



Scholars Research Library

Archives of Applied Science Research, 2012, 4 (4):1850-1856
(<http://scholarsresearchlibrary.com/archive.html>)



Growth and Characterisation of Pure and Strontium added $(\text{NH}_4)_3\text{Sb}_2\text{F}_9$ Single Crystals

R.Mary Jenila^{1*}, T. R. Rajasekaran², J. Benet Charles¹

¹Materials Research Centre, St. Xavier's College (Autonomous), Palayamkottai, Tirunelveli - 627002, Tamil Nadu, India

²Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India

ABSTRACT

Single crystals of pure and strontium doped Tri Ammonium Fluoro Di Antimonates $(\text{NH}_4)_3\text{Sb}_2\text{F}_9$, an electro optic crystal were grown by slow evaporation technique. The grown crystals were subjected to various studies such as single crystal X-ray diffraction (XRD), UV-Vis studies, Fourier Transform Infrared (FTIR), TG-DTA, Vickers's Micro hardness, DC Conductivity of the grown crystals were also measured. Single crystal X-ray diffraction studies reveals both the crystals belongs to orthorhombic crystallographic system. Microhardness studies reveals the incorporation of SrF_2 makes the crystal more softer than that of the pure $(\text{NH}_4)_3\text{Sb}_2\text{F}_9$ crystals. The details are presented and discussed in this paper.

Key Word: Slow evaporation, Superionic conductors, X-ray diffraction, TG-DTA, DC conductivity

INTRODUCTION

Trivalent Antimony Fluoride complexes represent an extensive class of inorganic compounds among which many substances exhibits unusual electro physical [1-3], Optical [4] and other properties which stimulated their thorough investigation by different physic chemical methods [5]. It has also been reported that a number of fluorides have high ionic conductivity and super ionic properties [6]. These compounds are of considerable interest due to the assumption that the presence of liable NH_4^+ in a crystal lattice, which is likely to lead to higher values of conductivity than in the cations of heavy alkali metals [7]. The ionic conduction of several Ammonium Fluoro Antimonates are reported earlier [8]. Some of the fluoro antimonates such as $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{NH}_4)_3\text{Sb}_4\text{F}_{15}$ are classified as super ionic conductors [9]. This fluoro complexes are the promising compounds for producing different purpose materials which includes piezoelectric [10-13] and biologically active compounds [14]. The growth, Dielectric and Microhardness studies of Sodium, Potassium and Ammonium are reported earlier [15-19]. Motivated by this, an attempt was made to study the growth and physical characteristics of a new Tri Ammonium Fluoro Di Antimonate crystal $(\text{NH}_4)_3\text{Sb}_2\text{F}_9$ (TAFDA) and reported in this paper.

MATERIALS AND METHODS

2. Experimental Studies:

2.1 Crystal Growth:

Crystals of TAFDA and Strontium doped TADFA were grown by solution growth employing slow evaporation technique at room temperature. Appropriate proportions of Ammonium Fluoride (NH₄F), Antimony tri oxide (Sb₂O₃) and Hydro fluoric acid (HF) were mixed together to prepare the solutions of TAFDA crystals. The homogenous saturated solution was kept in PVC containers for slow evaporation. Transparent single crystals were obtained in a period of one month. For the growth of Sr²⁺ doped TAFDA crystals, 2 mole percentage of strontium fluoride (SrF₂) was added to the solution of TAFDA. Single crystals of size 15 x 12 x 2 mm³ with good transparency were obtained in a period of 30 days.

2.2 Characterization:

The single crystals of pure and Sr²⁺ doped AFA were subjected to single crystal XRD studies using ENRAF NONIUS CAD4 diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) to determine the unit cell dimensions and morphology. The optical transmission range of the crystals was examined between 100 - 1100 nm using Shimadzu UV -1061 UV - Vis -NIR spectrophotometer. The infrared spectroscopy is effectively used to identify the functional groups to determine the molecular structure of the grown crystals. The FTIR spectra of the samples were recorded using FTIR 460 spectrometer by KBr pellet technique in the range 400 - 4000 cm⁻¹. The Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of the sample crystals were carried out using Seiko Thermal Analyzer at a heating rate of 10 °C/min for a temperature range of 30-600 °C. Microhardness measurements were done using a Vickers's microhardness indenter using Leitz Weitzier Hardness Tester. The indentation time was fixed as 10 s. Vicker's Hardness Number (Hv) is calculated using the relation

