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Growth and characterization of a new semiorganic nonlinear optical crystal-Bis (thiourea) lithium chloride

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Abstract

Single crystals of a new semiorganic nonlinear optical material bis(tiourea) lithium chloride (BTLC) were successfully grown by slow evaporation solution growth technique. Chemical composition of the synthesized material was confirmed by elemental analysis. The BTLC crystals were characterized by powder diffraction analysis and the crystallite size was calculated. The presences of functional groups were identified through Fourier transform-infrared technique. The optical transparency was studied through UV–Vis spectrophotometer. The thermal stability of the crystal was determined from thermogravimetric and differential thermal analysis curve. The second harmonic generation behavior of BLTC crystal was tested by Kurtz–Perry powder technique. The fluorescence spectrum of the crystal was recorded and the optical band gap is about 2.3 eV.

Keywords: Bis(tiourea) lithium chloride; Growth from solution; X-ray diffraction; Thermal analysis; Nonlinear optical material; Fluorescence

1. Introduction

Nonlinear optics has been recognized for several decades as a promising field with important application in the domain of opto-electronics and photonics [1,2]. High-performance electro-optic switching element for telecommunication and optical information processing are based on materials with high nonlinear optical properties. Hence a variety of materials have been investigated for their nonlinear optical properties. A lot of organic chromophores exhibit extremely high and fast nonlinearities much better than those observed in inorganic crystals but they are thermally unstable. Hence, recent search is focused on semiorganic materials due to their large nonlinearity, high laser damage threshold, good mechanical and thermal stability [3,4]. At present metal complexes of thiourea and its derivatives has been investigated. Examples of these types are potassium thiourea chloride [5], potassium thiourea iodide [6], thiosemicarbazide cadmium chloride monohydrate [7,8]. Thiourea is a centrosymmetric molecule, when coordinated with metal ions it becomes noncentrosymmetric materials showing nonlinear optical activity. Many lithium complexes possess NLO property. Among them, lithium iodate, lithium niobate and lithium hydrogen oxalate [9] have attracted the researchers due to their potential applications.

In this paper, we report the growth of a new semiorganic NLO crystal BTLC. The grown crystals were characterized by Fourier transform-infrared

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technique (FT IR), powder XRD, optical absorption, TGA/DTA analysis, photolumiscence and NLO studies.

2. Experimental

BTLC was synthesized from aqueous solutions of lithium chloride and thiourea in the stiochiometric ratio 1:2, following reaction

$$LiCl + 2[CS\ (NH_2)_2] \rightarrow Li\ [CS\ (NH_2)_2]_2\ Cl$$

The saturated solution was taken in a beaker and the solvent evaporation technique was employed to grow single crystals of BTLC. Care was taken to minimize the temperature fluctuations and mechanical disturbance. Optical quality needle-shaped single crystals of the title material of size $5 \times 2 \times 2$ mm were harvested in a span of 25–30 days time. The photograph of the as-grown crystals is shown in Fig. 1.

3. Result and discussion

3.1. Elemental analysis

The elemental analysis was carried out for BTLC crystal using Elemental Vario EL III elemental analyzer. The results of elemental analysis (Table 1) confirms the stiochiometric and hence the molecular formula of the synthesized crystal. The experimental values are close to the theoretically values.

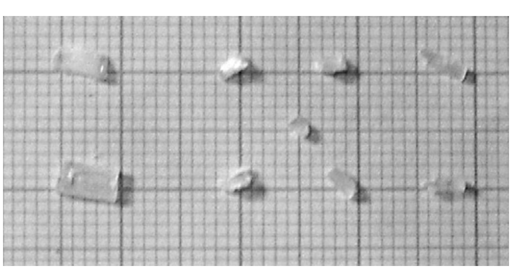

Fig. 1. As-grown BTLC crystals.

Table 1. Elemental analysis of BTLC crystals.

Element	Experimental value (%)	Theoretical value (%)
C	14.10	12.34
H	4.92	4.14
N	29.12	28.78
S	30.64	32.94

3.2. Powder X-ray diffraction

The grown crystals were characterized by powder X-ray diffraction using a JEOL JDX service instrument with Cuk$_\alpha$ radiation (1.5406 Å). The sample was scanned in the range 10–90 °C at a scan rate of $2^\circ\,min^{-1}$. The diffraction pattern of BTLC is shown in Fig. 2. The well-defined Bragg's peak reveals the high crystalline nature of the crystal. The d spacing and their relative intensities of the diffraction peaks are tabulated in Table 2. The crystallite size (D) was calculated using Scherer's formula from the full-width at half-maximum (FWHM)

$$D = k\lambda/\beta\cos\theta$$

where β is the broadening of diffraction line measured at half of its maximum intensity, λ the X-ray wavelength (1.5406 Å), θ the Bragg's angle and k the constant (0.9). The calculated average crystallite size is about 93 nm.

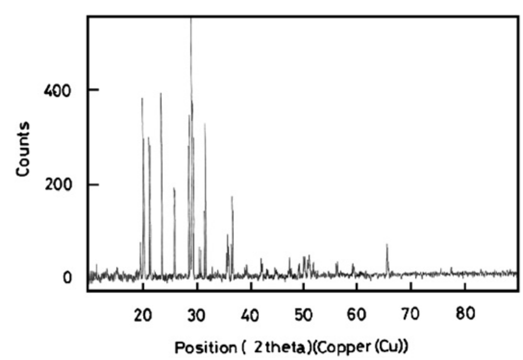

Fig. 2. Powder XRD patterns of BTLC crystals.

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

2θ	d-spacing (Å)	FWHM
19.5071	4.55071	0.1673
20.0778	4.42262	0.1338
21.0287	4.22474	0.1506
23.4922	3.78699	0.1673
25.7554	3.45912	0.1506
28.6582	3.11500	0.1840
29.1807	3.06041	0.2007
30.5336	2.92782	0.1338
31.5830	2.83290	0.1673
35.7562	2.51125	0.2342
36.5241	2.46020	0.1673
39.2865	2.29335	0.8029
42.0698	2.14784	0.2007
47.3024	1.92173	0.1673
50.0737	1.82168	0.2342
65.4862	1.42418	0.3264