Physica B 406 (2011) 1872–1876

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Synthesis, crystal growth and characterization of a chiral compound (triphenylphosphine oxide cadmium iodide): A new semiorganic nonlinear optical material

R. Santhakumari [a], K. Ramamurthi [b,*], Helen Stoeckli-Evans [c], R. Hema [d], W. Nirmala [e]

[a] Department of Physics, Government Arts College for Women, Pudukkottai 622 001, Tamil Nadu, India
[b] Crystal Growth and Thin Film Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli 620 024, Tamil Nadu, India
[c] Institute of Physics, University of Neuchatel, Rue Emile-Argand 11, CH-2009 Neuchatel, Switzerland
[d] Department of Physics, Seethalakshmi Ramasamy College of Arts and Science, Tiruchirappalli 620 002, Tamil Nadu, India
[e] Department of Physics, Rajah Serfoji Government College, Thanjavur 613 005, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 29 October 2010
Received in revised form
15 February 2011
Accepted 16 February 2011
Available online 20 February 2011

Keywords:
Characterization
Growth from solution
Organic compound
Nonlinear optical material

ABSTRACT

Synthesis of semiorganic material, triphenylphosphine oxide cadmium iodide (TPPOCdI), is reported for the first time. Employing the temperature reduction method, a crystal of size $16 \times 7 \times 6\ \text{mm}^3$ was grown from dimethyl sulfoxide (DMSO) solution. Three dimensional crystal structure of the grown crystal was determined by single crystal X-ray diffraction study. The complex crystallizes in the chiral orthorhombic space group $P2_12_12_1$. FTIR study was carried out in order to confirm the presence of the functional groups. UV–vis–NIR spectral studies show that the crystal is transparent in the wavelength range of 290–1100 nm. The microhardness test was carried out, and the load hardness was measured. Thermogravimetric and differential thermal analyses reveal the thermal stability of the crystal. Second harmonic generation efficiency of the powdered TPPOCdI, tested using Nd: YAG laser, is ~0.65 times that of potassium dihydrogen orthophosphate.

1. Introduction

In the last several decades, Nonlinear Optical (NLO) materials have attracted much attention due to their potential use in many fields, such as telecommunication, optical computing, optical information processing and color displays [1,2]. Nonlinear optical materials, which can generate highly efficient second harmonic blue–violet, are of great interest for various applications, including laser fusion reactions, laser remote sensing, color display and medical diagnostics. Organic molecules containing π electron conjugation systems asymmetrized by the electron donor and acceptor groups are highly polarizable entities for NLO applications [3–5]. Furthermore, in metal-organic complexes, the metal–ligand bonding is expected to display a large molecular hyper-polarizability because of the transfer of electron density between the metal atom and the conjugated ligand system [6,7]. More importantly, the diversity of central metals, oxidation states and ligands make it possible to optimize the charge-transfer interactions. In the case of metal-organic coordination complexes, group (IIB) metals are extensively chosen as their compounds, usually to achieve high transparency in the UV region because of their closed d^{10} shell [8,9]. The stronger the ligands, the greater the energy difference between the split in the high and low 3d groups. Complex ion formed by d-block elements (e.g. Zn and Cd), which is colorless, because 3d orbitals are full, no electrons are able to move up to the higher gap [10]. Regarding the organic ligands, small π-electron systems such as thiocyanate $(SCN)^-$, urea $[OC(NH_2)_2]$ and thiourea $[SC(NH_2)_2]$ have been used with remarkable success. These ligands and their metal (group IIB) complexes are always colorless. Potential NLO materials like bisthiourea cadmium chloride (BTCC) and triallyl thiourea cadmium chloride (ATCC) are examples of this approach [8]. Further, triphenylphosphine oxide derivatives are interesting candidates, as they bind well to most transition metals of groups 7–10. Hence in the present investigation, we report for the first time on the synthesis, growth, crystal structure, optical, mechanical and thermal properties and the powder nonlinear optical efficiency of the title compound, triphenylphosphine oxide cadmium iodide.

