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BULK CRYSTAL GROWTH AND CHARACTERIZATION OF SEMIORGANIC NONLINEAR OPTICAL MATERIALS

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High quality bulk single crystals of novel NLO semiorganics : L-arginine tetrafluoroborate (L-AFB) and L-histidine tetrafluoroborate (L-HFB) measuring 78 × 50 × 35 mm^3 have been successfully grown from solution by temperature lowering methods. Solubility curves of these materials have been determined in different solvents, such as water, ethanol and acetone to determine the most suitable solvent. The results of the various studies on synthesis, solvents, solubility, crystal growth, effects of seed orientation on morphologies, second-harmonic-generation (SHG), transparency range, differential scanning calorimetry are presented. The published results of crystal growth of other analogues of LAP crystals are also presented.

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1. Introduction

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics. Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. Within the last decade much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients. However, most of the organic NLO crystals are constituted by weak van der Walls and hydrogen bonds with conjugated π electrons. So they are soft in nature and difficult to polish and these materials also have intense absorption in UV region. In view of these problems, new types of hybrid NLO materials have been explored from organic-inorganic complexes with stronger ionic bond such as L-arginine phosphate monohydrate (LAP) and others [1-2] have been synthesized and single crystals have been grown. LAP crystals are used for second, third and fourth harmonic generation from the fundamental radiation 1.06 µm and also sum and difference frequencies generation in wide spectral range from UV to IR. LAP has three times the nonlinearity, two or three times high damage threshold of KDP, chemical stability, and also lower cost. A problem related with LAP growth is the presence of micro-organisms arising during growth, which leads to deterioration in LAP crystal quality. So, it was thought interesting to synthesize, and grow bulk single crystals of L-histidine tetrafluoroborate (L-HFB), L-arginine tetrafluoroborate (L-AFB) and others. In this paper, the results of work done in our group, on LAP, L-HFB and L-AFB synthesis, growth and their characterizations are described.

2. Experimental

2.1 Synthesis and growth

L-arginine phosphate (LAP) crystalline powder is not currently commercially available. Thus, the LAP was synthesized in our laboratory by dissolving the stoichiometric amount of L-arginine and

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orthophosphoric acid in excess of water at 50 °C. The fully reacted solution was filtered and crystalline LAP was obtained by evaporation of filtered solution. The crystalline LAP so formed was further purified by re-crystallization process in deionised water [3].

L-arginine tetrafluoroborate (L-AFB): L-arginine (more than 98% pure) procured from Fisher Scientific Company, USA, was purified by repeated crystallization from the hot de-ionized water solution by slow cooling. The tetrafluoroboric acid (48 wt% in water solution, from Aldrich Chemical Company) was used as the reagent for L-AFB crystal growth. L-arginine tetrafluoroborate was synthesized by dissolving one equivalent of L-arginine in de-ionized water containing one equivalent of tetrafluoroboric acid.

L- histidine tetrafluoroborate (L-HFB): was synthesized by dissolving one equivalent of histidine in de-ionized water containing one equivalent of tetrafluoroboric acid. The solubility of L-HFB is very low in acetone or ethanol. It is less then 2 g in 100 ml ethanol and 3g in 100ml acetone at 45 ºC. Even though in water, the solubility is only 18 g per 100 ml at 45 ºC, but is adequate for growing crystals by temperature lowering or evaporation. L-HFB crystals were grown with temperature lowering technique between 34 ºC and 28 ºC with lowering rate of about 0.1ºC per day. The solubility of the above compounds was measured in solvents as described above using the method described elsewhere [2].The crystals seeds with perfect shape and free from macro-defects were formed by spontaneous nucleation in a supersaturated solution at room temperature.

The crystals were grown by solution temperature lowering technique using a crystallizer as shown in Fig. 1. The photograph of the L-arginine tetrafluoroborate (L-AFB) crystal is shown in Fig. 2. The details are given in our earlier publication [2].

