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Growth and characterization of semiorganic single crystal of bis-glycine manganese chloride

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ABSTRACT

Semiorganic single crystals of bis-glycine manganese chloride (BGMC) of dimension $5 \times 3 \times 3$ mm^3 were grown from aqueous solution by slow evaporation method at room temperature. The crystal structure and lattice parameters were determined for the grown crystal by the single crystal X-ray diffraction studies. BGMC was subjected to FT-IR and FT-Raman spectral analyses. The lower cutoff wavelength observed from UV–vis–NIR transmittance spectrum is 271 nm. The mechanical strength of the grown crystal was estimated using Vickers microhardness tester. The dielectric response of the grown crystal was analyzed at different temperatures in the frequency range from 50 Hz to 2 MHz. Thermal properties were investigated by thermogravimetric, differential thermal and differential scanning calorimetric analyses. Chemical etching study shows the distribution of etch figures of various shapes in the grown single crystal. The third order nonlinear optical properties of BGMC were investigated by Z-scan technique employing He–Ne laser radiation of wavelength at 632.8 nm.

1. Introduction

Investigations on the growth and studies of the semiorganic nonlinear optical materials (NLO) gain importance because these crystals possess good thermal and mechanical properties with large NLO coefficients [1,2]. In this context among a wide variety of amino acids and their complexes L-arginine and L-arginine phosphate are proved to be the efficient second harmonic generators which find applications in devices such as optical parametric amplifiers [3,4]. Triglycine sulphate has been the important material for the fabrication of infrared detectors and target part of vidicon operating at room temperature [5]. Glycine ($H_2N—CH_2—COOH$), the simplest amino acid has no asymmetric carbon atom and is optically inactive [6–8]. Michel Fleck carried out detailed studies on the structures of several compounds of halogenides and metal halogenides combined with glycine [9]. Some of the complexes of glycine with alkali metals [10–15], alkaline earth metals [16–18], transition metals [19–21] and halogens [22–24] were synthesized and their structural, mechanical, thermal and optical properties were reported. Literature survey shows that two reports are available on the bis-glycine manganese chloride material. The ferroelectric behavior of diglycine manganese chloride dihydrate was reported by Pepinsky et al. [25]. Three dimensional X-ray crystal structure of bis-glycine manganese chloride (BGMC) was reported by Narayanan and Venkataraman [26] for the first time. They reported that BGMC belongs to triclinic system with cell parameters $a = 4.97$ Å, $b = 6.98$ Å, $c = 7.92$ Å, $\alpha = 107.4°$, $\beta = 115.9°$ and $\gamma = 87°$. But systematic studies are yet to be reported on the growth and the properties of bis-glycine manganese chloride. Hence in the present work bis-glycine manganese chloride crystal were grown from aqueous solution and were characterized by single crystal X-ray diffraction, FT-IR and FT-Raman, UV–vis–NIR optical transmittance, thermal, microhardness, etching and third order nonlinear optical studies.

2. Experimental

2.1. Synthesis

Dissolving AR grade glycine and manganese chloride tetrahydrate in 2:1 stoichiometric ratio in distilled water bis-glycine manganese chloride salt was synthesized. The chemical reaction is given below

$$2(CH_2NH_2COOH) + MnCl_2{\cdot}4H_2O \rightarrow CH_2NH_3COO—Mn—OOCNH_3CH_2{\cdot}Cl_2 + 4H_2O$$

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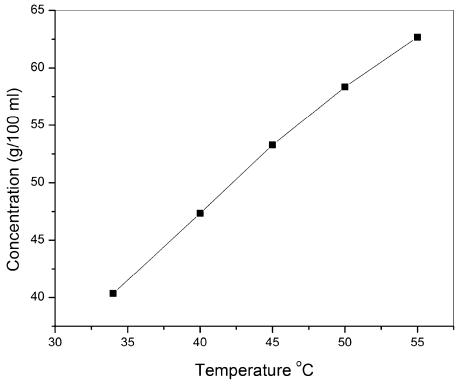

Fig. 1. Solubility curve of BGMC single crystal.

Resultant solution was stirred well and the slow evaporation of the solvent at room temperature yielded BGMC salt.

2.2. Solubility

The solubility of BGMC was determined at five different temperatures namely 34, 40, 45, 50 and 55 °C. A constant volume of 100 ml of the saturated solution was used in this experiment. BGMC salt was dissolved in double distilled water taken in an airtight container which was maintained at a experimental temperature with continuous stirring. After achieving the saturation by adding BGMC salt carefully the equilibrium concentration of the solute was estimated gravimetrically [27]. The same procedure was repeated to measure the solubility of BGMC at different experimental temperatures and the results are shown in Fig. 1 which shows the solubility increases with increase of temperature.

