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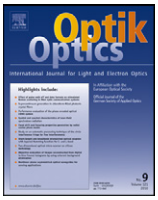

Synthesis, growth, spectral, thermal and photoluminescence properties of a new semiorganic NLO crystal—Thiosemicarbazide lithium chloride [TSLC]

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ABSTRACT

Thiosemicarbazide lithium chloride [TSLC] a new semiorganic nonlinear optical crystal has been synthesized. Single crystals by TSLC have been grown by slow evaporation solution growth technique at room temperature. Chemical composition of the synthesized material was confirmed by elemental analysis. Powder X-ray diffraction (XRD) pattern of the grown crystal has been studied. Functional groups present in the materials were identified by FT IR spectral analysis ranging between 4000 and 450 cm^{-1}. The optical transmission was studied through UV–vis spectrophotometer. Thermal analysis is carried out on the crystal and inferred to be stable at 176 °C. The second harmonic generation (SHG) of the TSLC crystal was confirmed using Nd:YAG laser and also fluorescence spectral analysis is carried out for the TSLC crystal.

1. Introduction

For the past few decades organic nonlinear optical crystals have been the major focus of numerous scientific interests attracting much attention owing to their non-linearity quick response, tailorabilty and flexibility [1–4]. Organic crystals fall short of vital technological properties including mechanical strength, chemical stability and performance at low and high temperature. In order to overcome the shortcoming of the organic materials, some new classes of metal–organic NLO crystal have been developed [5]. The limitations on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device grade organic single crystals have egged on scientists to adopt alternate strategies. Obviously began the development of hybrid organic–inorganic materials. The achievement to have high efficient optical quality organic based NLO materials in semiorganic class is to form compound in which a polarizable organic molecule is stoichiometrically bonded to inorganic host [6–8].

Recently metal complexes of thiourea derivative analogs have been explored. Thiourea derivative is a centrosymmetric molecule, when coordinate with metal ion it becomes non-centrosymmetric material to exhibit non-linear optical activity. In the recent past, the nonlinear optical properties of products of thiourea [9–12] have attracted a great deal of interest. The aspiring metal–organic materials have the potentials for combining high optical nonlinearity and the chemical flexibility of organics with thermally stable and mechanically robust inorganic molecules resulting in useful nonlinear optical properties.

In the present study lithium chloride is combined with thiosemicarbazide to form a new semiorganic (metal–organic) nonlinear optical material. This paper reports the synthesis, crystal growth and characterization studies of TSLC single crystal grown by solution method. The title compound subjected to X-ray diffraction, absorption, NLO studies, thermal analysis, FT IR, elemental and photoluminescence are presented and discussed.

2. Experimental technique

The new semiorganic material thiosemicarbazide lithium chloride [TSLC] was synthesized by mixing an aqueous solution of lithium chloride combine with thiosemicarbazide in the ratio 1:2. The chemical reaction is given in Scheme 1.

As thiosemicarbazide has a coordinating capacity to form a variety of metal–thiosemicarbazide complexes the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. Care was taken to minimize the temperature fluctuations and mechanical disturbance. The single crystals of TSLC were grown by slow evaporation technique at room temperature. Transparent colorless crystals were obtained in 20–25 days. The photograph of the as-grown crystals is shown in Fig. 1.

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$$LiCl + 2[CHNS(NH_2)_2] \rightarrow Li[CHNS(NH_2)_2]_2Cl$$

Scheme 1. Chemical reaction of TSLC.

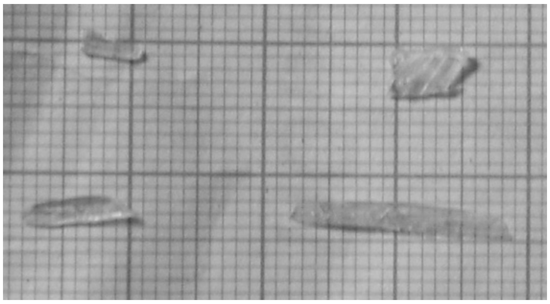

Fig. 1. As-grown TSLC crystals.

Table 1
Elemental analysis of TSLC crystals.

Element	Experimental (%)	Theoretical (%)
C	13.80	11.69
H	5.63	4.86
S	27.05	28.54

3. Result and discussion

3.1. Elemental analysis

The percentage compositions of the constituent elements present in thiosemicarbazide lithium chloride [TSLC] crystals were determined by Vario EL III Elemental. The percentages of carbon, hydrogen and sulphur are presented in Table 1. The experimental values are close to the theoretically values.