$$Hv = 1.8554 \frac{P}{d^2} \quad \text{kg mm}^{-2} \quad (1)$$

Where P is the load applied in kg and d is the diagonal length of the indented impressions in mm. DC conductivity measurements were carried out for pure and Sr²⁺ doped AFA crystals using the conventional 2-probe technique at various temperatures ranging from 40°C to 150 °C. The resistance of the crystals was measured using a milli Meg ohm meter. The observations were made while cooling the samples [20]. The conductivity (σ_{dc}) of the crystal was calculated using the relation

$$\sigma_{dc} = \frac{d}{RA} \quad (2)$$

Where R is the measured Resistance, d is the thickness of the sample and A is the area of the crystal. The Activation energy were calculated using the relation

$$\sigma_{dc} = \sigma \frac{\exp(-E_{dc})}{KT} \quad (3)$$

Where K is the Boltzmann's Constant, T is the absolute temperature and σ is the constant depending on the material.

RESULTS AND DISCUSSION

3.1 Single Crystal X-ray Diffraction:

TAFDA crystallized in the orthorhombic system and the lattice parameters are found to be $a = 6.48 \text{ \AA}$, $b = 14.16 \text{ \AA}$, $c = 6.80 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ for pure TAFDA crystals and $a = 6.44 \text{ \AA}$, $b = 14.11 \text{ \AA}$, $c = 6.74 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ for Sr²⁺ doped TAFDA crystals. The photograph of the grown crystals are displayed in fig .1(a-b)

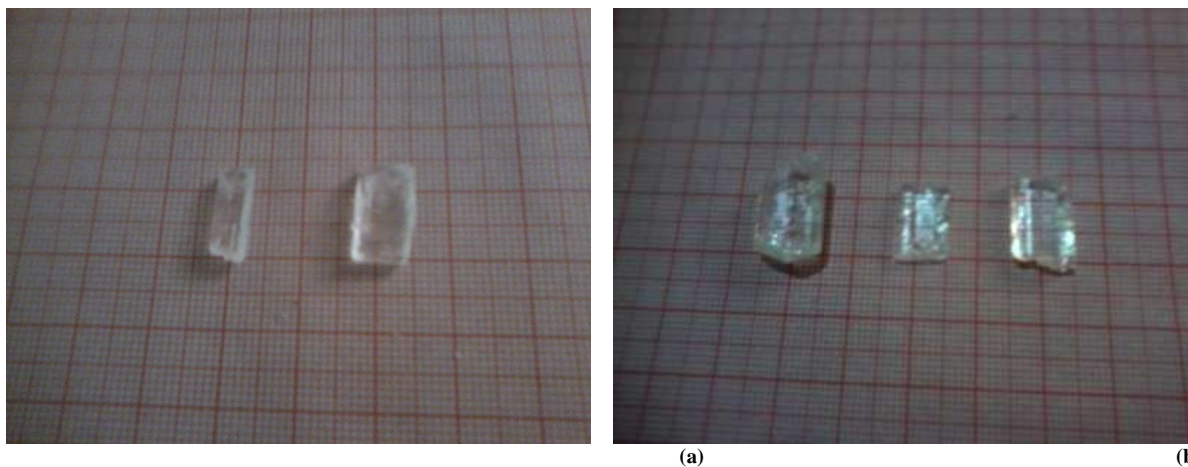


Fig .1. The Photograph of (a) as Grown pure & (b) Sr^{2+} doped (b) TADFA Crystals

3.2 UV -Vis Studies:

The recorded transmittance spectra for pure and Sr^{2+} doped TADFA crystals in the wavelength range 190 - 1100 nm are shown in fig.2a,b.

