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Comparative Study of Thiourea Family Crystals

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Abstract

In the recent years, nonlinear optical (NLO) crystals have attracted the researchers due to their potential applications in various fields. Thiourea is a centro symmetric molecule and has the ability to form an extensive network of hydrogen bonds. Most of the thiourea complexes are metal organic coordination complexes some of the nonlinear crystals of the metal complexes of thiourea reported are bisthiourea zinc chloride, bisthiourea cadmium chloride and zinc thiourea sulphate. This paper aims to analyze the impact of doping of different materials on optical, mechanical and thermal properties.

Key words: Thiourea complexes, optical, thermal property.

Introduction

In recent years several studies dealing with organic, inorganic and semi organic molecules and materials called nonlinear optics (NLO) are being reported due to the increasing need for photonics applications. The nonlinear (NLO) responses induced in various molecules in solution and solids are of great interest in many fields of research [1-6]. Thiourea is an interesting inorganic matrix modifier due to its large dipole moment and it forms a good network of hydrogen bonds effectively. It is the family of orthorhombic crystal system. However, most of the thiourea complexes crystallize in centro symmetric form at room temperature and do not show second harmonic generation (SHG). Only a few of thiourea complexes viz, zinc thiourea sulphate [2] , ATCC [4] , cadmium thiourea acetate [6] , bis thiourea cadmium chloride , allyl thiourea mercury bromide , thio semicarbazide cadmium bromide and bismuth thiourea bromide crystallize in non centro symmetric structure and show second harmonic generation.

This paper aims to analyze the effect of doping of amino acids (L-Histidine and Glycene) and metals in thiourea complexes [6-10].

Experimental

All the crystals were grown by slow evaporation technique. The materials are chosen in stoichiometric ratio and mixed in double distilled water. The solution was thoroughly mixed for homogeneous mixture of the solution. This solution was maintained at constant temperature. Then the solution was filtered using Waterman filter paper and poured in to petri dishes. The solution was then left for slow evaporation. After few days the crystals were harvested.

The details of growth periods of the crystals were tabulated in Table1. It is evident that the L-Histidine doped thiourea crystals were growing fast whereas the nickel doped thiourea crystals were growing slowly. In general the amino acids when doping can easily form the nucleation and helps for fast growth of crystals. On the other hand the heavy metals slow down the process of nucleation and growth.

Result and discussion

UV – Vis Studies

Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. The cut off wavelength of the grown materials were tabulated in Table.2.

Table.1. Growth periods of thiourea crystals

Crystals	Growth period
Glycine thiourea	20 days
L-histidine thiourea	8 days
Bis-thiourea nickel bromide	110 days
Thiourea cadmium bromide	20-25 days
Thiourea cadmium chloride	3 weeks
Bis -thiourea cadmium bromide	20-25 days

Table.2. Cut off wavelengths of grown crystals

Sample	UV cut off λ	Transparent region	Absorption of light in visible region	Optical band gap eV
GT	250	300 – 1100	Absence	4.70
TCC	258	300 – 1100	Low	4.81
TCB	225	300 – 1100	Low	4.88
TZS	260	300 – 1100	Low	4.77
BTNB	248	300 – 1100	Low	4.73
BTCB	269	300 – 1100	Low	4.45
LHTU	278	300 – 1100	Low	5.53

From the table, it is observed that the amino acid doped crystals (GT, LHTU) lowers the transmission property. It is because increasing bulk group. However heavy metals increases the transparent nature of the thiourea crystals

Micro-hardness

Hardness is a measure of the resistance to plastic deformation. This permanent deformation can be achieved by indentation, bending, scratching or cutting. The hardness of the crystal carries information about the mechanical strength, chemical bindings, yield strength and elastic constants of the material

Table.3. Hardness of grown crystals

It is concluded from the above table, BTNB has high hardness. Generally bromide is more electro negative element. Cadmium, nickel are electro positive element. But compared to cadmium, nickel has more electro positive in nature. This nature is responsible for strong bond nature in BTNB and hence high hardness.

XRD Studies

Powder X-ray diffraction studies confirms whether the material possesses crystalline nature or not.

S.No	Sample	a(A·)	b(A·)	c(A·)	Angle	Crystal System
1.	Thiourea	7.66	8.54	5.52	α =β =γ =90·	Orthorhombic
2.	Glyciene Thiourea	5.32	11.90	5.85	B =95.78	Monoclinic
3.	TCC	5.80	6.74	13.05	α =β =γ =90·	Orthorhombic
4.	TCB	5.97	12.97	13.45	α =β =γ =90·	Orthorhombic
5.	BTCB	5.6949	6.6051	7.5937	α =β =γ =90·	Orthorhombic
6.	BTNB	6.1310	8.0907	9.1131	α =β =γ =90·	Orthorhombic
7.	LHTU	5.129	7.263	18.509	α =β =γ =90·	Orthorhombic

The crystalline nature of the material is not altered by the doping materials. The crystal parameters of all the doped crystals except glycine doped thiourea crystals are almost same. It indicates all the doping materials occupied the intersetial sites in the crystal lattices. However, glycine enters in to the crystal lattices and increases axial lengths and axial angles.

S. No	Sample	Load(g)	Vicker´s Hardness(/d²Kg/ mm²)
1	Glyciene Thiourea	25-100	1.8544
2	Thiourea	25	39.3
3	BTCB	50	52.4
4	BTNB	100	71.7

Conclusion

Thiourea is a centro symmetric crystal so that it does not show any non linear property. In addition it is not mechanically strong. The addition of any metal or amino acid enhances the optical, thermal and mechanical properties. To analyze, six crystals were taken for review. Among all the crystals, the amino acid doped crystals exhibit superior properties.

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