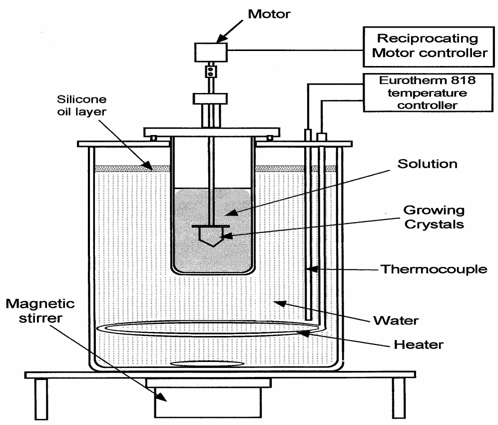

Fig. 1. A schematic diagram of a solution growth Crystallizer.

2.2. Optical properties

Optical absorption data were taken on a flat polished crystal sample about 3-5 mm in thickness, using a CARY 3E UV-VIS dual beam spectrophotometer between 190 and 900 nm.

2.3 Thermal properties

A thermo gram of samples was obtained by using the Perkin Elmer DSC-4 equipment having a thermal analysis data station (TADS) and a Perkin Elmer System 4 thermal analysis controller as accessories.

Fig. 2. A photograph of L-HFB crystal grown at Alabama A&M University.

3. Results and discussions

3.1 L-arginine phosphate (LAP)

L-arginine phosphate monohydrate ($C_6H_{14}N_4O_2H_3PO_4.H_2O$; known as LAP) has high nonlinear coefficient (>1 pm/V), high laser damage threshold (>15 J/cm^2), wide transmission rages (220 nm-1950 nm), low level of hygroscopicity and high frequency conversion efficiency (38.9 %). It is more sensitive compared to potassium dihydrogen phosphate (KDP), and replaces the requirement of KDP in the harmonic frequency generation for laser fusion experiments. The solubility curve of the LAP from 30 to 55 °C is shown in Fig. 3 at the pH of 4.3 [3]. To find out the optimum growth parameters for growing good quality LAP crystals, a systematic effort was made to study the effect of pH, stirring rate and temperature of solution of the growth and quality of LAP crystals. The growth kinetics as a function of pH of solution and stirring rate are investigated and it was found out that pH around 5 is the best to obtain good quality crystals without any visible defects. It has been found that crystal quality improves appreciably at high pH at the expense of growth yield. The addition of habit modifier like Li ions increases growth yield along with rectangular prismatic habit which is favourable for device fabrication.

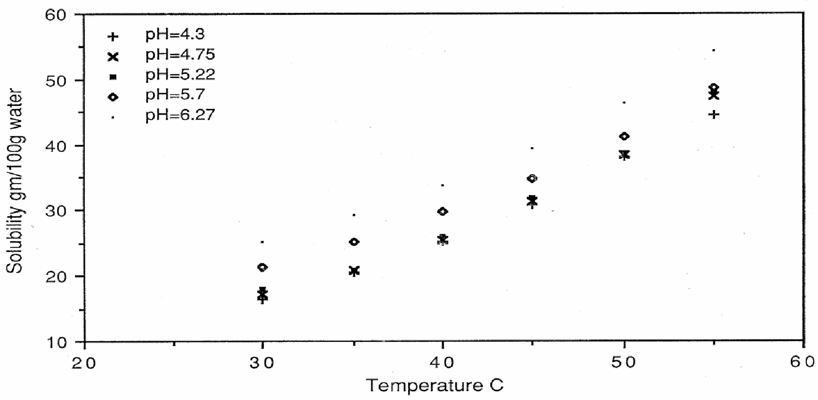

Fig. 3. Solubility of LAP in water at various pH values.