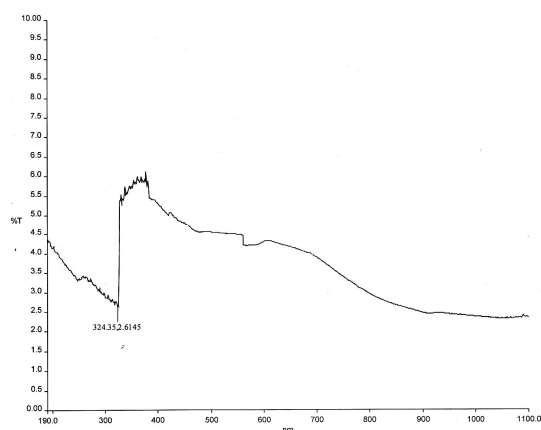


Fig 2a. Transmission Spectra of pure TADFA crystals

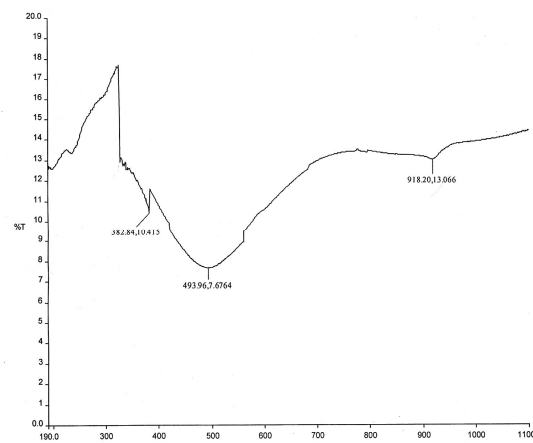


Fig2b. Transmission spectra of SrF^{2+} doped TADFA crystals

At about 324 nm, a sharp fall in the transmittance is observed and the crystals have sufficient transmission in the entire visible region and hence the crystals of this work are the potential candidates for opt electronics [21]. From the results, it is noticed that a lower cut off wave length for Sr^{2+} doped TADFA crystal are 493.96 nm. The forbidden band gap for the grown crystals of this work was calculated as 3.834eV and 2.5151eV. When TADFA crystals are doped with Sr^{2+} , the transmission is altered and the increase in transparency indicates the improvement of the quality of crystals [22].

3.3 FTIR Studies

The FTIR spectra of the grown crystals are displayed in fig .3 (a-b).

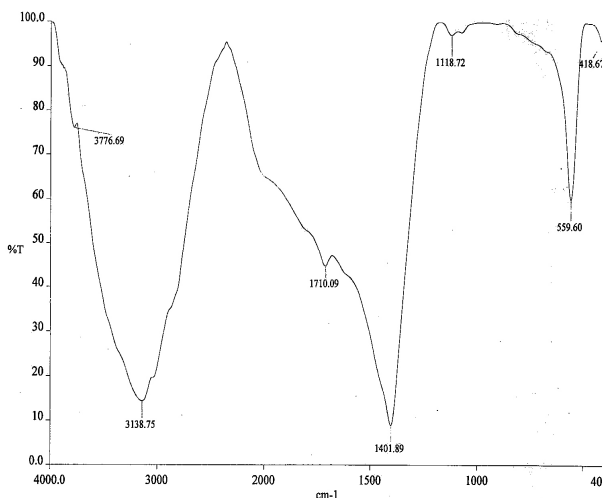


Fig 3a. Infrared Spectra of pure TADFA crystals

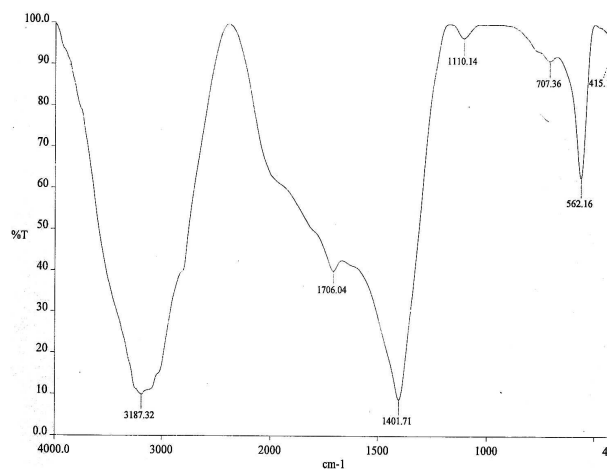


Fig 3b Infrared spectra of Sr²⁺ doped TAFDA crystals

The broad peak between 2500 cm⁻¹ and 3500 cm⁻¹ corresponds to the symmetric and asymmetric stretching modes of NH₂. The absorption peak at 1401 cm⁻¹ is due to the NH₄⁺ ions. The absorption peak at 1110 cm⁻¹ is due to the Sb - F vibrations. A sharp peak at 562 cm⁻¹ is due to the Sb - O symmetric stretching vibrations. Although the spectrum of Sr²⁺ doped TAFDA provides similar features as that of pure TAFDA, there is slight shifting and variations are observed for all peaks suggesting that it may be due to the incorporation of Sr²⁺ ions in the lattice of TAFDA.

