SYNTHESIS, OPTICAL AND DIELECTRIC PROPERTIES OF HIGHLY EFFICIENT ORGANOBIMETALLIC THIOCYANATE COMPLEX CRYSTALS

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Single crystals of Manganese Mercury Thiocyanate (MMTC) and its lewis base adduct Manganese Mercury Thiocyanate bis dimethyl sulfoxide (MMTD) have been grown by low temperature solution growth technique. Piezoelectric charge coefficient (d33 pC/N) of MMTC and MMTD at 110 Hz was found to be 3 pC/N and 8 pC/N respectively. Hysteresis loop parameters such as remnant polarization (P_r) and coercive field (E_c) of grown samples were also determined. The mechanical behaviors of the samples were studied using Leitz Weitzler hardness tester. The band gap of the samples was also measured.

1.Introduction

Recently, the organobimetallic crystals have fascinated Material Scientists because of their high nonlinearity, shorter UV cut-off wavelength, large optical transparency window, ability to grow easily in large dimension, high laser damage threshold and good physicochemical stability. Materials with large SONLO properties, short transparency cut off wavelengths and stable physicochemical performance are inevitable for laser applications. The metal thiocyanate complexes are capable of efficient frequency conversion of infrared laser radiation into visible and ultraviolet wavelengths and are
developed on the basis of the molecular engineering method and the double-ligand model [1].

Bimetallic thiocyanates of type AB (SCN)₄ with A=Zn, Co, Ni, Mn, Cd and B=Cd, Hg are one among those which satisfy the above mentioned features. Their crystal structure consists of two kinds of slightly flattened tetrahedral: AN₄ and BS₄. The most striking features are the –N=C=S– bridges, which connect the center atoms of the infinite three dimensional –A–N=C=S–B– networks. The metal ligand bonding in organometallics gives rise to the large macroscopic nonlinearities and excellent physicochemical stabilities due to the transfer of electron density between the metal atoms and the conjugated ligand systems. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with physical ruggedness and excellent transmittance of inorganic. Like organic materials, organometallic compounds also offer the advantage of architectural flexibility, 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[2]. Manganese mercury thiocyanate (MMTC) and its lewis base adduct, Manganese mercury thiocyanate bis dimethyl sulfoxide (MMTD) crystals are the two promising crystals in the family of thiocyanate complex. The SHG efficiency of MMTC and MMTD are 18 and 23 times of urea respectively [2,3].The MMTC belongs to tetragonal crystallographic system with space group I₄ while that of MMTD crystallizes in a orthorhombic structure with space group P2₁2₁2₁ . Both the crystals have moderate thermal stability and decomposition temperature of MMTC is around 620K, whereas MMTD is 418K [4,5]. The UV transparency with the lower cut-off wavelength of thiocyanate complexes is around 372 nm.

2. Experimental Procedure

Manganese mercury thiocyanate (MMTC) was synthesized by dissolving the analytical grade Potassium thiocyanate (KSCN), manganese chloride (MnCl₂) and mercury chloride (HgCl₂) in the molar ratio of 4:1:1 in de-ionized water. The MMTC is formed according to the following formula, 4KSCN+ MnCl₂+ HgCl₂ → MnHg (SCN)₄+4KCl . pH of the solution plays a crucial role in the growth of thiocyanate complex crystals. A large number of tiny crystals grown in the lower pH value were not transparent. So in order to get good quality transparent crystals, the pH of the solution was adjusted to 3.5 by adding HCl slowly. The synthesized compound was purified by successive recrystallization process and then the solution was allowed to evaporate at room temperature. Due to spontaneous nucleation optically clear tiny crystals were obtained in a period of 15-20 days. The defect free and well shaped crystals were chosen as seed crystals for further growth experiment.

For synthesizing the manganese mercury thiocyanate bisdimethylsulfoxide (MMTD), MMTC crystals were crushed and the powder was dissolved in mixed solvent
of DMSO and deionized water (1:3). The following reaction formula is expected to have taken place. \( \text{MnHg (SCN)}_4 + 2\text{C}_2\text{H}_4\text{OS} \rightarrow \text{MnHg (SCN)}_4(\text{C}_2\text{H}_4\text{OS})_2 \). As in the preparation of MMTC crystal, the pH of the MMTD solution was also adjusted to be 3.5. In the case of MMTC, nucleation was started after two weeks, but tiny MMTD crystals could be seen the very next day after it was kept for evaporation in the beaker. Defect free crystals chosen for further growth were hung with nylon thread and carefully suspended into the beaker containing super saturated solution. The solvent was allowed to evaporate at ambient temperature. The photograph of as grown single crystals of MMTC and MMTD are shown in Fig.1 and Fig.2 respectively. The interesting thing noted in the growth of these crystals is that when the MMTC dissolved in mixed solvent of DMSO and water, the entire structure of MMTC itself was changed and we got a new product showing different properties. From the photograph of the crystals we can easily differentiate the two crystals in terms of color.

