

Spectral Studies on Trimetallic ($\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}$) Thiocyanate Crystals

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Abstract: EDAX spectral analysis of the trimetallic thiocyanate crystals grown by slow evaporation technique confirmed the existence of metal ions in the grown crystals. Optical transmittance of the grown crystals was determined by UV-Vis spectroscopic studies which reveal that the crystal has a wide transparency in the region 350 to 800 nm. Functional groups present in the crystals and coordination of SCN with metal ions was confirmed by FT-IR spectroscopic analysis.

Keywords: Metallic thiocyanates, Optical transmittance, EDAX

Introduction

In recent years, the search for new materials with enhanced nonlinear optical (NLO) properties has increased as a result of wide range of applications in optical communication, photonics, electronics and optical storage systems. Hence, there is a demand for materials with large NLO efficiency, high resistance to laser damage, good environmental stability and overall high performance. Moderate environmental stability, poor mechanical properties and thermal stability restrict organic materials to be used for NLO applications¹. Consequently many researchers are focusing their attention towards semi-organic materials, which combine the advantages of both organic and inorganic materials. Thiocyanate (SCN) ligand based bimetallic crystals possess several advantages due to their high transparency, better nonlinear optical response and, moderate mechanical and thermal stability, which make them potential materials for crystal engineering based three dimensional (3D) coordination networks. Recent reports on metallic thiocyanates strongly favour the possible use of this class of materials for various nonlinear optical applications and photonics device fabrications²⁻⁴.

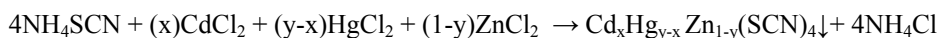
An important aspect of utilizing organometallic structures for nonlinear optics is in their unique charge transfer capability associated with charge transfer transitions either from metal

to ligand or ligand to metal. A wide variety of central metal atoms as well as the size and nature of the ligands, provide architectural flexibility to tailor NLO properties to a maximum. Organic ligands are usually found to possess more dominant NLO effects. Especially, the SCN organic ligand with medium sized π -electron systems such as benzene derivatives has its SHG efficiency higher than that of urea⁵. Metal-thiocyanate complexes have all the good characteristics, such as crystallizing in a non-centrosymmetric space group I4, pale colors and high thermal stability⁵⁻⁶. Bimetallic thiocyanates have been studied extensively by many workers and reported in the literature⁷⁻¹⁰.

The present study is focused on preparation and characterization of trimetallic thiocyanate compounds with the expectation that the presence of third metal ion in the crystal structure will improve the optical properties of the system. As far as we are aware of, no data is available in the literature on trimetallic thiocyanate compounds and this prompted us to carry out this work. The results obtained are presented herein.

Experimental

High purity (Merck, AR grade) starting materials of ammonium thiocyanate (NH_4SCN), cadmium chloride (CdCl_2), mercury chloride (HgCl_2) and zinc chloride (ZnCl_2) were used to synthesize cadmium mercury zinc thiocyanate using Millipore water. The following chemical reaction was expected.



The concentration of metal ions taken for study is tabulated in Table 1. The trimetallic thiocyanate ($\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}(\text{SCN})_4$) complex was formed as a white precipitate, which settled down in the bottom of the beaker. This was filtered and dried in a vacuum oven and used as the starting material for further studies.

Saturated solution of $\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}(\text{SCN})_4$ complexes were prepared using acetone-water (4:1) mixed solvent. The solution was stirred continuously for a period of 8 hours in a sealed container to avoid concentration gradient. Well stirred solution was then transferred to a 250 mL top sealed beaker with a perforated aluminum foil. The beaker was kept in a constant temperature bath (with an accuracy of ± 0.01 °C) at a predetermined temperature. Tiny crystals appeared at the bottom of the beaker in about 10 days time. The crystals were collected and characterized by SEM-EDAX, FT-IR (JASCO FT-IR spectrophotometer with ATR) and UV-Vis spectroscopic analyses (Shimadzu UV-Vis spectrophotometer)

Table 1. Concentration of metal ions taken for sample preparation

Sample	Concentration, in mole%		
	Cd (x)	Hg (y-x)	Zn (1-y)
1	0.4	0.3	0.3
2	0.3	0.4	0.3
3	0.3	0.3	0.4
4	0.6	0.2	0.2
5	0.2	0.6	0.2
6	0.2	0.2	0.6

Results and Discussion

Presence of metal ions (Zn, Cd and Hg) in the crystal grown was confirmed by SEM-EDAX analysis. EDAX spectrum recorded for $\text{Cd}_{0.4}\text{Hg}_{0.3}\text{Zn}_{0.3}(\text{SCN})_4$ is shown in Figure 1 and similar observations were recorded for other crystals also.