2. Experimental Procedures

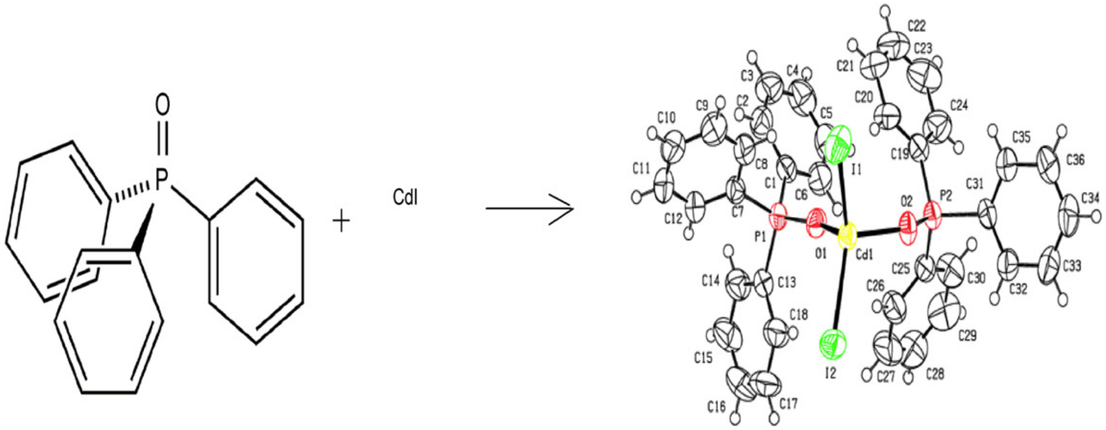
2.1. Material Synthesis

The title compound was synthesized from analytical reagent grade cadmium iodide (CdI) and triphenylphosphine oxide (TPPO) in 1:1 molar ratio. The calculated amount of CdI was dissolved in distilled water and the required amount of TPPO was dissolved in

---

[*] Corresponding author. Tel.: +91 431 2407057; fax: +91 431 2407045.
E-mail address: krmurthin@yahoo.co.in (K. Ramamurthi).

0921-4526/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2011.02.045



Scheme 1. Reaction mechanism involved in the synthesis of TPPOCdI.

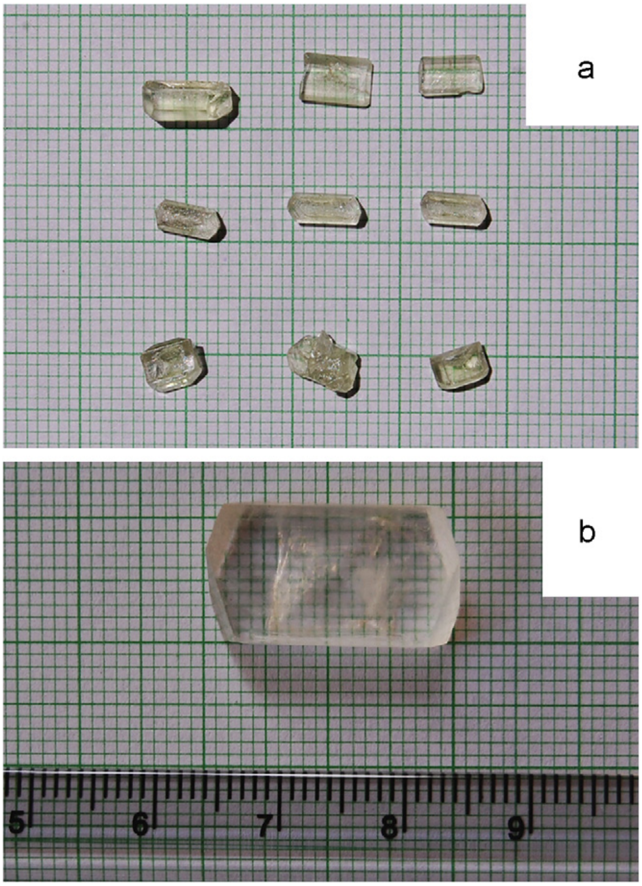


Fig. 1. (a) As-grown crystal of TPPOCdI by slow evaporation at room temperature. (b) As-grown crystal of TPPOCdI by temperature reduction method.

ethanol and mixed by continuous stirring. After refluxing it for 2 h at 100 °C, the mixture was allowed to cool slowly to room temperature, which yielded colorless crystalline powder solid of the compound. The purity of the synthesized material was improved by recrystallization process. The reaction mechanism involved in the synthesis of triphenylphosphine oxide is given in Scheme 1.

