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Growth and Characterization of Pure and Rare earth doped organometallic Nonlinear Optical single crystals of Manganese Mercury Thiocyanate (MMTC)

Bhushan Kumar Lanka, Nirmal Rajeev Yerramalla and Sandhya Cole*

Department of Physics, Acharya Nagarjuna University, Guntur, India.

***Corres.author: sandhya.cole@gmail.com**

Abstract: Good optical grade single crystals of Pure and Lanthanum doped Manganese Mercury Thiocyanate (MMTC) crystals were grown from aqueous solution by slow solvent evaporation technique at room temperature. The single crystal XRD studies confirmed that Pure and Lanthanum doped MMTC crystals crystallized in tetragonal system with space group $\mathrm{I}\bar{4}$. FT-IR spectrums are used to identify the presence of functional groups of the compounds. The TG/DSC studies reveal the thermal decomposition temperatures of Pure and Lanthanum doped MMTC crystals. The Second Harmonic Generation nature of Pure and Lanthanum doped MMTC crystals were measured by Kurtz-Perry powder method.
Key Words: NLO Crystals, Rare earth, XRD, FT-IR, SHG, Decomposition temperature.

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 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. Crystals such as BTCC, ZCTC, MMTC belong to this category and they are identified as promising materials exhibiting excellent physical and chemical properties [6-8]. In this paper, we are reporting the growth and characterization of good optical grade Pure and Lanthanum doped MMTC crystals grown from aqueous solution by slow evaporation technique.

Experimental Procedure

Pure MMTC was synthesized by taking appropriate amount of NH_4SCN, $MnCl_2$ and $HgCl_2$. All the starting materials were highly pure (AR Grade) and used as purchased. 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 same procedure was repeated for the growth of La^{3+} doped MMTC crystal by substituting 2% of Hg by 2% of La^{3+}. The growth period ranged between 80-90 days. Interestingly the colour of the crystals slowly changed from its initially pale greenish to golden yellow.

Results and Discussion:

X-ray diffraction studies

Single crystal X-ray diffraction studies are carried out to identify the structure of the grown crystals. The cell parameters of pure and La^{3+} doped MMTC single crystals are a=b=11.2437 Å, c=4.2649 Å with $\alpha=\beta=\gamma=90^0$ and a=b=11.297(8) Å, c=4.271(7) Å with $\alpha= \beta = \gamma=90^0$ respectively. Both pure and La^{3+} doped MMTC single crystals are tetragonal in structure with space group $I\bar{4}$. The results suggest that the presence of dopants has not altered the basic structure of the crystal. The XRD data of the present work coincides well with the reported ones [5].

FT-IR studies

The FT-IR studies of pure and La^{3+} doped MMTC single crystals were carried out in the region 4000-500 cm^{-1}. FT-IR spectrums of pure and La^{3+} doped MMTC single crystals are shown in Figure 1(a & b). A Comparison of FT-IR bands of pure and La^{3+} doped MMTC single crystals are shown in Table 1.

