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Growth and characterization of an organometallic nonlinear optical crystal of manganese mercury thiocyanate (MMTC)

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Abstract

A novel nonlinear optical single crystal of MMTC was grown at room temperature by slow evaporation technique. The sample was confirmed by single-crystal XRD and CHN analysis. The spectroscopic properties were investigated by FTIR and optical absorption spectra. The SHG efficiency and laser damage threshold studies confirm the superiority of this crystal over conventional laser materials. The dielectric response and photoconducting nature of the crystal were also investigated and reported. Microhardness studies on MMTC suggest that the crystal has a moderate VHN value. The thermal properties of the crystal were investigated by photopyroelectric technique.

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1. Introduction

Recently, the metal complexes of thiourea, thiocyanate and allyl thiourea have emerged as strong second order nonlinear optical materials (SONOLO) for laser applications [1–3]. The special interest on these materials is attributed to their large nonlinearity, high damage threshold, low UV cutoff and moderate thermal and mechanical properties. The double ligand model theory proposed by Xu et al. [4] facilitates the development of this new class of materials. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with physical ruggedness and excellent transmittance of inorganics. Like organic materials, organometallic compounds also offer the advantage of architectural flexibility and ease of fabrication and tailoring. An important aspect of utilizing organometallic structures for nonlinear optics is their unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal [5]. The engineering of organic or inorganic NLO crystals involves the basic question of noncentrosymmetry, only the II B metal complexes of Zn, Cd, Hg, and Mn crystallize in a noncentrosymmetric space group I4. Crystals such as BTCC, ZTS, ZCTC, ZMTC, MMTC, CMTC and CMTD belong to this category and they are identified as promising materials exhibiting excellent physical/chemical properties [6–8]. Among this class of organometallic crystals reported so far, MMTC is rated as the second best material in terms of second harmonic efficiency (18 times that of urea) [9], only ZCTC has better efficiency (51 times that of urea)

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than it [10]. MMTC belongs to the tetragonal crystallographic system, with cell parameters $a = 11.324\,\text{Å}$, $c = 4.270\,\text{Å}$, $V = 547.5\,\text{Å}^3$ and density $= 2.959\,\text{g/cm}^3$ [1]. MMTC has a fairly high thermal stability and its decomposition starts around 347.8 °C [1].

As a continuation of our ongoing research on novel organometallic crystals [11–13], in this paper we are reporting on the growth and characterization of MMTC, a prominent member of the above-mentioned category. In the present work, relatively large and good optical grade MMTC crystals were grown from aqueous solution by slow evaporation technique, and their optical properties were investigated by FTIR and UV–Vis–NIR absorption spectra. In addition, the dielectric, photoconducting, mechanical and thermal (PPE studies) properties of MMTC were studied and reported for the first time.

2. Experimental procedure

2.1. Crystal growth

MMTC was synthesized by taking appropriate amount of NH_4SCN, $MnCl_2$ and $HgCl_2$. All the starting materials were highly pure and used as purchased. The following is the reaction formula:

$$4NH_4SCN + MnCl_2 + HgCl_2 \rightarrow MnHg(SCN)_4 + 4NH_4Cl.$$

To ensure high purity the material was purified by successive recrystallization in double-distilled water. The recrystallized salt of known weight was dissolved in double-distilled water and tiny pale greenish yellow crystals of MMTC were formed by spontaneous nucleation within 7–10 d. Optically clear and defect-free crystals with perfect shapes were chosen as seeds to carry out the growth experiment. The seeds were seasoned and then hung in the beaker containing the supersaturated solution. The solvent was allowed to evaporate at a constant temperature of 305 K by covering the vessel with a perforated lid. Good quality crystals of dimension up to $12 \times 8 \times 6\,\text{mm}^3$ were harvested in a period of 50–60 d. As the days progress, the color of the crystal appeared to have undergone a change from greenish yellow to golden yellow. The photograph of MMTC crystals is shown in Fig. 1.

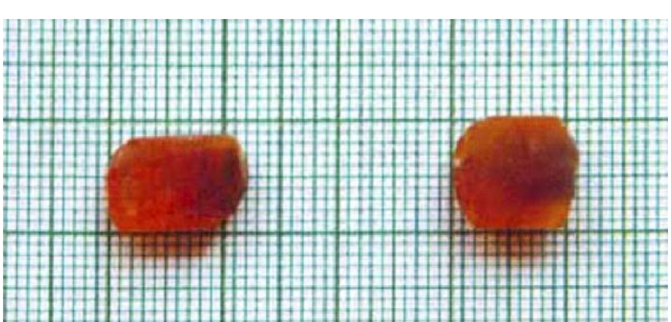

Fig. 1. Photograph of MMTC crystals.

2.2. Characterization

The single crystal X-ray analysis of MMTC crystal was carried out using Enraf Nonius CAD-4 X-ray diffractometer. The structure was solved by direct method and refined by the full matrix least-squares technique using the SHELXL program. The second harmonic efficiency of the powdered sample was studied using a Nd–YAG Q-switched laser with first harmonic output of 1064 nm and urea was taken as the reference material. The FTIR studies were carried out with freshly crushed sample of MMTC mixed with KBr in the ratio 1:10 and palletized using a hydraulic press. The FTIR spectrum was recorded in the range of $4000–400\,\text{cm}^{-1}$ using the instrument Thermo-Nicolet Avatar370. The optical absorption spectrum of MMTC was taken using VARIAN CARY 5000 spectrophotometer. The dielectric studies were carried out using HIOKIMODEL 3532-50 LCR HITESTER with a conventional two terminal sample holder (Westphal). Photoconductivity of the crystal was studied using Keithley 485 Picoammeter. The Vickers hardness number (VHN) of MMTC was studied using the Leitz Vickers microhardness tester. The percentage confirmation of S, C and N in the grown single crystals was established by CHN analysis using Elementar Vario EL III elemental analyzer.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

From the single crystal XRD data it is observed that MMTC crystal belongs to tetragonal crystallographic system with cell parameters $a = 11.3099\,\text{Å}$ and $c = 4.2537\,\text{Å}$ with cell volume $543.15\,\text{Å}^3$. The XRD data is in good agreement with the powder XRD report of Wang et al. [1], and thus confirm the grown crystal.

3.2. Non-linear optical (NLO) studies

In order to find out the NLO property of MMTC, second harmonic efficiency test was performed by the Kurtz and Perry powder technique using Q-switched, mode locked Nd–YAG laser operating at the fundamental wavelength 1064 nm, generating about 6 mJ/pulse. This laser can be operated in two modes. In the single shot mode the laser emits a single 8 ns pulse. In the multishot mode, the laser produces a continuous train of 8 ns laser pulses at a repetition rate of 10 Hz. In the present study, the single shot mode of 8 ns laser pulses with a spot radius of 1 mm was used. The experimental set up used a mirror and $\frac{50}{50}$ beam splitter, to generate a beam with pulse energy of 6 mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. For the SHG efficiency measurements, we have used microcrystalline material of