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Spectroscopic Investigations of Undoped and Rare Earth Doped NLO Single Crystals of Manganese Mercury Thiocyanate Bis-Dimethyl Sulfoxide

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ABSTRACT

Good optical grade single crystals of pure, lanthanum (La^{3+}) and neodymium (Nd^{3+}) doped manganese mercury thiocyanate bis-dimethyl sulfoxide (MMTD) crystals are grown from aqueous solution by slow solvent evaporation technique at room temperature. Single crystal X-ray diffraction (XRD) data reveals that the grown crystals belong to the orthorhombic crystallographic system with the non-centrosymmetric space group $P2_12_12_1$. The crystals are characterized using optical absorption, Fourier transform infrared (FT-IR), Fourier transform Raman (FT-Raman), energy dispersive X-ray analysis (EDAX) studies. The second harmonic generation (SHG) efficiencies of the grown crystals are also measured using Kurtz and Perry powder technique. The nonlinear optical (NLO) activity of the pure MMTD significantly enhances due to rare earth dopants.

1. Introduction

The rapid growth in several important areas like microelectronics and communication technologies is due to the highly demanded progress in the field of crystal growth [1]. In spite of considerable research in this field, it is often considered as a fine combination of science, technology and art to grow new materials in single crystal forms at the optimum growth conditions [2]. An important aspect of utilizing organo-metallic structures for nonlinear optical applications is their unique charge transfer transitions, either from metal to ligand or from ligand to metal. Thiocyanate (SCN) is a highly versatile ligand with two terminal modes and thirteen multidentate bridging modes of coordination. Based on the concept developed by Pearson [3] on the hard and soft acids and bases rationalizes that soft cations show a pronounced affinity for coordination with softer ligands, while hard cations prefer coordination with harder ligands. The SCN-ligands in $MnHg(SCN)_4$ bridge the tetrahedrally coordinated N-bonded Mn atoms and the tetrahedrally coordinated S-bonded Hg atoms into a 3-D network with the non-centrosymmetric space group. $MnHg(SCN)_4$ has been identified to exhibit high hyperpolarizability due to the extended π-conjugation of the Mn-NCS-Hg bridges and their parallel alignments in the 3-D crystal structure [4].

Recent studies indicate that the Lewis-base adducts of these crystals have been identified to possess superior NLO property compared to their parent metal SCN crystals. The metal SCNs and their Lewis-base adducts are some of the interesting themes of structural chemistry [5]. This encouraging switch-over is mainly attributed to the enhancement in the NLO activity, by the addition of Dimethyl sulfoxide (DMSO) ligand. The introduction of DMSO aids in better electronic oscillations in SCN ligand, leading to an improvement in NLO efficiency. The present study deals with the growth and characterization of pure and rare earth doped manganese mercury thiocyanate bis-dimethyl sulfoxide (MMTD), Lewis-base adducts of MMTC [4]. In the structure of MMTD, the hard Mn^{2+} ion is coordinated with the harder N-(SCN) and O-(DMSO) ligands, while the soft Hg^{2+} is coordinated with the softer S-(SCN) ligands. The Hg^{2+} ion is coordinated with four SCN S-atoms and is in a tetrahedral geometry [6].

The present investigation deals with the growth and characterization of pure, La^{3+} and Nd^{3+} doped Manganese mercury thiocyanate bis-dimethyl sulfoxide (MMTD) crystals, grown from a mixed solvent of water and DMSO.

2. Experimental Methods

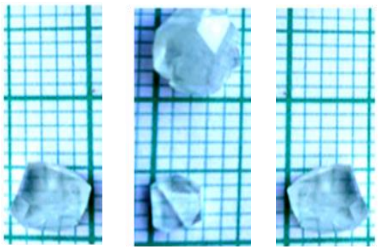
Pure MMTC was synthesized by taking appropriate amount of NH_4SCN, $MnCl_2$ and $HgCl_2$. The chemicals were dissolved in double distilled water and stirred well for about 12 hours. The following is the reaction formula.

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

The seed crystals were obtained using dimethyl sulfoxide as a ligand to react with MMTC in a mixture of dimethyl sulfoxide and de-ionized water. The chemical reaction is:

$$MnHg(SCN)_4 + 2C_2H_6OS \rightarrow MnHg(SCN)_4(C_2H_6OS)_2$$

After vigorous stirring, the pH of the solution was adjusted to be between 2 and 3 by slowly adding dilute HCl, and then allowed to evaporate at room temperature.



(a) (b) (c)

Fig. 1 Photographs of (a) pure, (b) La^{3+} and (c) Nd^{3+} doped MMTD single crystals

The same procedure is repeated for the growth of La^{3+} and Nd^{3+} doped MMTD crystals by substituting 2% of Hg by 2% of La^{3+} and Nd^{3+} respectively. Optically clear defect free and well-shaped crystals were

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chosen and used as seed crystals. The growth period ranged from 90-100 days. The photographs of the pure and doped MMTD crystals are shown in Fig. 1. The optical properties of the grown crystals have been studied by recording their FT-IR, FT-Raman spectra. Energy Dispersive X-ray analysis (EDAX) studies were also carried out.