3.2 L-arginine tetrafluoroborate (L-AFB)

The solubility of L-HFB was measured (Fig. 4), in water, acetone and ethanol by the method described earlier (4), since the key to solution growth is proper choice of solvent for growing crystals of the desired morphology. The crystal structure of L-AFB belongs to the orthorhombic system with symmetry class 222 and space group $P2_12_12_1$. L-AFB has a transmission range extending from 196 to 900 nm. Therefore, bulk single crystals of L-AFB are potential materials throughout the visible and UV spectral region. The solubility of L-AFB is very low in methanol, ethanol, and acetone. Taking certain precautions it was possible to grow single crystals from a saturated solution by the temperature lowering method. It was observed that, the growth of the seed in the [001] direction was higher than in the [100] or [010] directions. In our experiments the largest single crystal of L-AFB in size 78 x 50 x 35 mm^3 was grown in eight weeks using de-ionized water as solvent. The L-AFB single crystals have good chemical stability and when stored at room temperature with a relative humidity of 50-60% showed no degradation for several months. The details of growth and its characteristics are given elsewhere [4].The optical absorption spectra of L-AFB is shown in Fig. 5. The absorption edge at 198 nm and a strong absorption at 900 nm were measured. The useful transmission range of solution grown bulk crystal L-AFB extends from 198 to 900 nm which makes it valuable for applications that require blue green light. Although we have not investigated the nonlinear optical properties of L-AFB in detail, it seems likely that this crystal, a chemical analogue of L-arginine phosphate (LAP), will be a promising nonlinear optical material for applications in high power large aperture harmonic generation. Preliminary characterization of the crystals was carried out for the second-harmonic-generation (SHG) efficiency. A Q-switched Nd : YAG laser (1064nm) was used and the SHG efficiency has been found to be more than the phase-matched potassium dihydrogen phosphate (KDP) crystal. A plot of the DSC results for the L-AFB crystal grown is given in Fig. 6. The DSC plot shows no phase transition before the L-AFB crystal melting point (242.7 °C). However, there are two peaks detected at 257.1°C and 280.1°C, respectively. These peaks are probably caused by super cooling and decomposition of L-AFB melt.

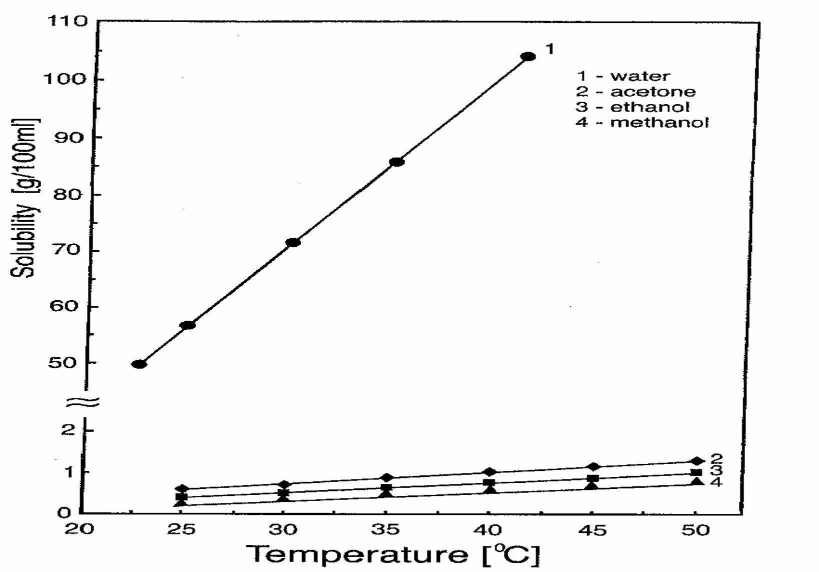

Fig. 4. Solubility of L-Arginine tetrafluoroborate (L-AFB) in various solvents.

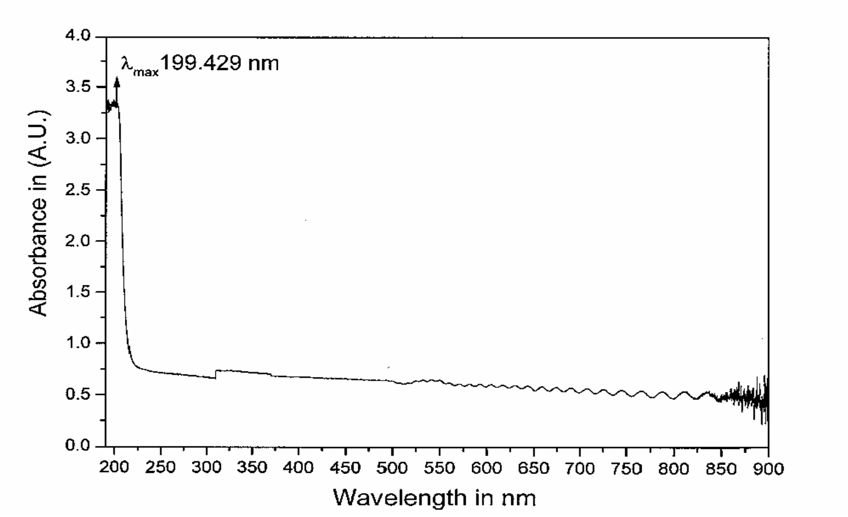

Fig. 5. Optical spectra of L-Arginine tetrafluoroborate L-AFB.

