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Investigation on the influence of nickel chloride on bisthiourea manganese chloride—An organometallic crystal

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ABSTRACT

Single crystals of bisthiourea manganese chloride (BTMC) mixed with nickel chloride were grown by slow evaporation solution growth technique using water as solvent in a constant temperature bath designed by the authors. The lattice parameters of the grown crystals are measured from X-ray diffraction studies. Infrared spectra were recorded to determine the symmetries of the molecular structure. The observed infrared bands were also assigned and discussed. The optical transmission spectral study was carried out to test the transmitting ability of these crystals in the visible range. The second harmonic generation test of BTMC revealed that the linear nature of the pure BTMC crystal gets transformed into non-linear nature when mixed with nickel chloride. The TGA/DTA curves recorded for the investigated crystals depict small changes upon mixing.

1. Introduction

Non-linear optical (NLO) materials play a major role in optical modulation, fibreoptic communication and optoelectronics as they are capable of producing multiple values of original frequency. Continuous effort is on in growing organic, inorganic and semiorganic materials with wide range of transparency and higher nonlinear coefficient which make them suitable for device fabrication [1,2]. Poor physical strength and higher degree of polarization are the characteristics of organic materials whereas greater physical strength and lesser degree of polarization are the characteristics of inorganic materials. For NLO materials, we require greater physical strength and higher degree of polarization which prompted the development of hybrid organic–inorganic materials called semiorganics [3]. Among the semiorganic NLO materials, metal complexes of thiourea having lower cut off wavelengths, applicable for frequency conversion are of interest as both organic and inorganic components in it contribute specifically to the process of SHG [4–10]. Bisthiourea manganese chloride a material which was reported as organometallic crystal by the authors [11] earlier is taken to study the influence of nickel chloride for the present investigation. Bisthiourea nickel chloride crystals reported by the authors [12] gave SHG output whereas BTMC crystals show no output when subjected to SHG test showing that it is purely a linear crystal. The present work is carried out to investigate the influence of nickel on the linear nature of BTMC crystals by gradually increasing the percentage of nickel chloride in it.

2. Experimental

In the present investigation single crystals of bisthiourea manganese chloride (BTMC) mixed with nickel chloride were grown by using slow evaporation solution growth method. The main drawback in slow evaporation solution growth is the random variation of room temperature. This may result in spurious growth. To overcome this drawback a constant temperature bath was designed by the authors and was used for growing these crystals at a temperature of 33 °C. A 25 l water tank was constructed with a glass window. A water heater with 1000 W power was fixed at the bottom of the tank and two stirrers were provided at the top and middle part of the tank for uniform distribution of heat. The temperature of water in the tank was controlled digitally by using INTEL microprocessor 8085. Here microprocessor with the interfacing of ADC 0808, monitored the temperature. When the temperature is set and switched ON, the heater supplies heat so that the water in the tank attains the set temperature. When the set temperature of water varies due to fluctuations in room temperature, the microprocessor with the aid of ADC controls the current through the heater so that the temperature of water remains constant. Variation in temperature of the bath can be tuned to an accuracy of ±0.1 °C. Three different mixed crystals were grown with higher percentage mixing of nickel chloride (25%, 50%, 75%).

