Available online at **www.scholarsresearchlibrary.com**

Scholars Research Library

Archives of Applied Science Research, 2010, 2 (1) 191-197
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Optical, Microhardness, Dielectric and Conductivity Studies of Na_2SbBF_8 Single Organic Crystal

A. Cyrac Peter[a,b*], M. Vimalan[c], P. Sagayaraj[a] and J. Madhavan[a]

[a]*Department of Physics, Loyola College, Chennai, India*
[b]*Thirumalai Engineering College, Kanchipuram, India*
[c]*S. T. Hindu college, Nagercoil, India*

Abstract

Single crystals of Na_2SbBF_8 are grown by slow evaporation technique at ambient temperature. The improved transparency of grown crystal was investigated using UV-Vis spectral analysis. The Mechanical properties and work hardening coefficient of the grown crystal have been studied using Vickers microhardness tester. The dielectric constant constant (ε_r) and dielectric loss (tan δ) were determined as a function of frequency in the range 50 Hz to 5 MHz at different temperature. It was found that both the dielectric constant and dielectric loss decrease with increase in frequency. The electrical conductivity studies of Na_2SbBF_8 crystal in the temperature range 35 to 115 °C. The effects of frequency, and temperature on the electrical conductivity (σ_{ac}) were studied for Na_2SbBF_8. Analysis of the results shows that σ_{ac} increases with increase of frequency and the change in independent of temperature. The cole-cole plots indicates shift in the distribution of relaxation time.

Key words: solution growth, UV-Vis-NIR Spectrum, microhardness, dielectric constant, and ac conductivity

---

Introduction

Flouride single crystals, owing to their unique properties such as large band gap, has many advantages as optical materials. Colquiriite type fluoride single crystals are especially promising materials for UV laser and optical lithography applications [1]. Flouro complexes of sodium and ammonium are gaining interest because of their electro- optic (Na_2SbF_5) and superionic [$(NH_4)_2SbF_5$] properties [2-3]. The crystal chemistry of water-soluble crystal of fluoroantimonates and their related compounds have been reported in the literature [4-8]. It was also reported that a number of fluoro complexes of antimony (III) with the alkali fluorides are of considerable interest, because of their high optical homogeneity and other pertinent characteristics. The potassium fluoroantimonate $KSbF_4$ show high ionic conductivity [9]. The infrared absorption spectra of Na_2SbF_5, $NaSbF_4$, $NaSb_2F_7$ and $NaSb_4F_{13}$ have been recorded in the range down to 400 cm^{-1} and the structures of these compounds have also been discussed by Kharitonov et al. Micro hardness studies of this component were reported by Benet Charles et.al.[10-12]. Growth, Microhardness and crack pattern studies of $NaSb_2F_7$ and $Na_3Sb_2F_9$ single crystals have also been reported [13-15]. In this paper, we report the results of dielectric, absorption and hardness studies of Na_2SbBF_8 single crystal.

Materials and Methods

Experimental

The starting material is synthesized by stoichiometric incorporation of Sb_2O_3, NaF, HF(48%)and HBF_4 (50%) in the appropriate molar ratio according to the chemical reaction.

$$0.5Sb_2O_3+HBF4 + 2\ NaF + 6HF \longrightarrow Na_2SbBF_8 + 3H_2O$$

The growth experiments were carried out by slow and controlled evaporation of the water solvent at constant temperature 305K using polyethylene container and stirrers. The seed crystals are obtained by spontaneous nucleation. The single crystals are grown of Na_2SbBF_8 in a period of 60 days up to dimensions 22 X 20 X 8 mm^3 and are as shown in Fig. 1. The size of the crystal grown in the present work is better than the earlier reported work [11]