3. Results and Discussion

3.1 Single Crystal X-Ray Diffraction (XRD) Analysis

From the single crystal XRD data, it is observed that the pure and doped MMTD crystals belong to the orthorhombic crystallographic system with the non-centrosymmetric space group $P2_12_12_1$. The unit cell parameters of the pure and doped MMTD crystals are shown in Table 1. The calculated cell parameters match well with those obtained by Wang et al. [7].

Table 1 Comparison of unit cell parameters of pure, La^{3+} and Nd^{3+} doped MMTD single crystals

Lattice parameters	Pure MMTD	La^{3+}	Nd^{3+}
a (Å)	8.6523	8.6605	8.6627
b (Å)	8.7043	8.7125	8.7232
c (Å)	27.8750	27.8820	27.8937
α = β = γ (deg)	90	90	90
Volume (Å)^3	2099.32	2103.82	2107.82
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$

3.2 Optical Absorption Studies

It is well known that an efficient NLO crystal has an optical transparency at lower cut-off wavelengths between 200 and 400 nm [8]. It is observed from the spectra (Fig. 2) that pure and doped MMTD crystals have a wide transmission window. The UV cut off wavelengths of the pure, La^{3+} and Nd^{3+} doped MMTD crystals are observed to be 374 nm, 348 nm and 354 nm respectively. The results agree well with the reported values [9]. Hence the doped samples of MMTD are found to be superior than compared to their parent MMTD. In the entire visible region, the optical absorption spectra are flat and constant. This wide transmission range in the entire visible region is a desirous useful property for opto-electronic applications.

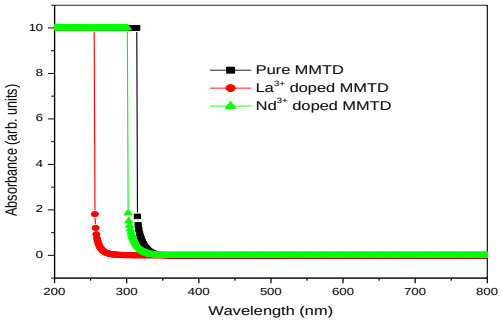


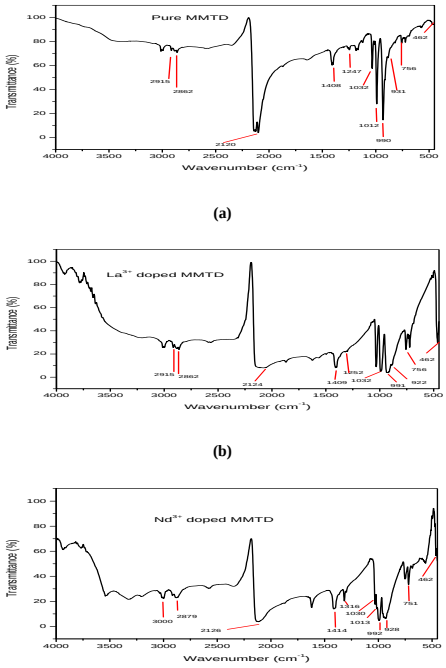
Fig. 2 Optical absorption spectra of pure, La^{3+} and Nd^{3+} doped MMTD single crystals

3.3 FT-IR Studies

Fig. 3 shows the FT-IR transmission spectra of the pure, La^{3+} and Nd^{3+} doped MMTD crystals. The main IR spectral data of pure and doped MMTD with MMTC and DMSO are presented in Table 2. It is well known that the C-N stretching vibration often lies above 2100 cm^{-1}, the C-S stretching vibration lies between 860 and 780 cm^{-1} (N-bonding) or between 720 and 690 cm^{-1} (S-bonding) and SCN bending vibration lies near 480 cm^{-1} (N-bonding) or 420 cm^{-1} (S-bonding) [10, 11]. The strong band observed at 2100 cm^{-1} which is attributed to stretching vibration of C-N in MMTD, is now shifted to 2081 cm^{-1}/ 2117 cm^{-1} due to the presence of La^{3+}/Nd^{3+} ions. The weak and sharp band at 756 cm^{-1} which is assigned to the C-S stretching in MMTD is now observed to be shifted to 751 cm^{-1} due to the presence of Nd^{3+} ions. The S-O vibration frequencies in pure and doped MMTD are now shifted to lower values when compared to that of DMSO. This could be attributed to the coordination of O atoms with the Mn atoms, which cause weaker bonds between O and S in the coordinated DMSO molecule [9]. The stretching and bending modes of C-H in pure and rare earth doped MMTD are also found to be shifted from the frequencies of free DMSO. This confirms that the molecular structure of DMSO in MMTD is different from that of the free DMSO, which can be attributed to the fact that the DMSO molecule combines with Mn as a monodentate ligand through O atom.