2.2. *Crystal growth*

Saturated solution of TPPOCdI was prepared at 35 °C from recrystallized salt, and this solution was filtered with microfilters. About 250 ml of this solution was taken in a beaker and placed in a constant temperature bath maintained at 35 °C with an accuracy of ± 0.01 °C. One of the better quality crystals obtained from slow evaporation of the solvent at room temperature was used as a seed crystal (Fig. 1a). Single crystal of TPPOCdI was grown by reducing the temperature from 35 to 31.3 °C at the rate of 0.1 °C per day. Optically clear and well-shaped crystal of size $16\times7\times6\ \mathrm{mm}^3$ was harvested in a growth period of 37 days and shown in Fig. 1b.

3. Results and discussion

The three dimensional crystal structure of TPPOCdI was determined by single crystal X-ray diffraction analysis. Suitable crystals of TPPOCdI were obtained as colorless blocks by slow evaporation technique. The intensity data were collected at 293 K (20 °C) on a Stoe Mark II-Image Plate Diffraction System [11] equipped with a two-circle goniometer and using MoKα graphite monochromated radiation. The structure was solved by direct methods using the program SHELXS-97 [12]. The refinement and all further calculations were carried out using SHELXL-97 [13]. TPPOCdI crystallizes in the orthorhombic system with space group $P2_12_12_1$. In the title compound, the CdII atom is ligated by two I atoms and two O atoms from two triphenylphosphine oxide ligands in a distorted tetrahedral arrangement. While the O–Cd–I angles vary from 106.67 (7) to 111.23 (7), the O–Cd–O angle is 88.60 (10) and the I–Cd–I angle is 125.47 (2). The crystal structure is stabilized by van der Waals forces only [14].

The Fourier transform Infrared (FTIR) spectrum of TPPOCdI was recorded in the region of 400–4000 cm^{-1} (Fig. 2), employing the Perkin Elmer Fourier transform infrared spectrometer using KBr pellet technique. The stretching vibration of P=O is observed at lower frequency of 1109 cm^{-1}, which clearly indicates the presence of oxygen to metal bonds in the coordination compound. This is also confirmed by single crystal X-ray diffraction analysis. The band appears at 537 cm^{-1} is attributed to the Cd–O bonds. The peak at 3454 cm^{-1} is assigned to the stretching vibration of the O–H bond of water molecules absorbed by KBr [15]. The presence of heteroaromatic type structure is best recognized by the presence of –C–H stretching vibration near 3030 cm^{-1}. In this region, the absorption bands are less affected by the substitutional pattern and the presence of conjection with the double bonds of the ring. The peak at 3056 cm^{-1} is designated to C–H stretching vibration. The in-plane and out-of-plane vibrations of C–H group are identified at 1020 and 854 cm^{-1}, respectively. The peak at 1641 cm^{-1} is the bending vibration of OH group. The C–O stretching mode is observed at 1425 cm^{-1}.

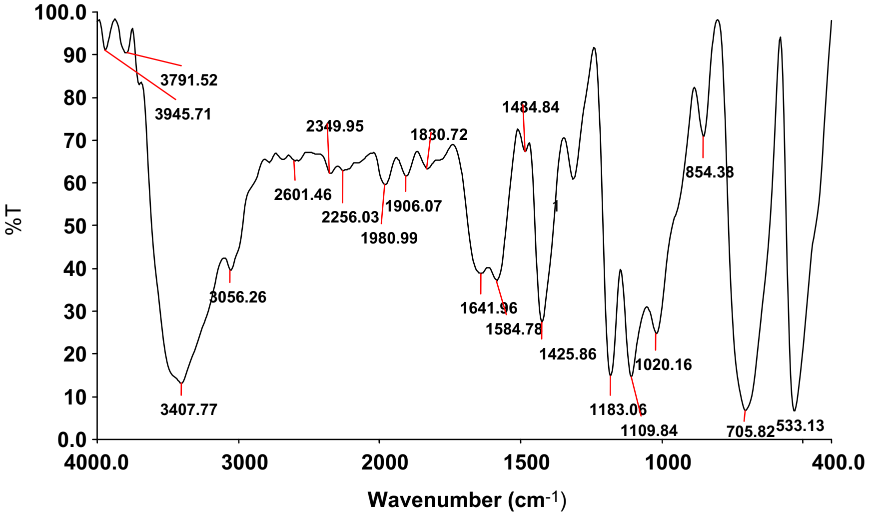


Fig. 2. FTIR spectrum of TPPOCdI.