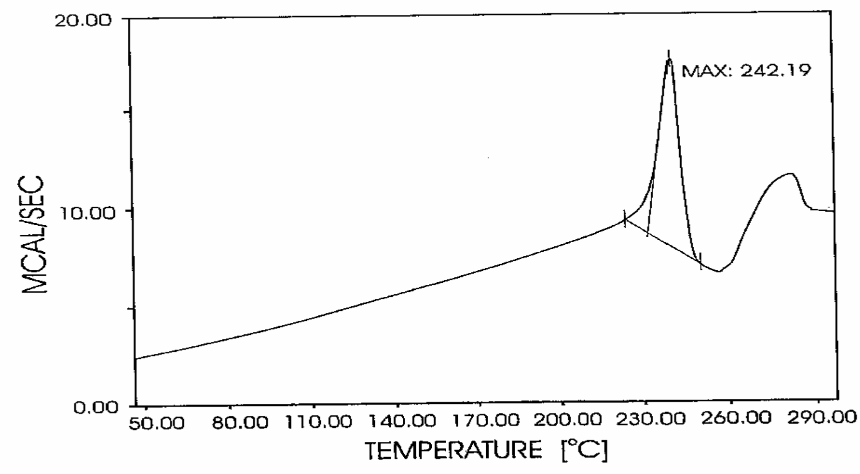

Fig. 6. Differential thermal calorimeter thermograph of L-Arginine tetrafluoroborate (L-AFB).

3.3 L- histidine tetrafluoroborate (L-HFB)

L-hystidine tetrafluoroborate (L-HFB) is a novel NLO crystal material with molecular formula $C_6H_{10}0_2$ = N_3BF_4. The crystal structure of L-HFB belongs to the monoclinic system with point group 2 and space group $P2_1$. The SHG intensity of L-HFB crystal is five times that of the KDP. The transmission range of L-HFB crystal has been measured to be 250 to 1500 nm, thus green and blue light can be obtained with L-HFB single crystals. The power threshold figure-of-merit compares favourably with BBO and LBO single crystals. It exhibits interesting potential uses in high average powder frequency conversion in the near UV to the near IR. Besides, the L-HFB built from organic-inorganic complexes in which the high optical nonlinearity of a purely organic compound is combined with the favourable mechanical and thermal properties of an inorganic. Therefore, single crystals of L-HFB are promising materials throughout the blue and near UV spectra region. The solubility of L-HFB in various solvents is shown in Fig. 7. The largest single crystals of L-HFB in size $20 \times 20 \times 10$ mm^3; were grown in two weeks using with de-ionized water as solvent (Fig. 2), the transparency of single crystals was poorer than crystals grown by the evaporation technique.

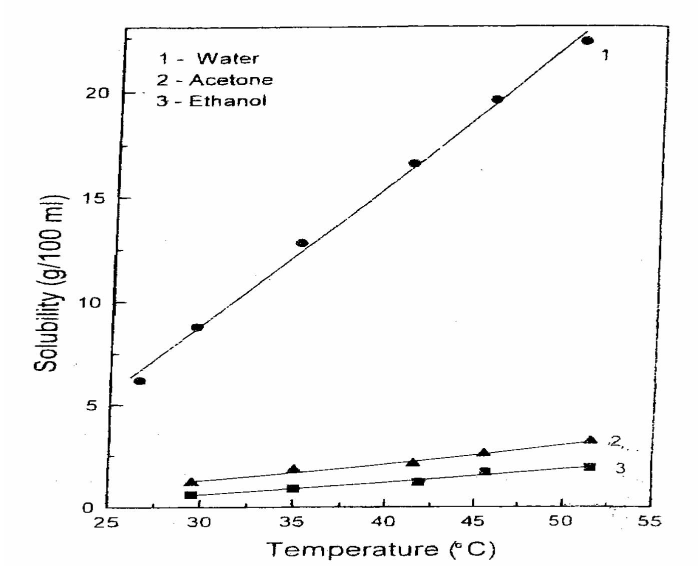

Fig. 7. Solubility of L-histidine tetrafluoroborate L-HFB in various solvents.