Table 2 Comparison of FT-IR bands of pure and doped MMTD single crystals with DMSO and MMTC

Assignments	DMSO (cm^{-1})	MMTC (cm^{-1})	MMTD (cm^{-1})	La^{3+} (cm^{-1})	Nd^{3+} (cm^{-1})
CN stretching	---	2118	2120	2124	2126
CS stretching	---	778	756	756	751
SCN bending	---	463	462	462	462
2SCN bending	---	896, 939	931, 990	922, 991	928, 992
CH stretching	2913, 2999	2905, 3009	2862, 2915	2862, 2915	2879, 3000
SO stretching	1050	---	1012, 1032	1032	1013, 1030
CH bending	1436, 1406, 1314	---	1408, 1247	1409, 1252	1414, 1316

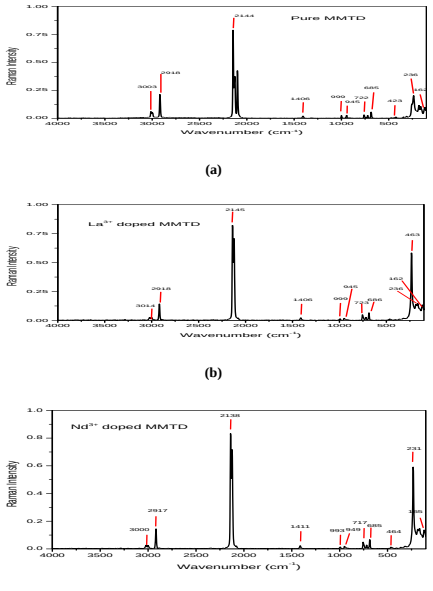


(a) (b) (c)

Fig. 3 FT-IR spectra of (a) pure, (b) La^{3+} and (c) Nd^{3+} doped MMTD single crystals

3.4 FT-Raman Studies

Fig. 4 shows the FT-Raman spectra of the pure and doped MMTD crystals. The observed bands along with their vibrational assignments are listed in Table 3.



(a) (b) (c)

Fig. 4 FT-Raman spectra of (a) pure, (b) La^{3+} and (c) Nd^{3+} doped MMTD single crystals

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Table 3 Comparison of FT-Raman spectral assignments of pure and doped MMTD single crystals with MMTC

Assignments	MMTC(cm^{-1})	MMTD(cm^{-1})	La^{3+}(cm^{-1})	Nd^{3+}(cm^{-1})
CN stretching	2146	2144	2145	2138
CS stretching	779	685, 722	686, 723	685, 717
SCN bending	447	423	463	464
2SCN bending	898, 940	945, 999	945, 999	949, 993
CH stretching	2901, 2932	2918, 3003	2918, 3014	2917, 3000
CH bending	1461	1406	1406	1411
SHgS bending	160	162	162	165
NMnN bending	231	236	236	231

3.5 EDAX Analysis

The exact weight percentages of La^{3+} and Nd^{3+} ions present in the doped crystals were determined using EDAX analysis. The results show that only 0.48 % of La^{3+} and 0.69 % of Nd^{3+} were present in the respective samples out of 2 % of the dopant (Fig. 5).

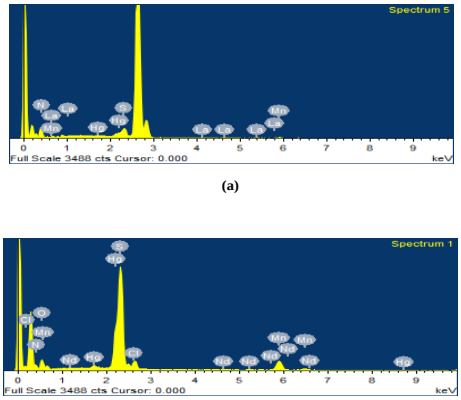

Fig. 5 EDAX spectra of (a) La^{3+} and (b) Nd^{3+} doped MMTD single crystals

3.6 Nonlinear Optical (NLO) Studies

For a laser input of 6.2 mJ, second harmonic signals of 532 nm were produced at 91.66 mW, 2273.16 mW, 2340.07 mW and 2384.99 mW for urea, pure, La^{3+} and Nd^{3+} doped MMTD crystals respectively. The experimental data confirms the second harmonic efficiencies of the pure, La^{3+} and Nd^{3+} doped MMTD crystals to be nearly 24.8, 25.53 and 26.02 times higher than that of urea. Thus the SHG efficiencies of pure and doped MMTD crystals are very much higher than CMTC, CMTD and BTCC of organometallic family [12, 13], as well as the conventional laser materials like KDP, LAP and BBO [14, 15].

4. Conclusion

The growth of single crystals of MMTD with rare earth substitution is achieved successfully by slow evaporation technique. The structure of the grown crystals and their compositions were confirmed by single crystal XRD and EDAX elemental analysis. The second harmonic efficiencies of the pure, La^{3+} and Nd^{3+} doped MMTD crystals are found to be 24.8, 25.53 and 26.02 times higher than that of urea. The good optical properties combined with very high SHG efficiency suggest that MMTD crystals with rare earth substitution can be exploited for future application in photonic device fabrications.

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