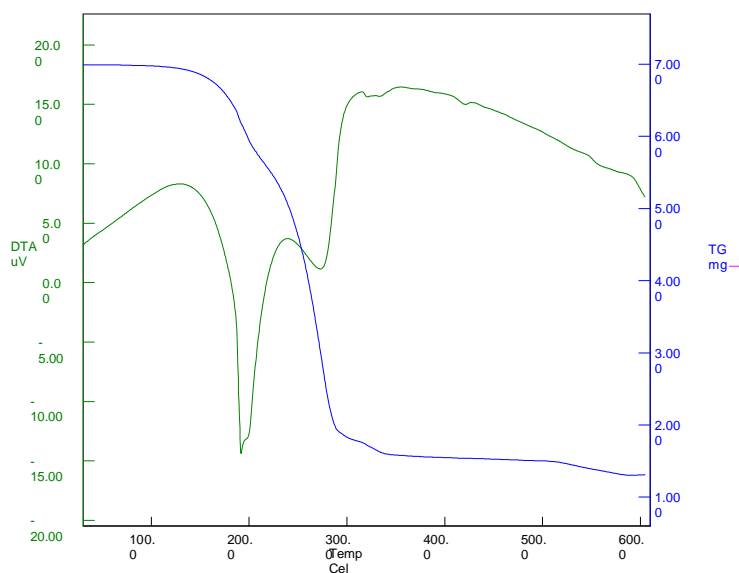


Fig 4a. TG /DTA studies of pure TAFDA single crystals

3.4 TG-DTA Studies:

TGA - DTA curves of the grown crystals are displayed in fig.4 (a-b). DTA curve shows that pure AFA crystal melts at 155°C and it undergoes endothermic transitions at 185°C and 285 °C. TGA curves shows that there is a weight loss in the temperature range 190 -280°C due to the liberation of volatile substances such as antimony in the compound. For Sr²⁺ doped TAFDA crystal, there is no weight loss in the

temperature range up to 165°C and there fore it is thermally stable upto 165°C. It is observed that there is a weight loss of about 75% in the range of 165 - 285°C. Beyond 320°C, the weight loss is found about 20 wt% of the initial mass.

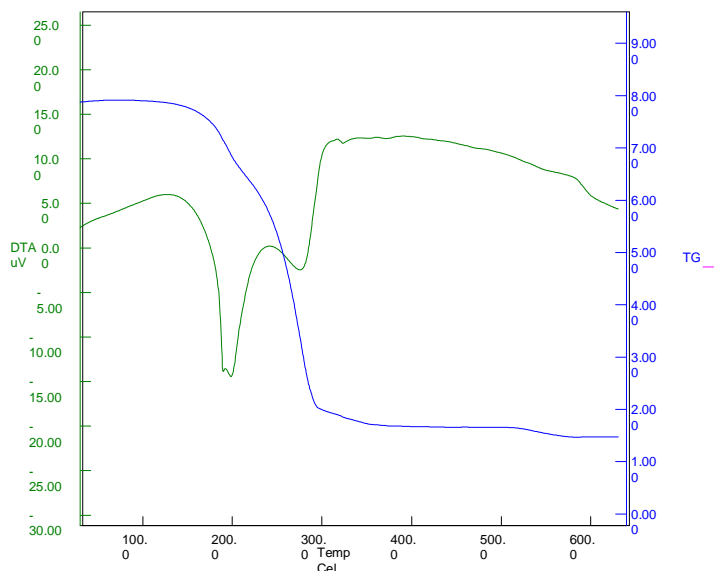


Fig 4b. TG / DTA studies of SrF₂ added TAFDA single crystals

3.5 Microhardness Studies:

A plot between the load P and hardness number H_v is shown in fig .5.