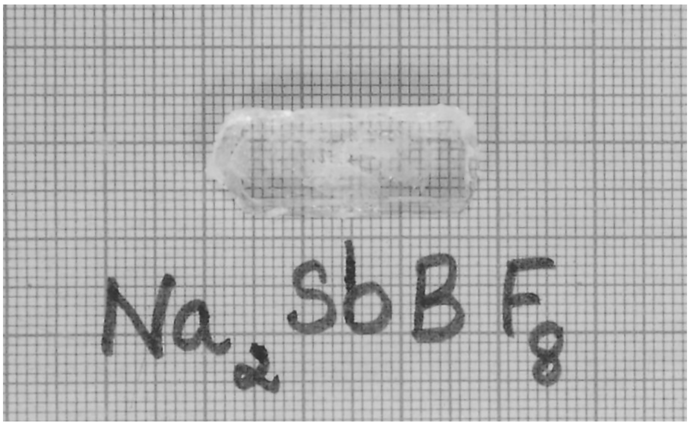

Fig.1. As grown crystal of Na_2SbBF_8 single crystal

Characterization of the crystal

The grown crystals have been characterized by optical absorption using Shimadzu UV-260 spectrophotometer. The microhardness was determined using a Leitz-Wetzler microhardness tester attached with a Vickers diamond pyramid indenter. The capacitance and dissipation factor of the specimen were measured as a function of frequency in the range from 50 Hz to 5000 KHz using AND0 model AG-4311 LCR meter.

3.1 UV- Vis Studies

The optical absorption spectra of Na_2SbBF_8 crystal is shown in Fig. 2. From the spectrum, a strong absorption was observed at 250nm, it has been observed that the lower cut-off wavelength is about 800 nm, above which the transparency conveniently extends to 2500 nm. The percentage of transmission is about 68%.We plotted $(\alpha h\nu)^{1/n}$ vs $h\nu$ for Na_2SbBF_8 the best fit was obtained for n = 1/2 indicating an indirect gap of 2.46 eV by the plot of $(\alpha h\nu)^2$ vs $h\nu$ as shown for in the Fig. 3.

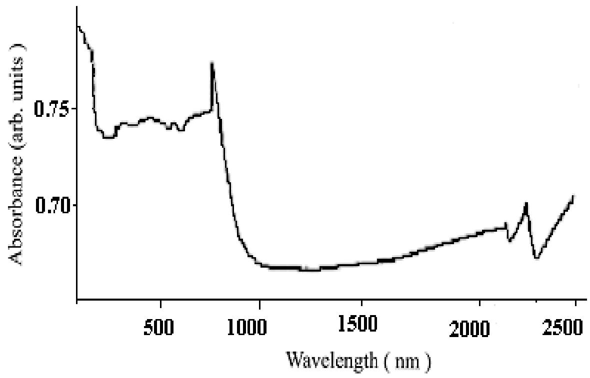

Fig. 2. UV-Vis Absorbance spectrum of Na_2SbBF_8

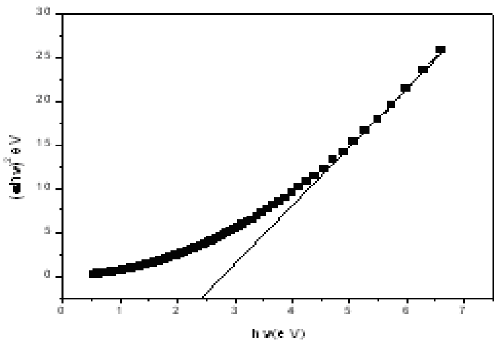

Fig. 3. Plot of hν Vs $(\alpha h\nu)^2$

3.2 Microhardness studies

Microhardness of a crystal is its capacity to resist indentation. Physically hardness is the resistance offered by a material to the localized deformation by scratching or by indentations. For the static indentation test, all the indentation measurements were made at room temperature using freshly cleaved sample Na_2SbBF_8 crystals over a fixed interval of time (15 seconds) and removed. The indented impressions were square. The surfaces were indented at different sites. Diagonal lengths of the indented impressions obtained at various loads were measured using a calibrated micrometer attached to the eye piece of the microscope. Several indentations were made on Na_2SbBF_8. The average value of the diagonal lengths of the indentation mark for each load was used to calculate the hardness. The Vicker's micro hardness number was determined from the relation

$$H_v = 1.8544\ P/d^2\ \mathrm{Kg/mm^2}$$

where P is the load in gm, d the length of the diagonal of the indentation impression in mm and H_V the Vickers hardness in kg/mm^2. The hardness values and corresponding load are shown in Table 1. A plot drawn between hard ness number and applied load is shown in Fig. 4. The hardness number was found to increase with load. The observed the low hardness value at low load, a steep increase at high load followed by a slower increase with load.