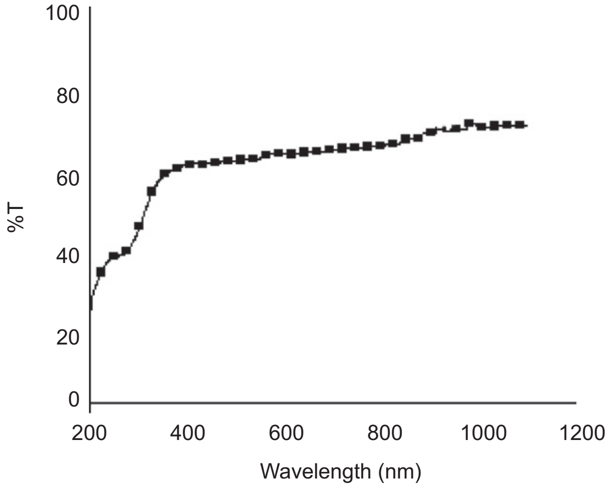


Fig. 3. UV–vis–NIR spectrum of TPPOCdI.

The transmission range is important for any NLO material because it can be of practical use only if it has wide transparency window. Optical transmission spectrum of TPPOCdI was recorded in the range of 200–1100 nm using Varian Cary 5E UV–vis–NIR spectrophotometer (Fig. 3). A transparent crystal of 2 mm thickness was used for this measurement. From the spectrum, it is evident that the compound has a very low UV cutoff wavelength at ~300 nm, which is sufficient for second harmonic generation of laser radiation of 1064 nm for frequency doubling process [16]. Kurtz and Perry [17] second harmonic generation (SHG) test was performed to estimate the NLO efficiency of powdered TPPOCdI crystal. The grown single crystal of TPPOCdI was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and was illuminated using Spectra Physics Quanta Ray DHS2 Nd: YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate of 10 Hz. A sample of potassium dihydrogen orthophosphate, also powdered to the same particle size as the experimental sample, was used as a reference material in the present measurement. The SHG radiations of 532 nm green light was collected by a photomultiplier tube (PMT-Philips Photonics-model 8563) after being monochromated (monochromator-model Triax-550). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered sample was chosen to be 3.4 mJ. Powder SHG efficiency obtained for TPPOCdI is about ~0.65 times that of potassium dihydrogen orthophosphate crystal. The relative efficiency of TPPOCdI is found to be greater than L-arginine hydrochloride, L-arginine hydrobromide and L-arginine hydrochloride bromide [18,19].

The thermal stability of TPPOCdI was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using SDT Q600 V8.3 Build 101 instrument between the temperatures 50 and 1100 °C at a heating rate of 20 °C/min in nitrogen atmosphere (Fig. 4). The initial mass of the material subjected to the analysis was 2.8600 mg. The TG analysis shows that between 62 and 153 °C the weight loss is about 4%. This indicates the loss of water hydration (H_2O). Only one major loss of weight of about 88% exists in the TG curve (between 223 and 310 °C), which may be due to the decomposition of the complex. The crystal is nearly stable upto 223 °C, which is higher temperature than for many other semiorganic NLO crystals like allyl thiourea mercury bromide (125 °C), bis(isothiocyanato)-bis(4-methylpyridine)zinc(II) (158 °C) [20,21]. In TG curve another weight loss of about 2% between 310 and 403 °C is due to dissociation of the substance and evaporation of volatile substances. There is no endothermic or exothermic peak up to 1000 °C in the DTA curve, whereas TGA shows almost complete weight loss and the residual weight obtained at 1000 °C is only 0.6626%.

