

A novel metal-organic coordination complex crystal: tris allylthiourea zinc bromide (ATZB) as a nonlinear optical material

Haiqing Sun^{*1,2}, Duorong Yuan¹, Xianqin Hou^{1,3}, Xinqiang Wang¹, Liqiang Liu², Dajiang Zhang², and Ye Han²

¹ State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China

² School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266510, China

³ School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

Received 15 March 2006, revised 21 July 2006, accepted 30 July 2006

Published online 15 December 2006

Key words crystal growth, solution, zinc compounds, nonlinear optical crystal.

PACS 42.70.Mp, 81.10.Dn

A new second order nonlinear optical coordination complex crystal tris allylthiourea zinc bromide was synthesized and grown from ethanol for the first time. Elemental analyses, X-ray powder diffraction and infrared spectroscopy confirmed the formation of the new material. The thermal characterization was determined by the differential thermal analysis and thermogravimetric analysis. The transmission spectrum of the crystal shows a wide transparent UV-Vis-NIR band. The powder SHG efficiency is higher than that of urea crystal.

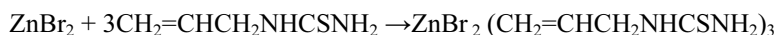
© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Second-order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in optoelectronic fields, i.e. laser technology, optical communication, optical data storage, etc. Much effort has been done in the search of new SONLO materials with high SONLO coefficients as well as stable physicochemical properties. Metal-organic coordination complex is a type of SONLO materials that fulfills the two points quite well. This type of materials consists of distorted polyhedra including organic conjugated molecular groups. They have advantages of both traditional inorganic and organic compounds as SONLO materials [1-3]. Among them allylthiourea (AT) is a good ligand to form complexes named ATMX with MX₂ (M = Zn, Cd or Hg, X = Cl or Br) resulting in high optical nonlinearity [1, 4-7]. They were found and grown as SONLO crystals by our research group. As a continuous work, here we report the synthesis and characterization of tris allylthiourea zinc bromide (ATZB), a new member of ATMX series of metal-organic coordination complexes.

2 Experimental

ATZB can be prepared in ethanol according to the following reaction:



ZnBr₂ and AT with molar ratio 1:3 were dissolved in suitable amount of ethanol, respectively. Then they were mixed together and stirred for half an hour. ATZB single crystal (Fig. 1) can be grown from this solution by solvent evaporation method under constant temperature.

* Corresponding author: e-mail: hqsun@sdust.edu.cn

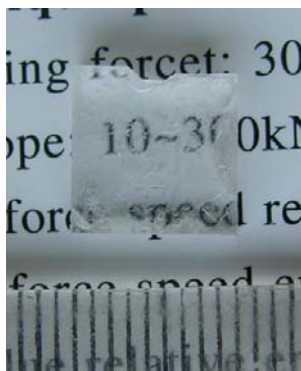


Fig. 1 As-grown ATZB crystal (0.9×0.9×0.37cm³).

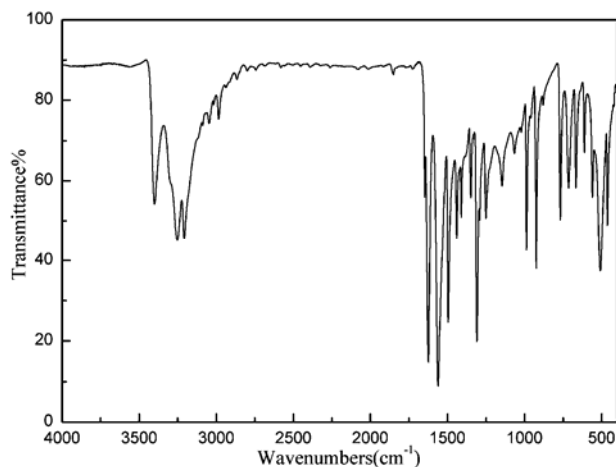


Fig. 2 IR spectrum of ATZB.

