Orientational disorder and geometrical isomeric effect on nonlinear optical properties of poly bis(glycine)cadmium chloride

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ABSTRACT

Poly bis(glycine)cadmium chloride (BGCC) crystals of both undoped and doped with thiourea (Tu) were grown from saturated solutions by a slow evaporation technique. The geometrical isomerism of the octahedral BGCC molecule is investigated using single crystal XRD, powder XRD and FT-IR. The significant difference between the two isomers namely facial (*fac*) and meridional (*mer*), is explained in terms of the different point group symmetries of C_3 and C_1, respectively. The loss of point group symmetry from C_3 to C_1 is attributed for the observed powder second-harmonic generation (SHG). Semi-empirical calculations from the optimized geometrical parameters also supported non-linear optical properties of the material.

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1. Introduction

Nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications in optoelectronics, optical communication, data storage, laser technology, etc. [1–3]. The design and development of efficient NLO materials requires a non-centrosymmetric structures that gives rise to a large hyperpolarizability (β). Molecules with large β often have large degrees of intramolecular charge transfer and usually posses a large dipole moment in their ground state. However, there is a strong tendency for the crystal structures of such molecules to be centrosymmetric [4]. But the criteria for SHG may also be satisfied by centrosymmetric molecules if they aggregate in a non-centrosymmetric manner and contributes to the bulk susceptibilities from intermolecular charge transfer [5]. Thus the macro second-order effects are also somewhat dependent on the molecular packing style [6]. Therefore there is hectic of research to induce the molecules into non-centrosymmetric environments with high value of β. The assembly of non-centrosymmetric segregation of centrosymmetric molecules can be achieved through various physical and chemical methods [7]. The selection of various organic host lattices with appropriate guest molecules as templates is crucial in the strategy of structural design and engineering [8]. The crystals of centrosymmetric α-glycine in its pure form show SHG upon occlusion of 'guest' molecules [9]. Even extremely small amounts (0.01 per cent weight) of guest can lead to a sufficient lowering of

the symmetry of the crystal for significant SHG to be possible [10,11]. In our earlier work on dye doped crystals, the crystal structure of pure BGCC was reported. It belongs to monoclinic system with space group P2$_1$/n [12]. In view of stereochemical flexible structure, good solubility in water and good basis for growing large single crystals of BGCC, efforts are directed to tune the centrosymmetric structure into a non-centrosymmetric by doping tailor made additives. Since thiourea is an interesting matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [13] it is tried as a dopant into BGCC. Through this communication the results of an attempt to create a non-centrosymmetric environment in centrosymmetric BGCC crystals by doping small amounts of thiourea are reported.

2. Experimental procedure

2.1. Synthesis and characterization

The BGCC single crystals were grown according to published procedures [12]. To get doped crystals Thiourea (Tu) is added (5 and 10 mol%) to the aqueous solution of BGCC. The transparent and good quality crystals were obtained from the slow evaporation technique in 15–20 day. Intensity data for the crystals was collected on Oxford XCalibur, Gemini diffractometer equipped with EOS CCD detector at 298 K. Monochromatic Mo K radiation ($\lambda = 0.71073$ Å) was used for the measurements. Absorption corrections using multi-scans were applied. Structure was solved using SHELXS-97 software [14]. Powder X-ray diffraction patterns were recorded on

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JEOL-JDX-8P X-ray diffractometer fitted with Cu Kα ($\lambda=1.54056$ Å). The data are then analyzed using PowderX software to obtain the lattice parameters and unit cell volume. The infrared spectrum of the pure and Tu doped BGCC crystals were recorded at room temperature using Nicolet NEXUS Spectrometer in the range of 400–4000 cm^{-1}. Semi-empirical quantum chemical calculations [15] were performed on the refined parameters using MOPAC2009 program to optimize the experimental structure with parameterization Model 6(PM6) approximation together with restricted Hartree Folk closed shell wave function; the minimization were terminated at r.m.s. gradient of less than 0.01 kJ-mol^{-1} Å^{-1}. The nonlinear optical conversion efficiency has been carried out using modified setup of Kurtz and Perry [16] at the Indian Institute of Science, Bangalore. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 2.9 mJ pulse^{-1}.