Vickers microhardness test was carried out on the prominent face of TPPOCdI crystal using microhardness tester fitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for loads 25, 50 and 100 g. The diagonal lengths of the impressions were measured using Shimadzu (Japan), Model HMV-2 hardness instrument. The indentation time was 25 s for all the loads. Vickers microhardness number (H_v) was evaluated from the relation $H_v = 1.8544(P/d^2)$ kg/mm^2, where P is the applied load in g and d is the diagonal length of the impression in mm. The variation in microhardness values with applied load is shown in Fig. 5. From Vicker's microhardness studies, it is observed that the hardness value increases up to a load of 100 g. For load above 100 g cracks started developing around the indentation mark, which may be due to the release of internal stresses [22].

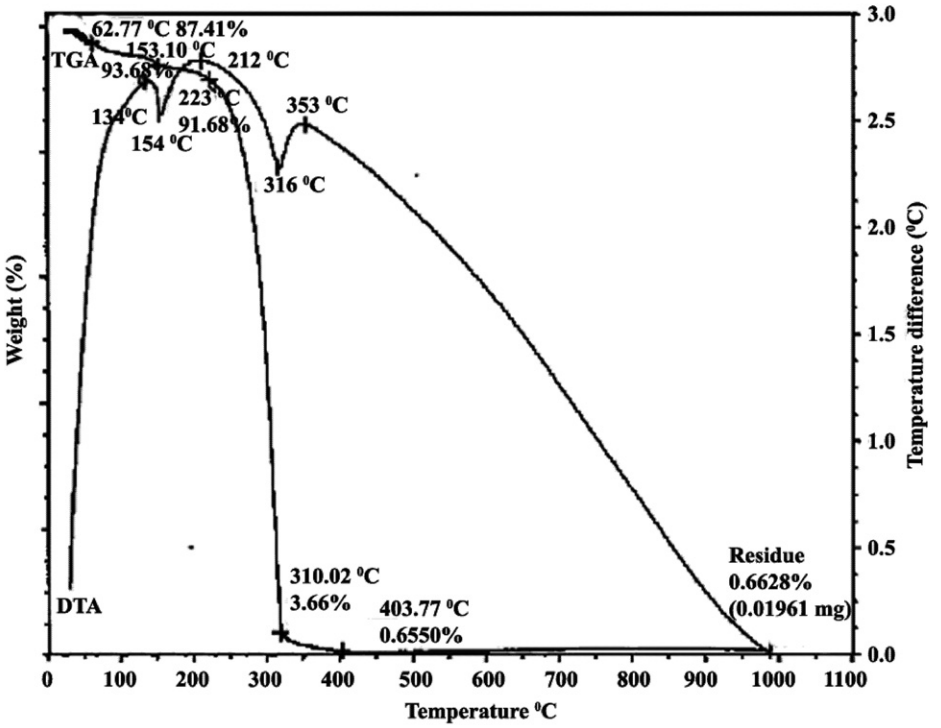


Fig. 4. TG/DTA of TPPOCdI.

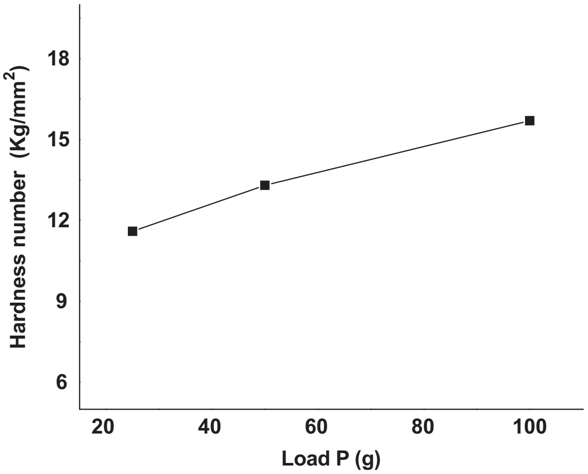


Fig. 5. Vickers microhardness values of TPPOCdI.