Table 1: The Hardness values for Na_2SbBF_8

Load (P) X 10^{-3} Kg	Diagonal Length X10^{-3} mm			Hardness value of H_V Kg/ mm^2
	d1	d2	d	
02	6.1	5.9	6	103
05	9.4	7.4	8.4	131.4
07	9.8	9.7	9.75	136.6
10	11	11.8	11.4	142.7
12	12.2	12.4	12.3	147.1

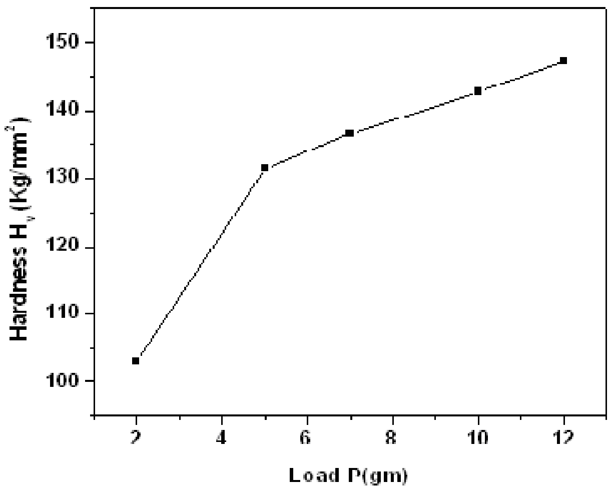

Fig. 4. Variation of Vicker's Hardness with Load

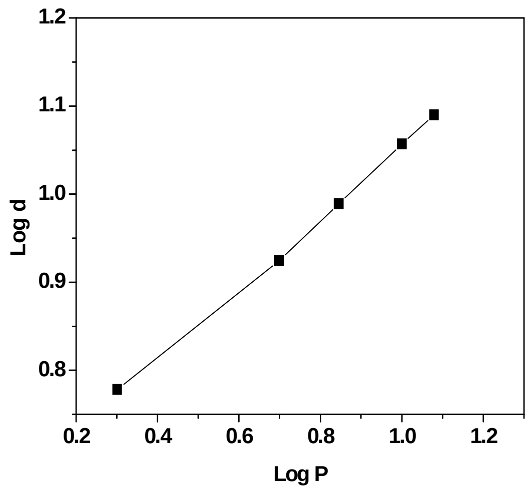

Fig. 5 .Plot of Log P Vs Log d

The plot log p Vs log d is shown in Fig. 5. The work hardening coefficients was computed using least squares fit method and found to be 2.22. Since the value of n is greater than 2, the hardness of the material is found to increase with the increase of load; it confirms the prediction of Onitsch [16], and also the reverse indentation size effect (RISE) [17–19].

3.3 Dielectric Studies

Sodium fluoroantimonate single crystal with high transparency and defect-free size was selected and used for dielectric measurements. Rectangular specimens of thickness approximately 3.5 mm and area of cross section of 113 mm^2 were used for dielectric measurements. A thin coating of silver paint was applied on both the surfaces of the samples for contact. From the capacitance data, the dielectric constant at each temperature is calculated using

$$\varepsilon_r = Cd/ \varepsilon_o A$$

Where C is capacitance, d is the thickness, ε_o the free space permittivity and A the Area sample. The variation of dielectric constant (ε_r) with frequency at different temperature for the Na_2SbBF_8 single crystal under investigation has been shown in Fig. 6. It was observed from these figures that the dielectric constant (ε_r) having higher values at lower frequencies and decreases with increasing frequency. The magnitude of ε_r depends on the degree of polarisation of charge displacement in the crystals. The dielectric constant of the materials is due to mainly the contribution of space charge polarization at low frequencies. The variation of dielectric loss with frequency has also exhibited similar behaviour as shown in Fig. 7.