3. Results and discussion

Although the structure of BGCC has been reported [12] we felt important to determine the structure of 5Tu BGCC to better understand the SHG property. The single crystal XRD data proves that the crystal still possesses monoclinic symmetry irrespective of doping

of thiourea molecule with $a=8.2864(2)$ Å, $b=9.0689(2)$ Å, $c=13.9464(5)$ Å, $\beta=108.598°$ and space group P2$_1$/c. The PXRD pattern is shown in Fig. 1. The unit cell parameters obtained from the powderX program [17] are listed in Table 1. Lattice parameters

Table 1
Unit cell parameters of pure and Tu doped BGCC crystals.

Sample	Cell parameters	
	Powder XRD	Single crystal XRD
BGCC	$a=8.2769$ Å	$a=8.2785$ Å
	$b=9.0769$ Å	$b=9.0807$ Å
	$c=13.7394$ Å	$c=13.7429$ Å
	$\beta=106.212°$	$\beta=106.230°$
5T BGCC	$a=8.2834$ Å	$a=8.2864$ Å
	$b=9.0678$ Å	$b=9.0689$ Å
	$c=13.9436$ Å	$c=13.9464$ Å
	$\beta=108.588°$	$\beta=108.598°$
10T BGCC	$a=8.2864$ Å	
	$b=9.0689$ Å	
	$c=13.9464$ Å	
	$\beta=108.598°$	
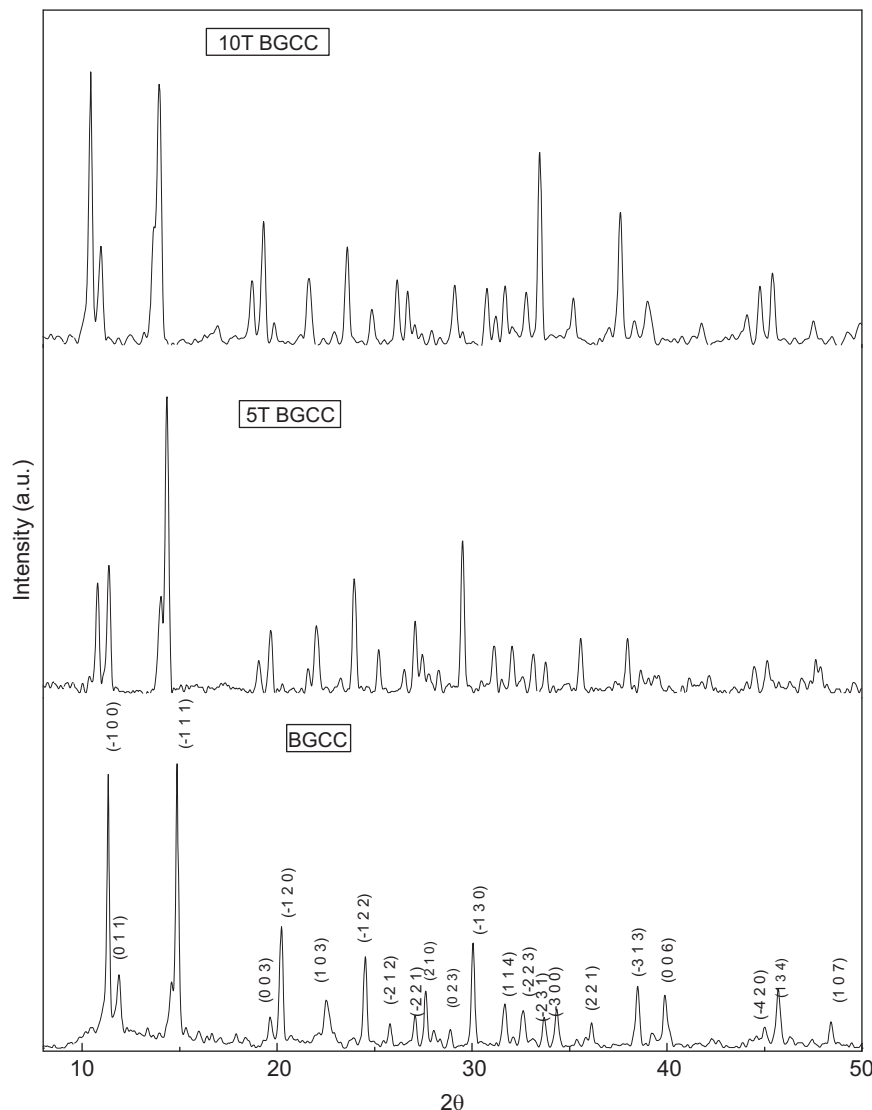
Fig. 1. PXRD pattern of pure and Tu doped BGCC.