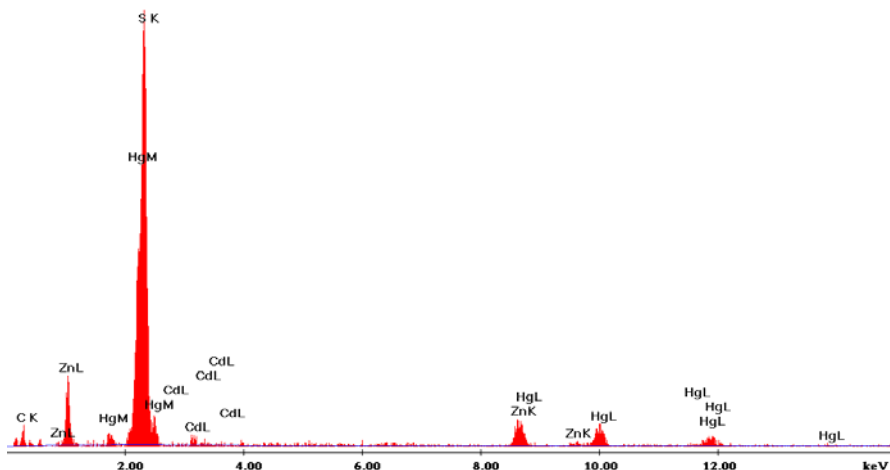


Figure 1. EDAX spectra of $\text{Cd}_{0.4}\text{Hg}_{0.3}\text{Zn}_{0.3}(\text{SCN})_4$ prepared in the present study

Figure 2 shows the FT-IR spectrum of $\text{Cd}_{0.4}\text{Hg}_{0.3}\text{Zn}_{0.3}(\text{SCN})_4$ crystal recorded in the present study. In general CN stretching vibration is expected to occur above 2100 cm^{-1} , CS stretching vibration between 860 to 780 cm^{-1} for *N*-bonding along with 720 to 690 cm^{-1} for *S*-bonding while the SCN bending vibration occurs around 480 cm^{-1} for *N*-bonding and 420 cm^{-1} for *S*-bonding¹¹. The observed very strong band at 2162 cm^{-1} confirms the presence of CN stretching in thiocyanate indicating that the thiocyanate group is coordinated to the metal ions through nitrogen and sulfur. The two weak absorption bands observed at 893 and 784 cm^{-1} are assigned to the CS stretching of *N*-bonded and *S*-bonded complexes respectively, which substantiates the characteristic feature of thiocyanate complexes. Similarly, the coordination of SCN ligand is manifested from the bending vibration mode of SCN observed as strong bands at 470 cm^{-1} and 445 cm^{-1} . The occurrence of the vibrational modes within the expected region further authenticates the existence of *N*-bonded and *S*-bonded nature in the prepared sample. Similar FT-IR spectra were obtained for all the synthesized samples in the present study.

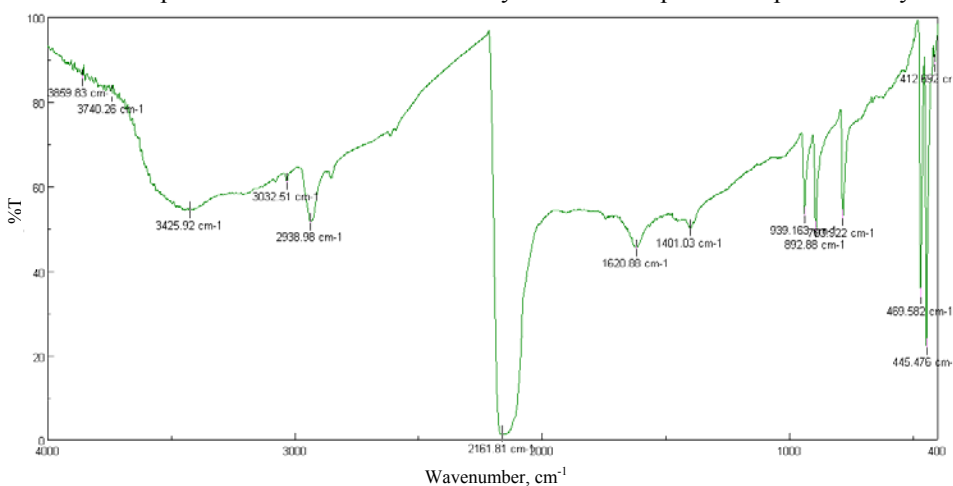


Figure 2. FTIR spectra of $\text{Cd}_{0.4}\text{Hg}_{0.3}\text{Zn}_{0.3}(\text{SCN})_4$ crystals

The UV-Vis spectra of all the six crystals grown in the present study are presented in Figure 3 and it reveals that the crystals are highly transparent showing which makes them potential candidates for optical applications.