The elemental analyses were performed on an Elementar VarioEL III analyzer. The IR spectrometry measurement of ATZB crystal powder (KBr disc) was carried out using a Nicolet 750 FTIR spectrometer in the 4000~400cm⁻¹ region at room temperature. The X-ray powder diffraction (XRPD) data were collected on a Rigaku D/Max-γA diffractometer. Intensities for the diffraction peaks were recorded in the 10-60° (2θ) range with a scan speed of 4°/min. The differential thermal analysis and thermogravimetric (DTA/TG) measurements were carried out (50~800°C) in static air using a Shangping ZRY-2P DTA/TG analyzer, at a heating rate of 5K/min. The UV-Vis-NIR transmission spectrum in the wavelength range of 200~2000nm was recorded by means of the Hitachi model U3500 Spectrophotometer. The second harmonic generation (SHG) efficiency of ATZB crystal powder was studied by the standard Kurtz and Perry technique [8].

Elemental analyses By analyzing the proportions of carbon, hydrogen and nitrogen elements in the complex, one can primarily confirm its formula. The elemental analyses results are summarized in table 1, which demonstrate the validity of the chemical composition of ATZB: C₁₂Br₂H₂₄ N₆S₃Zn.

Table 1 Elemental analyses of ATZB (C₁₂Br₂H₂₄ N₆S₃Zn, molecular wt. 573.76).

Element	C	H	N
Experimental (%)	25.03	4.198	14.46
Theoretical (%)	25.12	4.216	14.65

IR spectrum IR spectrum is used for analyzing the possible organic groups included in a complex. Fig.2. shows the IR spectrum of the synthesized ATZB. The main bands of free AT [9] with the corresponding ones of ATZB and their assignments are listed in Table 2. From this table, we can see that almost all the peaks of ATZB can find their counterparts in AT, which indicates the existence of AT ligand in the sample. The main differences between them are the ν(CN) and the low-frequency ν(C=S), which is the result of sulfur, not nitrogen coordination to metal atom [10]. Similar status can also be observed in some other AT coordination compounds [7, 9].

Table 2 Assignments of the main infrared (IR) bands (cm⁻¹) of ATZB and AT.

AT	ATZB	Assignment
3440(s)	3401(s)	ν _{as} (NH ₂)
3231(s)	3252(s)	ν(NH)
1629(s)	1624(s)	δ(NH ₂)
1542(s)	1561(s)	ν(CN), δ(NCN), ν(C=S)
1500(s)	1495(s)	ν _{as} (CN)
1316(s)	1309(s)	δ(NH)
1063(s)	1065(m)	ν(C'N), ν _s (CN)
998(vs), 929(s)	987(s), 924(s)	π(=CH)
778(s)	768(m)	ν(C=S)
570(s)	560(s)	τ(CN), π(NH)

X-ray powder diffraction Figure 3 shows the XRPD pattern recorded for the ATZB crystal. The peaks are indexed with the help of the DICVOL91 program [11, 12]. The indexed hkl values are listed with corresponding d and 2θ values in table 3. The calculation results show that ATZB belongs to the trigonal system and the lattice parameters are: $a = 11.59676\text{\AA}$, $c = 28.26919\text{\AA}$, $V = 3292.44\text{\AA}^3$. These are similar to those of the other four reported AT coordination compounds [1].

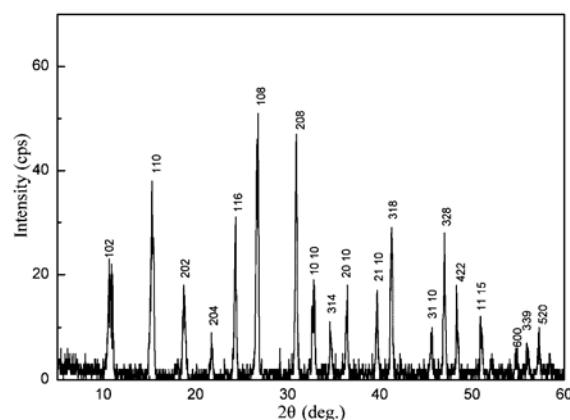


Fig. 3 XRPD pattern and diffraction indices of ATZB crystal.

