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Third-order nonlinear optical studies of Bis(4-methylbenzylammonium) tetrachloridocuprate metal-organic crystal with optical limiting behavior: Experimental and theoretical investigations

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Highlights

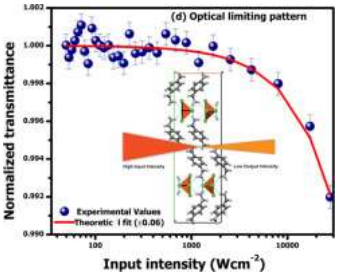
- NLO single crystal of Bis(4-methylbenzylammonium) tetrachloridocuprate (4MBA) has been successfully grown by slow evaporation solution growth technique.
- 4MBA single crystal was discovered to be triclinic system with space group Pnma by single crystal X-ray analysis and obtained optical band gap energy 3.71 eV from UV-Vis-NIR.
- TGA/DTA thermal studies reveal that 4MBA was thermally stable up to 310.8 °C.
- The dielectric properties attested its suitability in electro-optic devices.
- Optical limiting behavior of the crystal is used to protect the sensors and human eyes.
- Z-scan exhibited high third order optical nonlinearity for the grown crystal.

Abstract

The metal-organic nonlinear optical (NLO) compound Bis(4-methylbenzylammonium) tetrachloridocuprate (4MBA) was synthesized and grown by the slow evaporation method. X-ray crystal analysis revealed the crystal structure and conformation. Density functional theory (DFT) at B3PW91/LanL2DZ basis set level was applied and computed the optimized geometry, electronic structure, vibrational spectra, frontier molecular orbitals (FMO), molecular electrostatic potential (MEP), and natural bonding orbitals (NBO). UV–Vis-NIR spectroscopic measurements revealed the optical transparency range from 310 to 1100 nm and excited-state properties. The thermal behavior and stability of the compound were analyzed using TGA/DTA, and the suitability of the optical material is weighed. The dielectric parameters and AC conductivity were investigated as a function of frequency and temperature. Second-harmonic generation (SHG) efficiency was measured using the Kurtz and Perry powder approach and found 4MBA to be 0.8 times the KDP. The nonlinear refractive index (n_2), nonlinear optical absorption (β) and third-order nonlinear optical susceptibility ($\chi^{(3)}$) measured values are 1.548×10^{-9}cm^2 W^{-1}, 0.0538×10^{-4}cm W^{-1}, and 6.049×10^{-8}esu respectively, and shows that the 4MBA molecule is a third-order nonlinear optical material. The optical limiting threshold value is determined as 7.632×10^3W cm^2 for 532nm continuous-wave laser, representing that the 4MBA is a strong candidate for the optical limiting application. The static and dynamic nonlinear optical parameters were computed with three

different functions including B3PW91, M06 and PBE0 using LanL2DZ basis set. The outcomes revealed that the 4MBA molecule under study might be a promising NLO material for frequency generators and optical limiters applications.

Graphical abstract



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Introduction

Materials with high nonlinear optical (NLO) characteristics have recently attracted much attention due to their essential applications in optoelectronics, high-density, laser printing, optical logic, laser display, frequency shifting, optical parametric generation, and biophotonics [1], [2], [3]. Growing metal-organic materials with a wide transparency range and high nonlinear coefficient, appropriate for device fabrication, has been a continual effort [4], [5], [6]. Because of its significant and quick nonlinear response, their potential uses are implied in optical communication, optical data processing, and optical switching [7,8]. Organometallic complexes containing transition metal ions have novel features with various excited states in the complex system, and they are flexible to adapt to the metal-ligand interactions. Furthermore, such complexes exhibit a high molecular hyperpolarizability, resulting in an ultra-fast optical response and excellent third-order nonlinear effects. These are chemically favorable due to π-electron delocalization and electron transfer in the metal-ligand complex [9], [10], [11]. In the case of metal–organics, the polydentate ligand acts as a space linker to form a self-aggregated complex. As a prelude to the latter observations, there is a need to address the competitive metal-organic driven NLO materials found in the literature. Some of them are interesting and noticeable, such as bis(L-asparaginato)zinc(II), 4-dimethylaminopyridine potassium chloride, Bis(4-methylbenzylammonium) tetrabromidozincate and 4-methylbenzylammonium nitrate [12], [13], [14], [15]. Among the majority of the 4-methylbenzylamine-based crystals are centrosymmetric. Further, due to increased molecule polarizability, these crystals have enhanced nonlinear optical characteristics and find uses in high-speed signal transmission [16,17]. Methylbenzylamine and methylbenzylamine-based organic ligands are more attractive due to their ability to form strong hydrogen bonds through nitrogen atoms. Methylbenzylamine is an attractive ligand for building organic-inorganic cocrystals because of its metal complex ion properties [18]. On the other hand, due to its fascinating, complex ion formation potential, copper (Cu) has been extensively used to synthesize metal-organic hybrid crystalline solids [19], [20], [21], [22]. Cu is an outstanding choice among transition metals, offering enhanced charge transfer capabilities because it has a suitable hydrogen bond acceptor to an unpaired electron in the 4S state [23], [24], [25]. It emphasizes the copper complex as a promising supramolecular synthesis moiety. Because of the increased demand for crystals due to the electronic industry revolution, we must synthesize new NLO materials and improve existing materials' NLO characteristics. We synthesized and developed the methylbenzylamine and copper-based metal-organic nonlinear optical bis(4-methylbenzylammonium) tetrachlorocuprate (4MBA) single crystal with all of the above factors in mind.

In the current work, the 4MBA compound was synthesized and single crystals were grown by slow evaporation method, and further recrystallization yielded optically quality single crystals. X-ray single crystal structure, Fourier transform nuclear magnetic resonance (FT-NMR) studies, Fourier transform infrared (FTIR), Energy dispersive X-ray (EDX) analysis, Scanning electron microscopy (SEM), UV–vis–NIR spectrum, Thermal analysis (thermogravimetric analysis (TGA) and differential thermal analysis (DTA)), dielectric measurements and Hirshfeld surface analysis, was extensively implemented for the 4MBA compound. The measurement of second-harmonic generation (SHG) and third harmonic generation (THG) using Kurtz-Perry and Z-scan techniques was performed. Besides, theoretical study on the structure, vibrational spectra, Mulliken atomic charge, Frontier molecular orbital (FMO) and Natural bond orbital (NBO) analysis, static and dynamic of first and second hyperpolarizabilities were estimated using density functional theory (DFT) at three different functions including B3PW91, M06 and PBE0 using LanL2DZ basis set. In totality, our detailed study made on 4MBA material revealed full structure details and made us know how pertinent optical properties are worthwhile to claim the potential optoelectronic applications [26], [27], [28], [29], [30].

Section snippets

Material synthesis, crystal growth and morphology