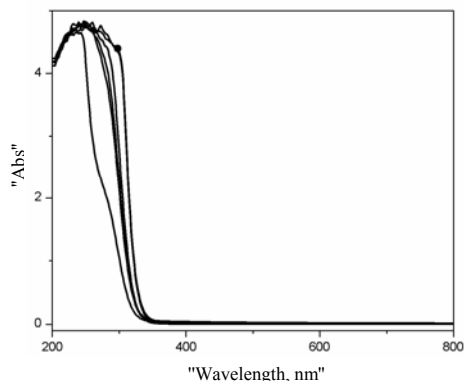


Figure 3. UV-Vis absorbance spectra of $\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}(\text{SCN})_4$ crystals

From the UV absorbance spectra, it is evident that the cut off wavelength of the compounds synthesized in the present study lies between 333 to 358 nm. By plotting graph of $(\alpha h\nu)^2$ versus $h\nu$ (Figure 4), it is possible to determine the direct band gap of the crystal. The band gap is obtained by extrapolating the linear part of the curve to zero of the ordinate and from this, E_g is found to vary between 3.82 to 4.06 eV (Table 2). It is quite clear that, the low wavelength absorption data are related to inter-band transitions (*i.e.*, excitation of an electron from the valence band to the conduction band). Similar observation has been reported for MMTC crystals¹².

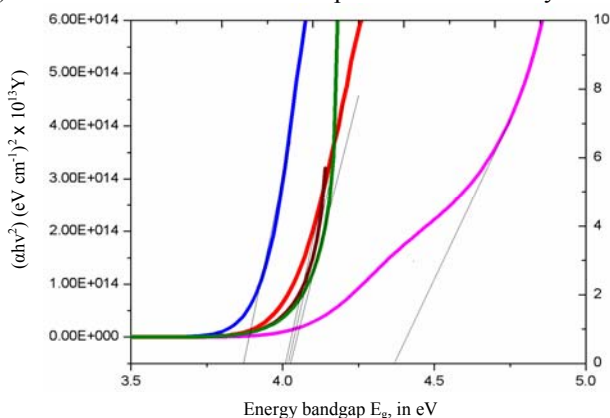


Figure 4. Tauc plots for determination of band gap energy of $\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}(\text{SCN})_4$ crystals

Table 2. Band gap energy of $\text{Cd}_x\text{Hg}_{y-x}\text{Zn}_{1-y}(\text{SCN})_4$ crystals

Sample	Bandgap energy (in eV)
$\text{Cd}_{0.4}\text{Hg}_{0.3}\text{Zn}_{0.3}(\text{SCN})_4$	3.82
$\text{Cd}_{0.3}\text{Hg}_{0.4}\text{Zn}_{0.3}(\text{SCN})_4$	3.90
$\text{Cd}_{0.3}\text{Hg}_{0.3}\text{Zn}_{0.4}(\text{SCN})_4$	4.03
$\text{Cd}_{0.6}\text{Hg}_{0.2}\text{Zn}_{0.2}(\text{SCN})_4$	4.06
$\text{Cd}_{0.2}\text{Hg}_{0.6}\text{Zn}_{0.2}(\text{SCN})_4$	4.00
$\text{Cd}_{0.2}\text{Hg}_{0.2}\text{Zn}_{0.6}(\text{SCN})_4$	3.96

Conclusion

Trimetallic ($Cd_xHg_{y-x}Zn_{1-y}$) thiocyanate crystals were successfully grown by slow evaporation technique using acetone-water mixed solvent. The presence of cadmium, mercury and zinc were confirmed by EDAX analysis. The optical absorption spectrum of the crystal showed a wide transparency window lying between 350 to 800 nm, indicating that these crystals are potential candidates for optical applications. The presence of all the major functional groups and the coordination of organic SCN ligand with metals were confirmed by FT-IR analysis.

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