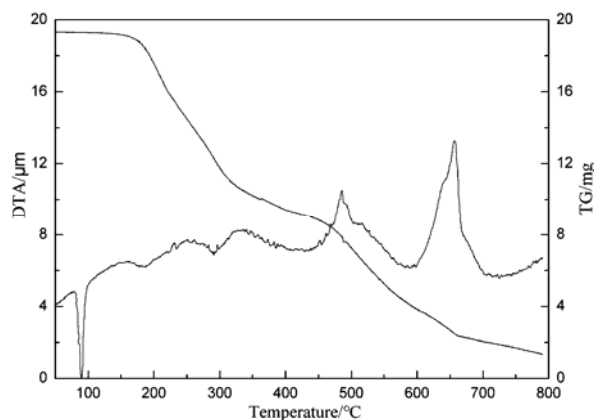


Fig. 4 DTA/TG curves of ATZB.

Table 3 Indexed XRPD data of ATZB crystal.

h k l	d_{obs}	d_{cal}	$2\theta_{\text{obs}}$	$2\theta_{\text{cal}}$
1 0 2	8.225	8.18691	10.756	10.806
1 1 0	5.788	5.7797	15.308	15.33
2 0 2	4.733	4.73181	18.748	18.752
2 0 4	4.084	4.09345	21.761	21.71
1 1 6	3.651	3.65658	24.379	24.341
1 0 8	3.327	3.33334	26.795	26.743
2 0 8	2.889	2.88985	30.952	30.943
1 0 10	2.721	2.72117	32.916	32.914
3 1 4	2.592	2.59144	34.604	34.612
2 0 10	2.462	2.46339	36.494	36.473
2 1 10	2.268	2.26726	39.741	39.755
3 1 8	2.185	2.18754	41.319	41.268
3 1 10	1.985	1.98411	45.705	45.726
3 2 8	1.932	1.93002	47.033	47.084
4 2 2	1.882	1.88108	48.361	48.386
1 1 15	1.793	1.79232	50.928	50.949
6 0 0	1.674	1.67385	54.84	54.845
3 3 9	1.645	1.64611	55.89	55.849
5 2 0	1.607	1.60778	57.333	57.302

Thermal analyses Simultaneously recorded DTA and TG curves of the ATZB sample are shown in figure 4. The TG curve shows that the weight loss takes place at around 167°C. Above 167°C there is a sustained weight loss until about 660°C, which shows the sample keeps decomposing to volatile products between 167~660°C. Above 660°C there is no weight change. According to the results of thermal analyses of ATCC [13] and some other metal-thiourea complexes [14], the residue is most likely ZnS and ZnO. The residue's weight percent (around 8%) is less than that of Zn element to the whole molecule (11.4%), which indicates that some Zn has fled off (probably in the form of ZnBr_2) before the formation of ZnS. The DTA curve shows one endothermic peak around 89°C and several exothermic peaks from 150 to 660°C. The former can be regarded as the melting point of ATZB as it is in the temperature range of no weight loss. There is no peak up to 660°C, which confirms the stability of the residue.

Optical properties The transmission spectra of ATZB crystal is shown in figure 5. One can see that the UV cutoff wavelength is 320nm, and the sample has good transmittance in the range of 400~1400nm, which is sufficiently wide and high for SHG by Nd:YAG or diode laser. The measured SHG efficiency of ATZB crystal powder is about 1.2 times than that of urea.