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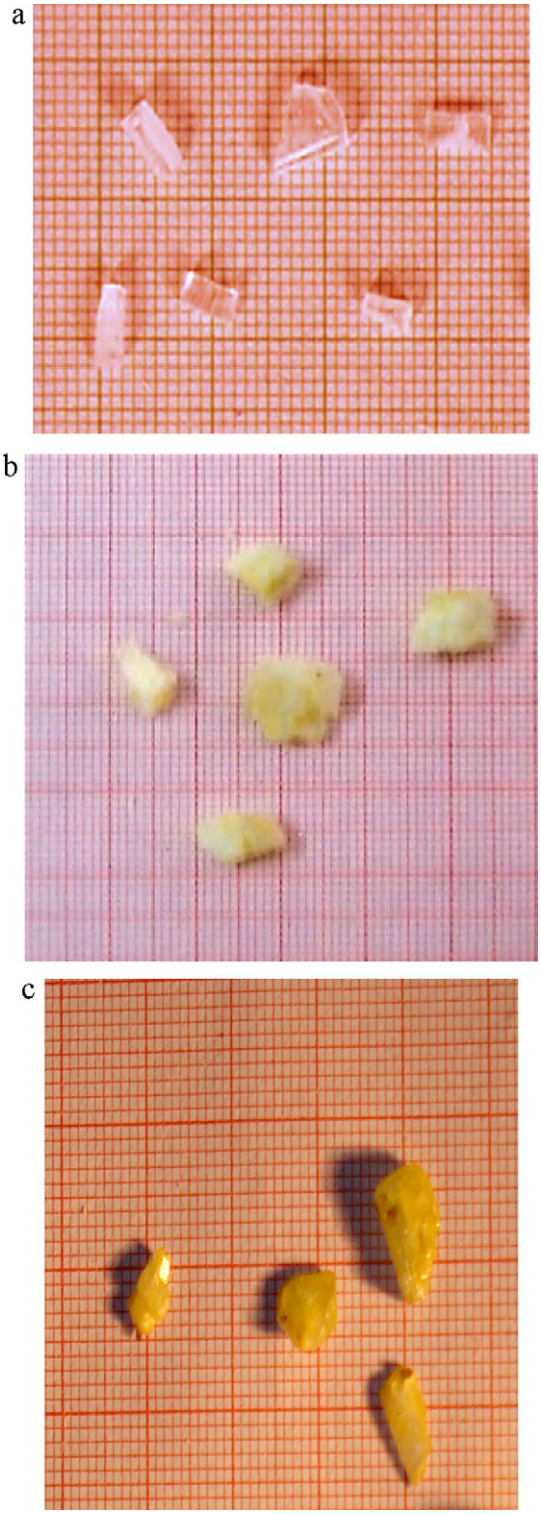

Fig. 1. Photographs of the mixed crystals of BTMC with nickel chloride.

This is done by preparing super saturated solutions of thiourea, manganese chloride and nickel chloride. The salts nickel chloride and manganese chloride were dissolved in water with molar ratio 1:3 for 25%, 1:1 for 50% and 3:1 for 75%. Good quality crystals were harvested in about 80 days. The photographs of the crystals are shown in Fig. 1a–c, respectively in the increased order of nickel mixing.

3. Characterization

The mixed crystals of BTMC with nickel chloride have been subjected to X-ray diffraction studies using an ENRAF NONIUS CAD4 X-ray diffractometer to determine cell parameters and morphology. The studies revealed that these crystals belong to orthorhombic system. The lattice parameters of BTNC, BTMC and mixed crystals of BTMC with nickel chloride are given in Table 1. The data reveals the fact that mixed crystals of BTMC with nickel chloride possess greater volume when compared with pure BTMC. This is due to greater atomic radius of nickel when compared with manganese.

4. Recording of spectra

4.1. IR measurements

The room temperature Infrared spectrum of BTMC mixed with nickel chloride were recorded in the region 450–4000 cm^{-1} at a resolution of $\pm 1\,cm^{-1}$ using a BRUKER IFS 66V Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source; boxcar apodization was used for the 250 averaged interferogrames collected for the sample.

5. Results and discussion

5.1. Analysis of the IR spectra of thiourea vibrations in mixed crystals of BTMC with nickel chloride

The IR spectra of BTMC and BTNC were reported earlier [11,12]. In the present study an attempt has been made to reveal the effect of coordination on the vibrational bands when nickel replaces manganese. The IR spectra of mixed crystals of BTMC with 25% nickel chloride, 50% nickel chloride and 75% nickel chloride are shown in Fig. 2a–c, respectively. In the IR spectrum of pure BTMC [11], the NH_2 rocking, N—C—N stretching and C—S stretching bands were observed whereas in the IR spectrum of BTMC mixed with 25% nickel chloride (Fig. 2a) they were observed with lesser intensity. These modes were not observed in the other two IR spectra Fig. 2b and c similar to the IR spectrum of BTNC [12]. This confirms the mixing of nickel chloride with BTMC. A comparison of IR modes is made between investigated crystals, thiourea, BTMC and BTNC (Table 2).

5.2. Optical absorption spectral studies

The optical absorption spectra were recorded using Varion Cary 5E UV-Vis-NIR spectrophotometer in the range 190–1100 nm with high resolution. The optical absorption spectra of mixed crystals of BTMC with 25% nickel chloride, 50% nickel chloride and 75% nickel chloride are shown in Fig. 3a–c, respectively. The low value of absorbance in the entire visible range shows the high transmission ability of the grown crystals. The lower cut off is found to be around 270–280 nm for these crystals which is an advantage in semi organic non-linear optical materials over their inorganic counterparts.

5.3. Second harmonic generation

The Second harmonic generation of the mixed crystals of BTMC with nickel chloride were studied using Nd:YAG laser (Model continuum YG501C, $\lambda = 1064$ nm). Powdered sample of the investigated crystal was taken in a glass capillary tube. It was irradiated