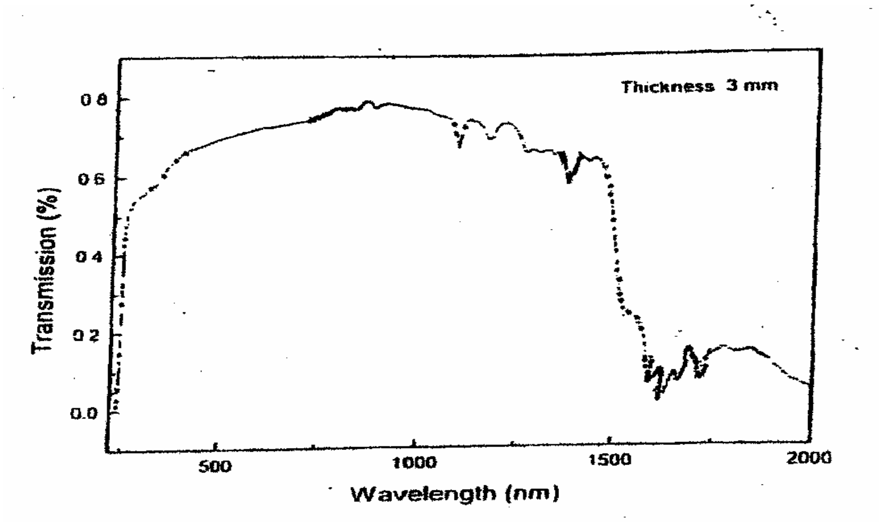

Fig. 8. Optical spectra of L-histidine tetrafluoroborate L-HFB.

Due to long period of crystal growth, it is difficult to control growth rate and morphology of the crystals. However, transparent good quality single crystals of L-HFB were obtained by the use of the [001] and [110] oriented seeds [5]. The major faces {110} and {100} were observed in the grown crystals. Optical transmission spectra for solution grown L-histidine tetrafluoroborate crystals is shown in Fig. 8. The absorption edge around 1083 nm is consistent with frequency doubling observed at 1064nm from Nd: YAG laser beams. Very low second harmonic conversion efficiency has been observed until now. Higher efficiencies are expected to be achieved by optimization of the phase matching angle, and improving crystal polish.

4. Survey of recent work

Recent survey shows that the research work [6-18] has been performed to grow various kinds of semi-organic crystals based on L-arginine phosphate type analogs with the aim of growing small size crystals, understanding their growth kinetics, thermograph and structure, and optical UV-VIS. absorption spectra. Yokotani et al. [6] reported the growth of DLAP crystals including the inhibition of microbes in the growth solution by adding H_2O_2. J.F. Carvalho et al. [7] solved the problem of microorganisms by growing LAP crystals by growing crystals by controlled evaporation technique in the presence of sodium azide, and also reported no significant change in optical properties. S. Mukerji et al. [12] found new semiorganic crystal: L-arginine hydrobromide (LAHBr). A.M. Petrosyan et al. [13] found new analog of LAP such as L-Arg.HCOOH, Arg.$2H_2PO_4$, Arg.2HCl and Arg.2HBr.H_2O. They completely characterized the crystals using infrared spectroscopy and X-ray. However, no efforts were made to grow larger size crystals. D. Rajan Babu et al. [14] reported the growth of L-alanine tetrafluoroborate (L-AlFB) crystals by slow evaporation. An L-AlFB crystal possesses orthorhombic structure and hexagonal morphology with slight elongation along its crystallographic c-axis. In powder form, it was found to have higher SHG efficiency than L-alanine. A.S. Haja Hameed et al. [15] examined the growth of sulfate mixed LAP (LASP) crystals, and Cu and Mg doped LAP crystals. Their hardness studies revealed that LAP crystals were harder than LASP crystals due to loosely bound sulfur in LASP crystals. R. Ittyachan et al. [16] reported the growth of L-arginine diphosphate (LADP) having dimensions upto 30X6X4 mm^3 by slow evaporation at constant temperature of 30°C from its aqueous solution. The grown crystals were characterized by employing UV-VIS spectrum, FTIR, DTA, TGA and X-ray diffraction. T. Pal et al. [17] reported the crystals growth of two NLO optical materials: L-arginine hydrochloride monohydrate (LAHCl) and L-arginine hydrobromide monohydrate (LAHBr) by slow evaporation and also by slow cooling of solution. It was found that mixed crystals are transparent down to 240 nm and its SHG efficiency for 1064 nm laser radiation is almost same as that of parent crystals: LAHCl and LAHBr. Damage threshold for mixed crystals was higher than LAHBr. R. Ittyachan et al. [18] reported for the first time, successful growth of L-histidine bromide (L-HB) by slow evaporation technique. In the entire visible region of the spectra, the absorbance was found to be less than 2 units.