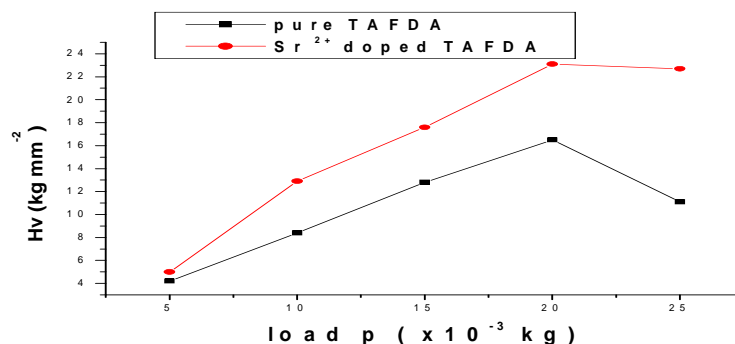


Fig.5 Variation of Hv with load for Pure and Sr²⁺ doped TAFDA crystals

This shows that the microhardness number increases with increasing load. On further increasing the load beyond 30 g, the Hv value started to decrease, indicating the starting of fracture on the surface of the crystal. Hardness number is found to be increasing with the doping concentration of Sr²⁺ in the lattice of TAFDA crystals. This can be attributed to enhancement of the strength of bonding due to the addition of Sr²⁺ into the lattice of TAFDA crystals. It is observed that scratching occurs in the crystal when the load is applied beyond 30g. The graph between log p against log d for pure and Sr²⁺ doped TAFDA crystals are drawn in fig .6.

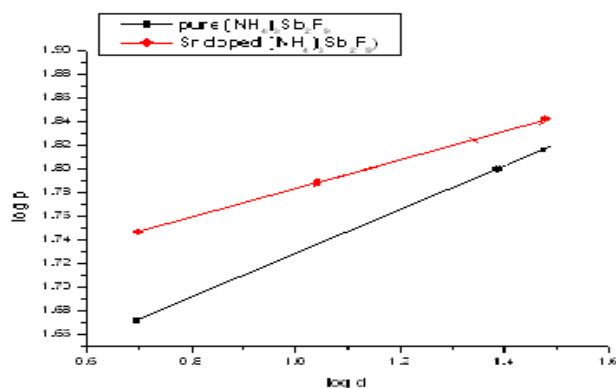


Fig. 6 log d Vs log P for Pure and Sr²⁺ doped and Sr²⁺ doped TAFDA crystals

The slope of the straight line gives the work hardening coefficient (n). The value for pure TAFDA is 1.540 and the work hardening coefficient for Sr²⁺ doped TAFDA crystal is 2.379. According to Onitsch [23], if n is greater than 1.6, the crystal belongs to soft category. As n is less than 1.6, pure TAFDA crystal is a hard material and Sr²⁺ doped TAFDA belongs to soft material and the hardness number increases with the load is also observed

DC Conductivity:

The DC conductivity of the pure and Sr²⁺ doped TAFDA crystals were calculated and the values of DC conductivity against Temperature are plotted in fig.7. It is observed that for both pure and Sr²⁺ doped TAFDA crystals, the DC conductivity increases with increase in temperature. The defect concentration increases with temperature and hence the electrical conductivity also increases. The addition of Sr²⁺ to the pure TAFDA increases the electrical conduction in the given range of temperature. The activation energies are calculated and it is found to be 0.5286eV for pure TAFDA crystal and 0.4108 eV for Sr²⁺ doped TAFDA crystals.

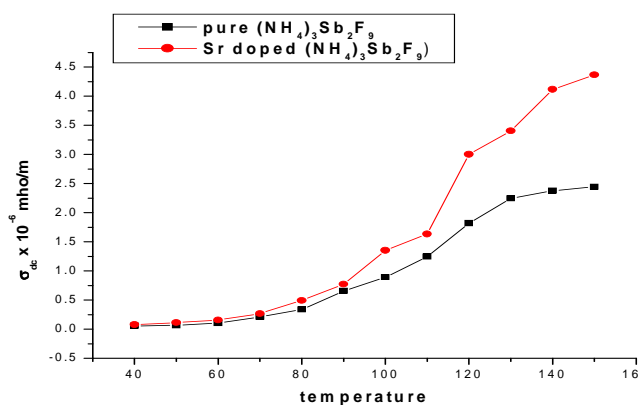


Fig. 7 .Temperature Vs DC Conductivity for pure and Sr²⁺ TAFDA crystals.

CONCLUSION

Single crystals of pure and Sr²⁺ doped AFA crystals were grown by solution growth. The grown crystals are transparent and have well defined external appearance. Single XRD studies confirm that both pure and doped TAFDA crystals crystallize in orthorhombic structure. The UV-Vis –NIR spectra shows that all the grown crystals of this work have good optical transmittance in the entire visible region. The FTIR trace reveals the shifting of bands due to the presence of alkali atoms in the lattice of TAFDA crystals. TG curves shows that both the crystals are stable upto 165°C. Microhardness studies show that the hardness number increases with increase of loads. The addition of Sr²⁺ makes the pure TAFDA crystal into softer category. Dc conductivity increases with temperature and the conductivity values are high for Sr²⁺ doped TAFDA crystals. The activation energies were calculated.