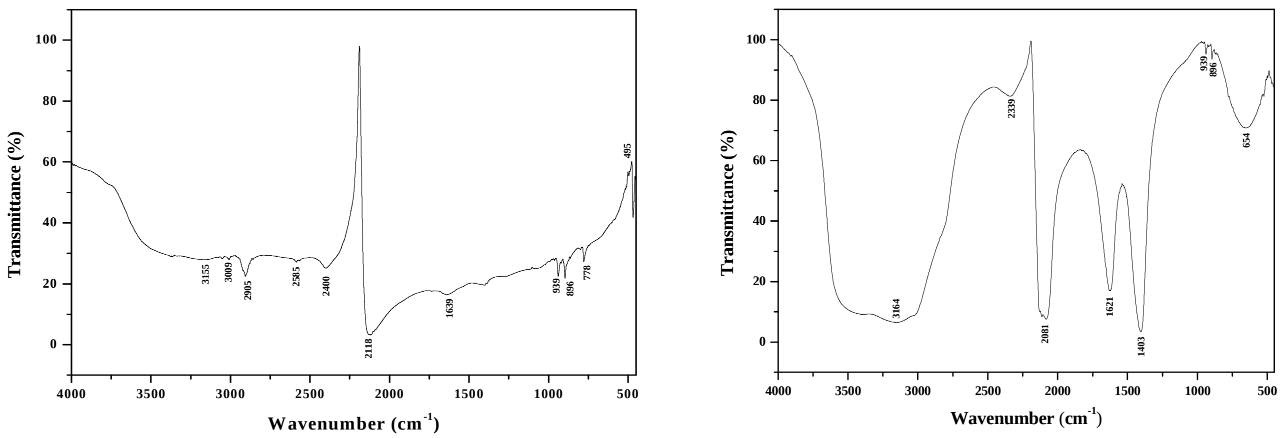

Fig 1. FT-IR Spectrums of (a) Pure and (b) La^{3+} doped MMTC single crystals.

TG/DSC studies

The thermo gravimetric (TG) and Differential scanning calorimetry (DSC) traces of pure and La^{3+} doped MMTC single crystals are shown in Fig 2 (a & b). The thermo grams appear nearly similar for the two samples with four steps of decomposition between 30^0C and 1400^0C. The first decomposition temperatures of Pure and La^{3+} doped MMTC single crystals are 360^0C and 362.6^0C respectively. Pure MMTC show four stages of weight losses of 24.81%, 37.18%, 11.89% and 4.02%, whereas La^{3+} doped MMTC show four stages of weight losses of 16.29%, 48.40%, 14.50% and 5.21%. Hence pure and La^{3+} doped MMTC single crystals have fairly high thermal stability.

Table 1. Comparison of FT-IR bands of pure and La^{3+} doped MMTC single crystals.

Wavenumber (cm^{-1})		Assignment
Pure MMTC	La^{3+} doped MMTC	
2118	2081	ν (CN)
778	654	ν (CS)
495	490	δ (NCS)
896, 939	896, 939	2δ (NCS)

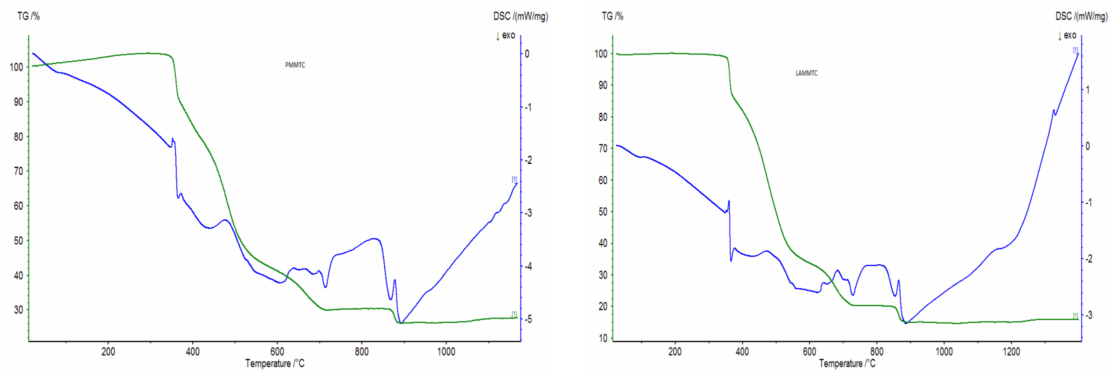

Fig 2. TG-DSC thermograms of (a) Pure and (b) La^{3+} doped MMTC single crystals.

NLO studies

The Pure and $La3^{+}$ doped MMTC single crystals were grounded into powder. The samples are tested using Q switched Nd-YAG laser of wave length 1064nm by Kurtz and Perry method. The second harmonic signals generated at the output confirm the Nonlinearity of the Pure and La^{3+} doped MMTC single crystals.

Conclusion

Pure and La^{3+} doped MMTC single crystals were synthesized and grown by slow evaporation technique from aqueous solution. The XRD studies of the grown crystals confirmed to crystallize in tetragonal system with noncentro symmetric space group $I\bar{4}$. FT-IR analysis confirmed the presence of various functional groups of the compounds. Thermal studies show that the Pure and La^{3+} doped MMTC single crystals show four stages of weight loss. The decomposition temperatures of the Pure and La^{3+} doped MMTC single crystals show that they possess high thermal stability. Nonlinear properties of the grown crystals are confirmed by Kurtz and Perry powder method.

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