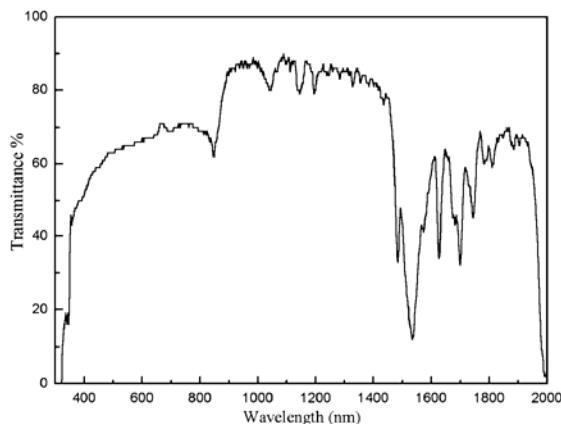


Fig. 5 Transmission spectrum of ATZB crystal.

3 Conclusions

The growth of a metal-organic coordination complex ATZB single crystal is reported for the first time. The elemental analysis, IR spectroscopy and XPRD studies have provided the basic structural and physical characteristics of the grown crystal. Although thermal analysis shows that ATZB has a relatively low melting point of not more than 100°C, the crystal shows no temporal degradation due to the oxydic, hygroscopic or efflorescent effects at room temperature. The optical transmission studies show that ATZB crystal has a UV transparency cutoff wavelength and also a UV-Vis-NIR wide transmission wave-band. The SHG effect of ATZB is measured to be higher than that of urea.

Acknowledgements This work was financially supported by the National Nature Science Foundation of China (NNSFC) 50372034.

References

- [1] D. R. Yuan, N. Zhang, X. T. Tao, D. Xu, Z. S. Shao, W. T. Yu, and M. H. Jiang, *Acta Optica Sinica* **13**, 456 (1993).
- [2] N. J. Long, *Angew. Chem. Int. Ed. Engl.* **34**, 21 (1995).
- [3] Owen R. Evans and Wenbin Lin, *Acc. Chem. Res.* **35**, 511 (2002).
- [4] N. Zhang, M. H. Jiang, D. R. Yuan, D. Xu, X. T. Tao, and Z. S. Shao, *J. Cryst. Growth* **102**, 581 (1990).
- [5] D. R. Yuan, N. Zhang, X. T. Tao, D. Xu, M. H. Jiang, and Z. S. Shao, *Chin. Sci. Bull.* **36**, 1401 (1991).
- [6] W. B. Hou, M. H. Jiang, D. R. Yuan, D. Xu, N. Zhang, M. G. Liu, and X. T. Tao, *Mater. Res. Bull.* **28**, 645 (1993).
- [7] H. Q. Sun, D. R. Yuan, X. Q. Wang, X. F. Cheng, C. R. Gong, M. Zhou, H. Y. Xu, X. C. Wei, C. N. Luan, D. Y. Pan, Z. F. Li, and X. Z. Shi, *Cryst. Res. Technol.* **40**, 882 (2005).
- [8] S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* **39**, 3798 (1968).
- [9] Dinorah Gambino, Eduardo Kremer, and Enrique J. Baran, *Spectrochim. Acta A* **58**, 3085 (2002).
- [10] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, Columba Curran, and J. V. Quagliano, *J. Am. Chem. Soc.* **80**, 527 (1958).
- [11] D. Louer and M. Louer, *J. Appl. Cryst.* **5**, 271 (1972).
- [12] A. Boultif and D. Louer, *J. Appl. Cryst.* **24**, 987 (1991).
- [13] H. Q. Sun, D. R. Yuan, X. Q. Wang, Y. Q. Lu, Z. H. Sun, X. C. Wei, X. L. Duan, C. N. Luan, M. K. Lu, and D. Xu, *J. Cryst. Growth* **256**, 183 (2003).
- [14] Janos Madarasz, Petra Bombicz, Masayuki Okuya, and Shoji Kaneko, *Solid State Ionics* **141-142**, 439 (2001).