However, no one has concluded that a particular crystal in LAP family of crystals is replaceable with KDP crystals. Further work is required to produce crystals of large size, ease of crystal growth and processing for their use in device applications with higher SHG efficiencies. However, it is clear that they have superior NLO, damage thresholds and mechanical hardness than KDP crystals.

5. Conclusion

The basic parameters of growth solution are studied extensively in order to grow large size crystals of these semi-organic materials. With optimised growth conditions, large size crystals of LAP, L-AFB and L-HFB have been successfully grown. The useful transmission range of L-AFB extends from 198 to 900 nm, which makes it valuable for applications that require blue-green light. A survey of recent literature suggests further research work is warranted to grow large size crystals of LAP type materials along with SHG efficiencies measurements so as to come to some concrete conclusion regarding their use in NLO devices.

Acknowledgements

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References

[1] D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono, G. Kennedy, IEEE J. Quant. Electronics **25(2)**, 179 (1989).

[2] M. D. Aggarwal, W. S. Wang, K. Bhat, B. G. Penn, D. O. Frazier, in "Handbbok of Advanced Electronic Materials and Devices", edited by H. S. Nalwa, (Academic Press, San Diego, CA 2001), vol. **9**, pp 193-228.
[3] S. M. Rao, C. Cao, A. K. Batra, R. B. Lal, Proc. SPIE **1557,** 283 (1991)
[4] C. Owens, K. Bhat, W. S. Wang, A. Tan, M. D. Aggarwal, B. G. Penn, D. O. Frazier, J. Cryst. Growth **225**, 465 (2001).
[5] M. D. Aggarwal, J. Choi, W. S. Wang, K. Bhat, R. B. Lal, A. D. Shields, B. G. Penn, D. O. Frazier, J. Cryst. Growth **204**, 179 (1999).
[6] A. Yokotani, T. Sasaki, S. Nakai, S. Yamanaka, J. Cryst. Growth,**99**, 815 (1990).
[7] J. F. Carvalho, A. C. Hernandes, F. D. Nunes, L. B. O. A. de Moraes, L. Misoguti, S. C. Zilio, J. Cryst. Growth **173**, 487 (1997).
[8] R. Kumar, N. Gopalakrishnan, R. Jayaver, P. Ramasamy, Cryst. Res. Technol. **34(10)**, 1265(1999)
[9] G. Arunmozhi, R. Jayavel, C. Subramanian, J. Cryst. Growth **178**, 387 (1997).
[10] K. Sangwal, S. Veintemillas, J. Torrent-Burgues, J. Cryst. Growth **155**, 135 (1995).
[11] M. D. Aggarwal, T. Gebre, A. K. Batra, M. E. Edwards, R. B. Lal, B. G. Penn, D. O. Frazier, Proc. SPIE Vol. **4813**, 52 (2002).
[12] S. Mukerji, T. Kar, Mat. Res. Bull. **33(4),** 619 (1998).
[13] A. M. Petrosyan, R. P. Sukiasyan, H. A. Karapetyan, S. S. Terzyan, R. S. Feigelson, J. Cryst. Growth **213**, 103(2000).
[14] D. Rajan Babu, D. Jayaraman, R. Kumar, R. Jayavel, J. Cryst. Growth **245**, 121 (2003).
[15] A. S. Haja Hameed, G. Ravi, M.D. M. Hossain, P. Ramasamy, J. Cryst. Growth **204**, 333 (1990).
[16] R. Ittyachan, P. Sagayaraj, J. Cryst. Growth **243**, 8356 (2002).
[17] T. Pal, T. Kar, X. Wang, G. Zhou, D. Wang, X. Cheng, Z. Yang, J. Cryst. Growth **235**, 523 (2002).
[18] R. Ittyachan, P. Sagayaraj, J. Cryst. Growth in press.