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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1667-1669, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Studies of Growth Parameters of ZTS Crystal Grown by Gel Technique

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Abstract: Zinc Tris (Thiourea) Sulfate (ZTS) is an efficient non-linear optical crystal which combines both organic and inorganic advantages. Usually, ZTS crystals have been grown by Slow Evaporation Solution Method, Aqueous solution by Slow Cooling Method, Free Evaporation and rarely using by Sankaranarayanan - Ramasamy (SR) Method. To attain better result Gel Technique has been adopted at ambient temperature. The reports of growth of ZTS single crystals by the Gel Technique, if any, have been very scant to the best authors' knowledge. The authors have been successfully grown ZTS crystals by Gel Technique and crystals were fairly good transparent and colourless. In order to get good transparent ZTS crystals, the influence of parameters such as density, pH and concentration of feed solution as well as mother solution have been experimented. The crystals size has been obtained the range about 5mm x 3mm x 2mm. The analytical technique (EDAX/EDS) has been carried out to determine chemical characterization of ZTS Crystal. The results are described.
Keywords: ZTS Crystal, Gel Growth Technique, Non linear optical crystal, Growth Parameters, EDAX Analysis.

Introduction and Experimental

Non linear Optical (NLO) materials have received much interest from several researchers in present time due to its significant applications in coming optoelectronic as well as photonic technologies. In current time, some technological complexities take place such as generationof blue light from near- Infrared (NIR) laser through Second Harmonic Generation (SHG) [1]. Such type of non linear optical process requires non linear medium, generally a crystal. In orderto come out from this significant problem, investigation for better non linear optical material is required.Zinc Tris (Thiourea) Sulfate (ZTS) havingmolecular formula Zn(NH2CSNH2)3SO4is one such a novel promising non-linear optical metal organic crystal having essential applications in the area of second harmonic generation device as well as laser tuned experiments [2]. While, a centro symmetric Thiourea molecule combines with inorganic material, it turns into non centro symmetric (NLO) complexes [3] which include both organic and inorganic advantages which known as semi organic material. This makes ZTS as a good candidate for non linear optical applications having 1.2 times more SHG efficiency than KDP crystal. ZTS crystal has been synthesized by various techniques such have needed of sophisticated instruments, very high or very low temperature. Even as Gel technique has been comparatively inexpensive and also easy to apply it. For

present study the authors have successfully grown ZTS crystals by Gel techniques at an ambient temperature. In order to prepare gel medium, Silica gel was used as a growth medium during the entire experimental study.Zinc SulfateHeptahydrate and Thiourea were taken in 1:3 ratio and 3N Thiourea prepared using stirrer with 48ºc temperature to avoid decomposition and poured in the gel medium as a mother solution or as a feed solution. After mixing pure Sodium Metasilicate Solution (SMS) with HClby distilled water, gel was prepared with required pH. Then, prepared gel solution was moved in different sized test tubes. Afterwards, gel solution was allowed to set at an ambient temperature. Gel setting time was obtained from 1 day to 17 days which was depended on concentrations of the reactants and specific gravity of SMS. After completing reaction between Zinc SulfateHeptahydrate and Thiourea, ZTS crystal was synthesized within 3-6 weeks depending on various parameters according to the reaction:

$$ZnSO_4 \cdot 7H_2O + 3CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]_3SO_4 + 7H_2O$$

Results and Discussion:

The recent experiment was set up with different three specific gravities and carried out with two different specific gravities of SMS with altered concentrations of the reactants. Good crystals were obtained with specific gravities as 1.06gm/cc and 1.04gm/cc. Mostly; crystals were acquired in upper and middle section and rarely in lower side of the gel medium in test tubes. In the case of specific gravity of 1.04gm/cc, the gel setting time with mother solution of Thiourea was decreased comparatively with mother solution of Zinc SulfateHeptahydrate.

Moreover, gel setting time was decreased in both sets with altered mother solutions after increasing pH. While better crystals obtained by the mother solution of Thioureawith the same specific gravity. In the case of specific gravity of 1.06gm/cc, gel setting period was decreased and crystal time was increased with increasing pH of solution. Also significant result has revealed that crystallization of ZTS crystals was occurred in gel technique by the condition of high pH with low sp.gravity and vice versa. Successfully grown crystals are shown in fig.1 and effect of parameter on gel growth is shown in Chart 1.Scanning Electron Microscope (SEM), an incredible tool identifies image of surface topology of ZTS crystal and an elemental identification of ZTS crystal was verified by EDS qualitative analysis shown in fig. 2(b) and 1(a).ZTS belongs to orthorhombic crystal system and its lattice parameters are a= 11.126, b= 7.773 and c=15.491 Aº with space group Pca21 (point group mm2) [4, 5] which confirmed by Powder X ray diffraction (PXRD) analysis was carried out with 2 theta value from range of 0 to 100ºwhich is shown in Fig.2(c). Experimental values of d spacing are excellent equivalent with theoretical d values as shown in table1[JCPDS card no. 76-0778].According to PXRD analysis, theoretical lattice parameters of ZTS crystals were confirmed with practical parameters as a=11.132, b= 7.793, c= 15.443(Å)and cell volume = 1339.7 ($Å^3$) which confirmed orthorhombic structure of ZTS crystal [6,7]. Nucleation rate can control greatly by the gel technique has confirmed with this experimental research.