![Figure 1. Photograph of MMTC](image1)

![Figure 2. Photograph of MMTD](image2)

3. Results and discussion

Piezoelectric studies of MMTC and MMTD were done using a Piezometer system, (Piezotest PM 300, 110 Hz), and the piezoelectric charge coefficient \( d_{33} \) was determined in conformation with piezoelectric effect. The P-E loop was traced by an indigenously built sawyer- tower circuit interfaced with computer controlled loop tracer at room temperature. Piezoelectric charge coefficient \( (d_{33}, \text{pC/N}) \) of MMTC and MMTD at 110 Hz was found to be is 3 pC/N and 8 pC/N respectively by applying a tapping force of 0.25N at room temperature. The Piezoelectric hysteresis loop of the MMTC and MMTD is shown in Fig.3and Fig.4 respectively. Hysteresis loop parameters such as remnant polarization \( (P_r) \) and coercive field \( (E_c) \) of MMTC were found to be 22.6µC/cm\(^2\) and 0.2706 kV/cm respectively while that of MMTD was 24.1µC/cm\(^2\) and 0.5728 kV/cm respectively.
Micro-hardness measurements were carried out on the MMTC and MMTD sample using Leitz Weitzler hardness tester fitted with a pyramidal diamond indenter by varying the applied loads from 5 to 30 g for an indentation time of 10 s. At least five indentation marks were obtained on each face for the same load, the distance between consecutive marks being kept more than three times the diagonal length of the indentation mark. The diagonal lengths of the indentation marks were measured using the micrometer eyepiece. The Vickers micro hardness number ($H_v$) was calculated using the equation: $H_v = 1.8544 \frac{p}{d^2}$ kg-mm$^{-2}$ where, $p$ is the applied load in kg and $d$ is the average diagonal length of the indentation mark in mm. Fig.5 shows the variation of micro hardness with the applied load for MMTC and MMTD crystals. The graph illustrates that the micro hardness number increases with increasing load. The work hardening coefficient ‘$n$’ of MMTC and MMTD was found to be 6.07 and 7.2 respectively, which indicate that both the crystals have a good hardness coefficient, and hence can find applications in device
fabri- cations. As per the concept put forward by Onitsch [6] the hardness increases with load when the hardness coefficient n is greater than 2 and the same is confirmed for MMTC and MMTD. The Vickers Hardness Number (VHN) of MMTC and MMTD were found to be 71.4 kg/mm² and 32.5 Kg/mm² for a load of 30 g. The result indicates that the VHN is higher than those for urea (6.5-11 kg/mm²) and N-methyl urea (12-19 kg/mm²), the well known organic NLO crystals [7]. A comparison of microhardness properties of organometallic crystals indicates that MMTC and MMTD have its VHN less than that of ZTS (116 kg/mm²), BTCC (136 kg/mm²) and CTA (81 kg/mm²) [8], but the VHN of MMTC is more than that of CMTD (47 kg/mm²)[9].

![Fig.5. Variation of Vicker hardness number with load](image)

An improved photopyroelectric technique [10] has been used to determine the thermal parameters of single crystal of MMTC and MMTD. The sample was illuminated by an intensity-modulated beam of light, which gives rise to periodic temperature variation by optical absorption. The thermal waves so generated propagate through the sample and were detected by the pyroelectric detector. A He-Cd laser of (wavelength $\lambda=442$ nm, KIMMON) output power 120 mW was used as the optical heating source. The light from the laser was intensity-modulated using a mechanical chopper (SR 540). A Polyvinylidene difluoride (PVDF) film of thickness 28 $\mu$m was used as the pyroelectric detector. The sample was attached to the pyroelectric detector by means of a thermally thin layer of a compound whose contribution to the signal was negligible. The signal output was measured using a lock-in amplifier (SR830). The values of thermal diffusivity ($\alpha$) and effusivity (e), the thermal conductivity (k) and heat capacity ($C_p$) of MMTC and MMTD for 40 Hz are shown in Table 1. Using Tauc’s relation a graph (Fig.6) has been plotted between $h\nu$ and $(\alpha h\nu)^2$ to determine the direct band gap value, where $\alpha$ is absorption coefficient and $h\nu$ is the energy of the incident photon, and found to be 3.20 eV and 3.32 eV for MMTC and MMTD respectively.
Table 1: Thermal Parameters of MMTC and MMTD crystals at 40Hz

| Sample Code | Thermal diffusivity, $\alpha$ (cm$^2$/s) | Thermal conductivity, $k$ (W/cm$^\circ$K) | Sp. Heat capacity, $C_p$ (J/g$^\circ$K) |
|-------------|------------------------------------------|----------------------------------------|----------------------------------|
| MMTD        | 0.4664                                   | 1.067                                  | 1.079                            |
| Thickness = 1.455 |                                           |                                        |                                  |
| MMTC        | 0.3489                                   | 0.9898                                 | 0.9585                           |
| Thickness = 1.455 |                                           |                                        |                                  |

4. Conclusion

Organobimetallic crystals of MMTC and MMTD of size 9 x 6 x 5 mm$^3$ and 11 x 10 x 6 mm$^3$ have been successfully grown by slow evaporation technique. The piezoelectric behavior of the grown samples was reported through hysteresis loop and $d_{33}$ measurements. The work hardening coefficient ‘n’ of MMTC and MMTD was found to be 6.07 and 7.2 respectively, which proved high mechanical strength of the thiocyanate complex materials. Thermal parameters of the MMTC and MMTD were also determined.

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