3.2. X-ray diffraction

The powder X-ray diffraction pattern of the synthesized compound is shown in Fig. 2. A JEOL JDX services instrument was obtained by the X-ray powder diffraction pattern. The observed intending of the peaks and its '*d*' values are given in Table 2. The prominent peak appears at 2θ values of 28.2169° and also includes many low intensity lines. The crystallinity of the synthesized compound is confirmed from the sharp and well-defined Bragg's peaks.

3.3. FT IR absorption studies

The FT IR spectra of TSLC crystal were recorded in the wave number range of 4000 to 450 cm^{-1} employing Thermo Nicolet 200 FTIR spectrometer by KBr pellet method in order to reveal the metal complex coordination. The FT IR absorption spectrum of TSLC is shown in Fig. 3. From the following observations the presence of the specific groups are confirmed. The FT IR spectra of TSLC when compared with the spectra of thiourea [13], a few peaks were found to be slightly shifted. In the complex, there are two possibilities by which the coordination of lithium with amniothiourea can occur. The coordination with lithium may occur either through sulphur or nitrogen of thiosemicarbazide. Most of the metals form a complex through sulphur [14].

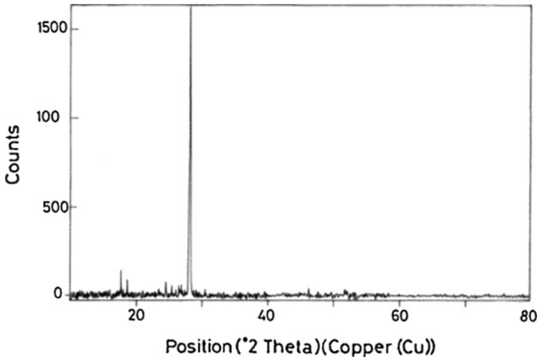

Fig. 2. Powder XRD patterns of TSLC crystals.

Table 2
X-ray powder diffraction data of TSLC crystals.

Peak	2θ (°)	*d*-Value
1	17.7404	4.9955
2	18.5992	4.7668
3	24.5045	3.6297
4	25.4604	3.4956
5	26.9805	3.3020
6	28.2169	3.1601
7	51.6629	1.7678

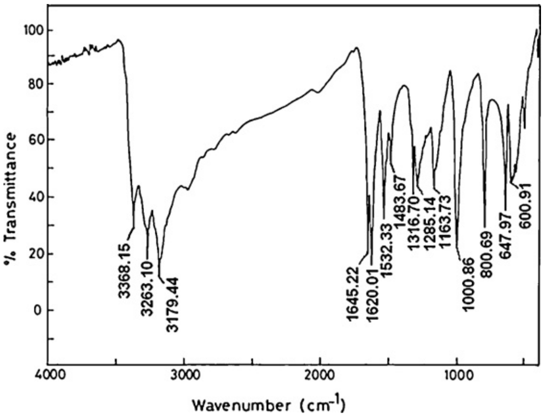

Fig. 3. FT-IR spectrum of TSLC crystals.

In the higher energy side there is a broad envelope positioned between 3368 and 3179 cm^{-1} which corresponds to the symmetric and asymmetric stretching modes of NH_2 grouping of amino thiourea. The medium and strong bands lying between 1645 and 1532 cm^{-1} are due to the absorption of the NH_2 bending and scissoring vibration .The absorption of the band at 1483 cm^{-1} is attributed to stretching vibration of N–C–N. The well resolved peaks between 1285 and 1000 cm^{-1} are due to C–N stretching. The bands observed at 647 and 600 cm^{-1} are assigned to C–Cl stretching respectively. The spectra dip lets a shift in frequency band in the low frequency region. The assignments confirm the presence of various functional groups present in the material, tabulated in Table 3.

Table 3
FT-IR data of TSLC crystals.

Wave number (cm^{-1})	Assignments
3263	N–H asymmetric stretching vibration of NH_2 groups
3179	N–H symmetric stretching vibration of NH_2 groups
1620	NH_2 deformation
1532	Asymmetric N–C–N stretching
1483	Asymmetric C=S stretching
1000	Symmetric N–C–N stretching
800	Symmetric C=S stretching
500	N–C–S bending