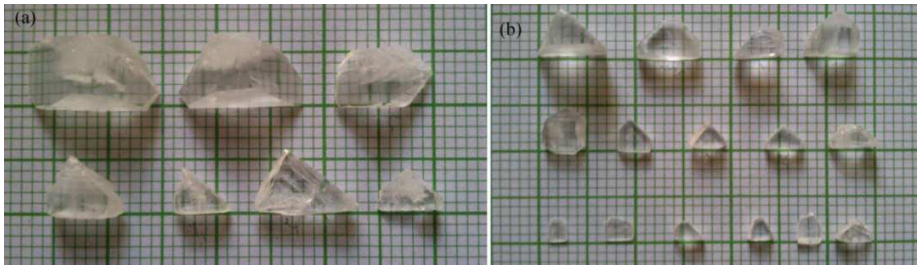
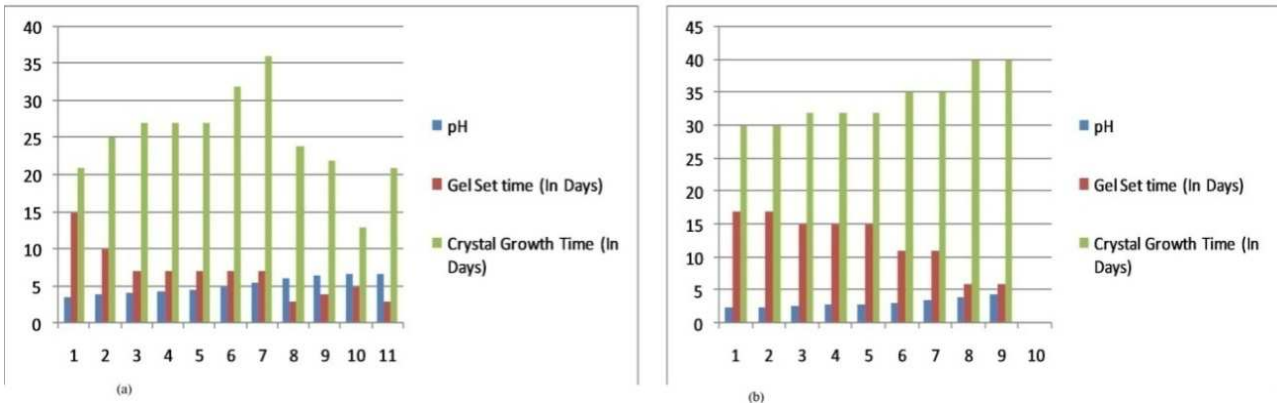


Figure 1:ZTS crystals grown at (a) pH 6.7 and (b) pH 6.6



Bar chart 1: Comparison bar chart; (a) for sp. Gr. of 1.04 and (b) for sp.gr. of 1.06

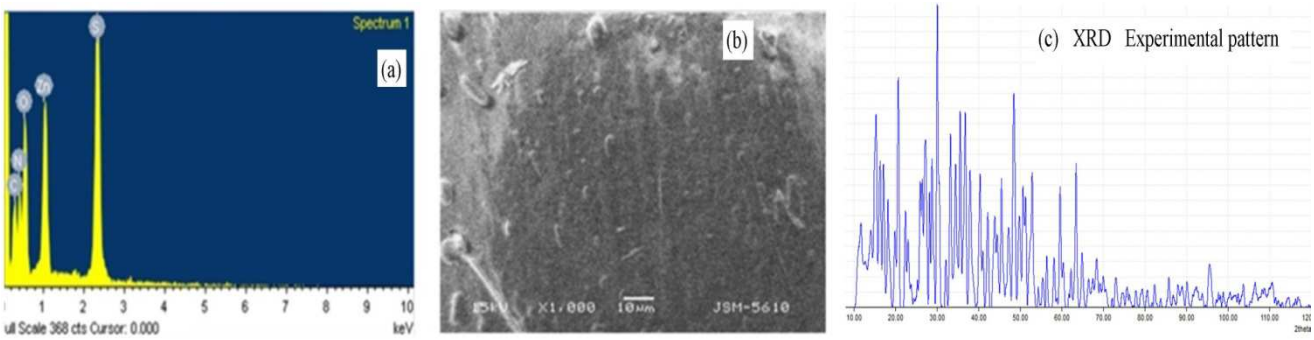


Figure 2:(a) EDS Spectra, (b) SEM micrograph,(c) XRD analysis of ZTS crystal

Table 1: Lattice parameter and Comparison of theoretical and experiential d-values and ZTS

No.	Dexp.(Å)	dtheo(Å)	hkl	No.	dexp(Å)	dtheo(Å)	Hkl	No.	dexp(Å)	dtheo(Å)	hkl
1.	4.94	4.9208	112	8.	3.27	3.2716	311	15.	2.01	2.0082	234
2.	5.48	5.4865	012	9.	3.07	3.0725	312	16.	1.93	1.9310	520
3.	4.53	4.5183	210	10.	2.99	2.9909	123	17.	1.88	1.8818	431
4.	4.34	4.3424	211	11.	2.94	2.9419	214	18.	1.84	1.8460	317
5.	4.01	4.0117	113	12.	2.46	2.4604	224	19.	1.84	1.8384	240
6.	3.90	3.9063	212	13.	3.39	2.3928	116	20.	1.76	1.7603	515
7.	3.88	3.8727	004	14.	2.24	2.2423	216	21.	1.75	1.7518	335

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