2.3. Crystal growth

A beaker containing saturated aqua solution of BGMC was covered with perforated polythene sheet and solvent was allowed to evaporate at room temperature. Well shaped optical quality single crystal of size $5 \times 3 \times 3\,mm^3$ was harvested in a growth period of 17 days (Fig. 2).

3. Results and discussion

3.1. X-ray diffraction analysis

One of the selected tiny crystals of BGMC was subjected to single crystal X-ray structure analysis using Bruker Nonius CAD 4 single crystal X-ray diffractometer with Cu $K\alpha$ ($\lambda = 1.5405$ Å) radiation. Structure of BGMC was solved by direct method with SHELXL-97 which reveals that BGMC crystal belongs to triclinic system. The calculated unit cell parameters agree well with the corresponding values reported by Narayanan and Venkataraman [26]. Crystallographic data and structure refinement details of BGMC are presented in Table 1. The unit cell packing diagram of BGMC is shown in Fig. 3. ORTEP diagram of BGMC crystal with atom numbering scheme is shown in Fig. 4. In the BGMC structure Mn cations are

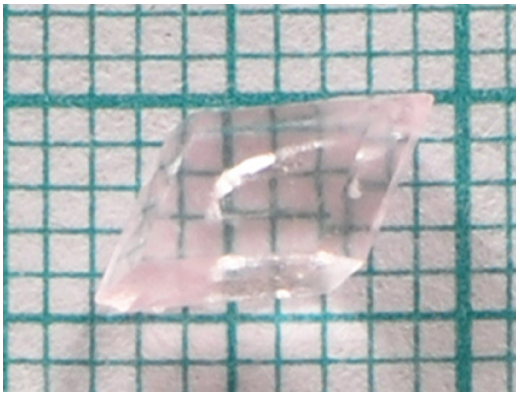

Fig. 2. As grown BGMC single crystal.

Table 1
Crystal data and structure refinement details for BGMC single crystal.

Formula	$C_4H_{10}Cl_2MnN_2O_4$
Formula weight	275.98
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 4.9500\,(9)$ Å $\alpha = 106.258\,(10)^\circ$
	$b = 6.5697\,(12)$ Å $\beta = 92.917\,(10)^\circ$
	$c = 7.8818\,(16)$ Å $\gamma = 107.100\,(9)^\circ$
	$b = 6.5697\,(12)$ Å $\beta = 92.917\,(10)^\circ$
	$c = 7.8818\,(16)$ Å $\gamma = 107.100\,(9)^\circ$
Volume	232.70 (8) Å^3
Z, calculated density	1, 1.969 g/cm^3

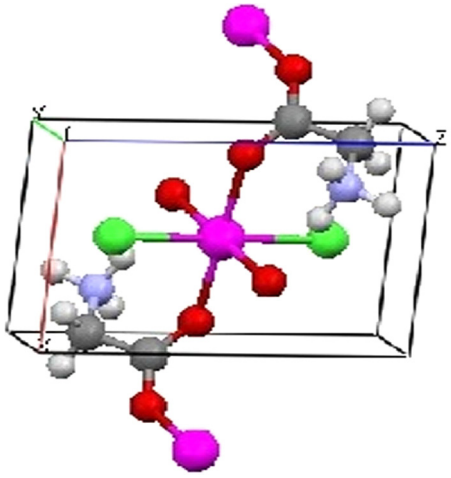

Fig. 3. Stereographic packing diagram of BGMC.

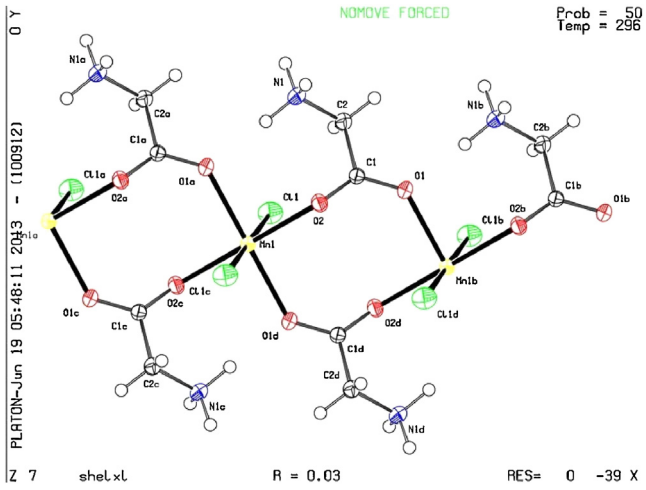

Fig. 4. ORTEP diagram of BGMC crystal showing the atom numbering scheme.