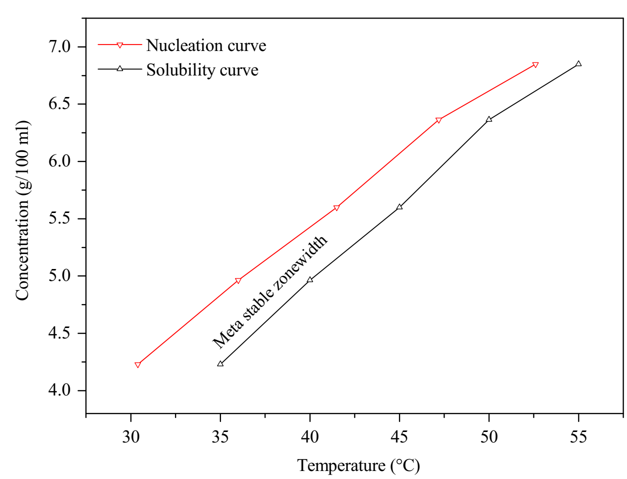

Fig. 2. The metastable zone of MLM solution in binary solvent of methanol and water.

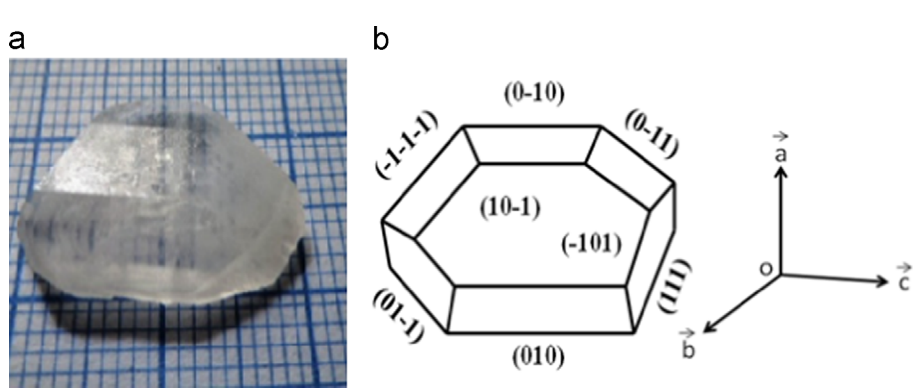

Fig. 1. Photograph of (a) as-grown and (b) morphology of MLM crystal.