Acknowledgement:

We would like to thank Dr. Shivaji and Mr. Soundararajan, Dept. of Nuclear Physics, Madras University, Chennai, for their help to carry out the research work.

REFERENCE

- [1] L.M.Avkhutsii, R.L.Davidovich, L.A.Zemnukhova, P.S.Gordienko, V.Urbonavicius and J.Grigas, *J. Phys. Stat. Sol. (b)*, 116 (1983) 483 - 488.
- [2] M. P. Borzenkova, F. V. Kalinchenko, A.V. Novoselova, *Zh. Neorg Khim.* 29, (1984) 703 - 705.
- [3] Yu. N. Moskvich, B. I. Cherkasov, A. M. Polykav, A. A. Sukhovskii and R. L. Davidovich, *Phys. Stat. Sol. (b)* 156 (1989) 615 - 631.
- [4] J. G. Bergman, D. S. Chemla, R. Fourcade, G. Macherpa, *J. Solid State Commun.*, 3 (1978) 187 - 190.
- [5] V. Ya. Kavun, L. A. Zemnukhova, V. I. Soriano, T. A. Kaidalova, R. L. Davidovich and N. I. Sorokin, *Russ. Chem. Bull.* 51 (2002) 1996 - 2002.
- [6] Elsamma Chacko, J. Mary Linet, S. Mary Navies Praia, *Indian J. Pure and Applied Phys.*, 44 (2006) 260 - 263.
- [7] V. Ya. Kavun, A. A. Udovenko, N. F. Uvarov, V. I. Sergienko, L. A. Zemnukhova, *J. Struct. Chem.*, 43 (2002) 246 - 251.
- [8] R. L. Davidovich, P. S. Gordienko, J. Grigas, *Phys. Status Solidi (b)*, 84 (1984) 387 - 392.
- [9] V. Ya. Kavun, V. I. Sergienko, N. I. Sorokin, L. A. Zemnukhova, T. A. Kaidalova and E. B. Merkulov, *J. Struct. Chem.*, 42 (2001) 570 - 577.
- [10] F. V. Kalinchenko, M. N. Borzenkova and A. V. Novoselova, *Zh. Neorg. Khim.*, 28 (1983) 2354 - 2357.
- [11] F. V. Kalinchenko, M. N. Borzenkova and A. V. Novoselova, *Zh. Neorg. Khim.*, 27 (1982) 2916 - 2919.
- [12] B. Ducourant and R. Fourcade, *Compt. Rend. Acad. Sci. Paris. Ser C.* 282 (1976) 741 - 745.
- [13] L. A. Zemnukhova, R. L. Davidovich, *Z. Naturforsch., A. Phys. Sci.*, 53 (1998) 573 - 577.
- [14] E. V. Kovaleva, L. A. Zemnukhova, V. M. Nikitin, *Zh. Prikl. Khim.*, 75 (2002) 971 - 975.
- [15] R. Rani Christu Dhas, J. Benet Charles, F. D. Gnanam, *J. Crys. Growth*, 137 (1994) 295 - 298.
- [16] R. Christu Dhas, J. Benet Charles, F. D. Gnanam, *J. Mater. Sci. Letters*, 12 (1993) 1395 - 1397.
- [17] J. Benet Charles and F. D. Gnanam, *Crys. Res. Tech.*, 12 (1990) 45 - 52.
- [18] J. Benet Charles and F. D. Gnanam, *J. Mat. Sci. Letters*, 9 (1990) 165 - 181.
- [19] C. Besky Job, K. Ganesan, *J. Benet Charles*, 3 (2011) 41 - 52.
- [20] S. Perumal, C. K. Mahadevan, *Physica B*, 367 (2005) 172 - 181.
- [21] G. Arunmozhi, E. M. deGomes, S. Ganesamoorthy, *Crys. Res. Tech.*, 39 (2004) 408 - 413.
- [22] C. Krishnan, P. Selvarajan, S. Pari, *Current. App. Physics*, 10 (2010) 664 - 669.
- [23] E. M. Onitsch, *Mikroskopie* 2 (1947) 131 - 232.