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Impact of intermolecular charge transfer interactions on structural, spectral and third-order nonlinear optical properties of a semiorganic crystal: Poly (bis 4-methoxybenzylammonium) tetra-μ-chlorido-cadmate (II)

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ABSTRACT

The correct crystal system and space group of the title crystal are reported. Powder X-ray diffraction (PXRD) study validates the crystal structure of poly (bis 4-methoxybenzylammonium) tetra-μ-chlorido-cadmate (II) (4MBACD) crystal. The crystal exhibits the optical transmittance from 270 to 1100 nm. The vibrations of different functional groups, formation of crystal, coordination of metal and the intermolecular hydrogen bonding impact in the crystal were analyzed by FT-Raman and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR spectrum of 4MBACD crystal is recorded in DMSO and D_2O solvent but the protonation of amino moiety is revealed only in DMSO solvent. The mechanical stability was determined by Vicker's microhardness study. The Z-scan analysis was carried out to know the nonlinear refractive index (n_2), the nonlinear absorption coefficient (β) and third-order nonlinear susceptibility ($\chi^{(3)}$). The result reveals that the crystal possesses saturable absorption and self-defocusing properties. 4MBACD crystal exhibits higher third order nonlinear susceptibility $\chi^{(3)} = 6.21 \times 10^{-6}$ esu compared to some well-known crystals due to the impact of intermolecular charge transfer interactions. This ensures the suitability of 4MBACD crystal for nonlinear optical (NLO) applications.

1. Introduction

The progress of single crystals led to the development of modern science and technology in various fields of photonics, lasers, sensors, optoelectronics and biomedical applications for the past few decades. NLO crystals are utiliszed mainly for optical devices such as optical modulators and frequency converters [1–5]. NLO crystals can be used to generate new frequencies that are not readily available with the present sources of laser. Recently researchers are keen on exploring novel semiorganic crystals which overcome the limitation of organic and inorganic crystals. To improve the efficiency of NLO crystals, it is essential to understand the relationship between macroscopic qualities and microscopic structures [6].

The title compound has the general formula AMX_4 where A is an organic 4-methoxybenzylamine (4MBA) cation, M is cadmium (Cd) II metal and X is Cl. 4MBACD is an effective semiorganic crystal, which has greater NLO coefficient influenced by the organic part and has high optical transmittance dominated due to the d^{10} configuration of metal ions [7]. The whole crystal system is

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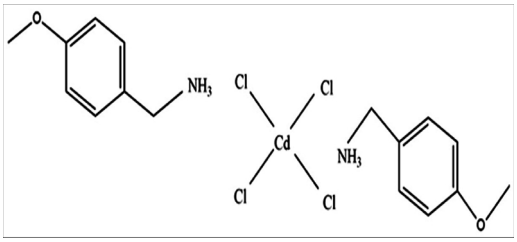

Fig. 1. Chemical structure of the title compound.

stabilized by the intermolecular hydrogen bonds connected between the organic cation and the inorganic anion. Kefi et al. [8] has reported the structure of the title compound as triclinic and space group as P $\bar{1}$ in the abstract and $P2_1/c$ in the crystallographic data, but the given lattice parameters suggest that the crystal system is monoclinic. To know the correct crystal system and space group of the crystal, we have again solved the crystal structure. It is observed that the crystal system and space group of the compound is monoclinic and $P2_1/c$, the lattice parameters are found to be a = 19.0861 (14) (Å), b = 7.4038 (3) (Å), c = 7.5068 (4) (Å) and β = 96.479 (4) (Å) respectively and the crystal is centrosymmetric in nature. The centrosymmetric crystals play a significant role in third harmonic generation. Nonlinear refractive index (n_2), nonlinear absorption (ß) and third-order susceptibility ($\chi^{(3)}$) are the important optical parameters to confirm the NLO activity of the crystal and are evaluated by the standard Z-scan method [9,10]. NLO behaviour of innumerable crystals have been investigated by many researchers and various mechanism have been proposed to enhance the nonlinearity [11]. Several methoxybenzylamine based structures were reported, but their properties were not analyzed to ascertain the NLO behaviour [12–14]. Functionalisation of the suitable inorganic part to the organic crystal is a good choice. Improvement in third order nonlinearity is due to the impact of intermolecular charge transfer interactions through hydrogen bonds and the incorporation of suitable metal in the organic ligand. In metal organic halogenides of 4MBACD, the hydrogen chloride transfers the proton between metal atom and the organic ligand. A strong metal-ligand bond is formed, due to the transfer of protons. This metal-ligand bond is responsible for higher molecular polarisability and greater susceptibility and therefore improves the NLO response [15,16].

In the present work, single crystal XRD analysis, powder XRD technique, UV–vis-NIR study, FT-Raman spectroscopy, ^{1}H NMR spectroscopy, Vicker's microhardness study and Z-scan techniques have been carried out to determine the properties of 4MBACD crystal. The crystal structure is reinvestigated. The structure-property relationship is analysed and reported.

2. Results and discussion

2.1. X-ray structure determination

The crystal is grown by solution growth method at low temperature by adopting the procedure as reported [8]. A colourless crystal of 4MBACD with size 0.25 × 0.20 × 0.20 mm^3 was used for data collection. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the data collection, the following softwares were used. For 4MBACD data collection: APEX2 [17]; cell refinement: APEX2/SAINT [17]; data reduction: SAINT/XPREP [17]; molecular graphics: ORTEP3 [18] and Mercury [19] and publication software: SHELXL-2014/7 [20]. The structure was solved by SIR92 [21] and refined using SHELXL-2014/7 [20]. Chemical structure of 4MBACD is displayed in Fig.1. The atomic numbering scheme of 4MBACD crystal is exhibited in Fig. 2. The crystal

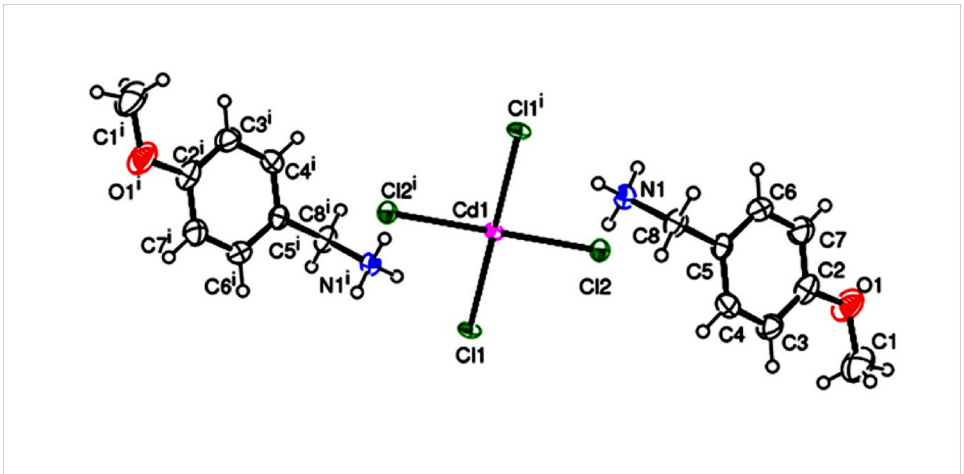

Fig. 2. The atomic numbering scheme of 4MBACD crystal.