4. Conclusion

A new semiorganic crystal TPPOCdI of dimension $16 \times 7 \times 6$ mm^3 was grown by the temperature reduction method. The crystal is transparent and colorless with a well-defined external appearance. Single crystal XRD shows that TPPOCdI crystallizes in the orthorhombic system. The observed unit cell parameters are $a = 10.5492(5)$ Å, $b = 17.7053(7)$ Å, $c = 19.1985(9)$ Å and $\alpha = \beta = \gamma = 90^\circ$, and the crystal belongs to the space group $P2_12_12_1$. FTIR spectral analysis confirms the presence of functional groups constituting TPPOCdI. The optical study shows that the crystal is transparent in the wavelength region of ~290–1100 nm. Its powder SHG efficiency is about ~0.65 times that of KDP. The microhardness studies reveal that the hardness of crystal is moderately good. Thus, TPPOCdI is a new NLO candidate with reasonable optical and mechanical properties, and relatively high thermal stability. Further efforts to modify this system with other possible derivatives may be expected to lead to new materials with improved properties.

Acknowledgments

The authors (RS and KR) thank Dr. K. Panchanatheeswaran, Professor in Chemistry (Rtd), Bharathidasan University, Tiruchirappalli, for fruitful discussions. Further one of the authors [RS] thanks University Grants Commission, Government of India, for financial assistance [File No. MRP 2976/2009 (RS)]. The authors acknowledge Prof. P.K. Das, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, for extending the laser facilities for the SHG measurement. One of the authors, Helen Stoeckli Evans, thanks the staff of the X-ray Application Laboratory of the CSEM, Neuchâtel, for access to the X-ray diffraction equipment.

References

[1] N.J. Long, Angew Chem. Int Ed. Engl. 34 (1995) 21.
[2] T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A.J. Persoons, Mater. Chem. 7 (1997) 2175.
[3] P. Tansuri, K. Tansuree, W. Gabriele, R.J. Lara, Cryst. Growth Des. 4 (2004) 743.
[4] B.J. McArdle, J.N. Sherwood, A.C. Damask, J. Cryst. Growth 22 (1974) 193.
[5] M. Aravindhan, K. Sankaranarayanan, K. Ramamurthy, C. Sanjeeviraja, P. Ramasamy, Thin Solid Films 2 (2005) 477.
[6] 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, D. Xu, J. Cryst. Growth 256 (2003) 183.
[7] P.M. Ushasree, R. Muralidharan, R. Jayavel, P. Ramasamy, J. Cryst. Growth 197 (1999) 216.
[8] M.H. Jiang, Q. Fang, Adv. Mater. 11 (1999) 1147.
[9] R. Sankar, C.M. Raghavan, R. Mohan Kumar, R. Jayavel, J. Cryst. Growth 305 (2007) 156.
[10] Guang Zhang, Mingguo Liu, Dong Xu, Duorong Yuan, J. Mater. Sci. Lett. 19 (2000) 1255.
[11] Stoe & Cie (2009). X-Area V1.52 & X-RED32 V1.48 Software, Stoe & CieGmbH, Darmstadt, Germany.
[12] G.M. Sheldrick, Acta Crysallogr. A64 (2008) 112.
[13] A.L. Spek, Acta Crysallogr. D65 (2009) 148.
[14] R. Santhakumari, R. Hema, K. Ramamurthi, Helen stoeckli Evans. Acta Crystallogr. E67 m114 (2011) doi:10.1107/S160053681005302X.
[15] Li Li, Zheng-ping Wang, Guang-ru Tian, Xin-yu Song, Si-xiu Sun, J. Cryst. Growth 10 (2008) 1016.

[16] C.N.R. Rao, Ultraviolet and Visible Spectroscopy of Organic Compound, Prentice Hall Pvt. Ltd., New Delhi, 1984.
[17] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
[18] T. Malik, T. Kar, J. Cryst. Growth 274 (2005) 251.
[19] T. Pal, T. Kar, W. Xin Qian, Z. Guang Ying, W. Pong, C. Xiu Feng, H.Y. Zhao, J. Cryst. Growth 235 (2002) 523.
[20] W.B. Hou, D.R. Yuan, N. Zhang, W.T. Yu, M.G. Liu, X.T. Tao, S.Y. Suo, M.H. Jiang, J. Cryst. Growth 133 (1993) 71.
[21] L.Y. Zhu, D. Xu, X.Q. Wang, C.J. Liu, G.H. Zhang, J. Cryst. Res. Technol. 12 (2006) 1226.
[22] P.M. Ushasree, R. Jayavel, C. Subramanian, P. Ramasamy, Bull. Electrochem. 14 (1998) 407.