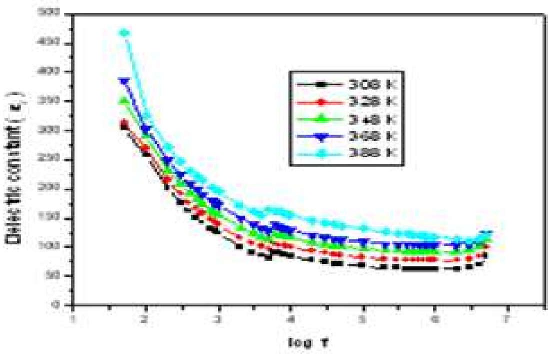

Fig. 6. Effect of frequency on dielectric constant at different temperature

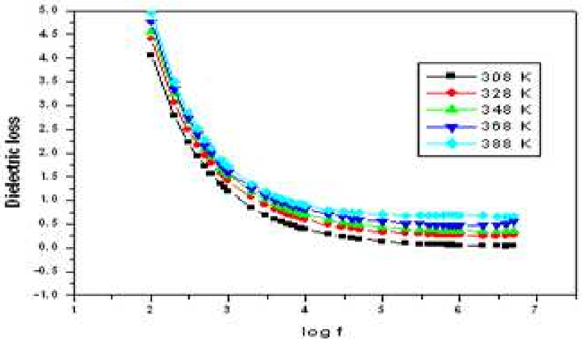

Fig. 7. Effect of frequency on dielectric loss at different temperature

Our measurements show that there is no abrupt change but only a smooth variation in "tan δ "over the entire frequency for all the crystals studied. The space charge polarisation will depend on the purity and perfection of the material. Its influence is small at low frequencies and it may be attributed to space charge polarisation due to lattice defects. However, the low values of "tan δ "suggests that the grown crystals are of moderately good quality.

The variation of dielectric constant and loss with temperature at different frequencies for Na_2SbBF_8 single crystal is studied. The Fig. 8 presents the variation of dielectric constant with temperature at different frequencies for Na_2SbBF_8 crystal shows that there is no abrupt change, and the rate of increase of ε_r with frequency is found. From Fig. 9, the variation of dielectric loss with temperature has also exhibited similar behaviour as shown in Fig. 8. Thus resulting in large proportions of space charge polarization, which ultimately causes larger increase of ε_r and tan δ values as observed.

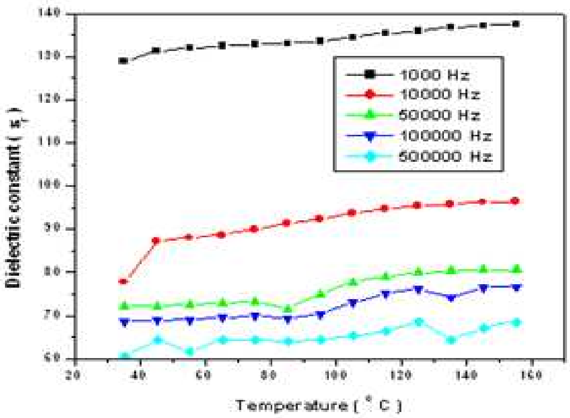

Fig. 8. Variation of dielectric constant with temperature at different frequency

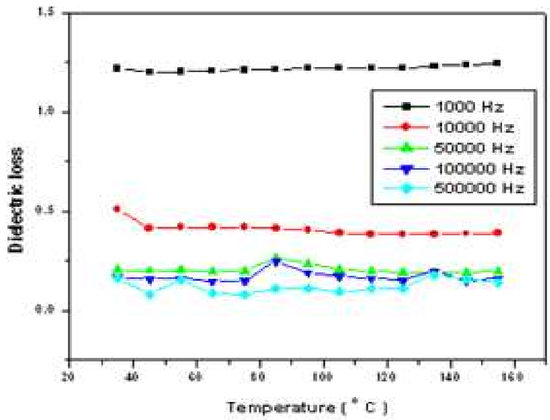

Fig. 9. Effect of frequency on dielectric loss at different frequency

The electric conductivity has been shown in Fig. 10 for Na_2SbBF_8. The AC conductivity (σ_{ac}) was calculated using the relation

$$\sigma_{ac} = \varepsilon_o \, \varepsilon_r \, \omega \tan \delta$$

where ε_0 is the permittivity of free space (8.85×10^{-12} farad/m) and ($\omega = 2\pi f$) is the angular frequency. Plots between ln (σ_{ac}) and 1000/ T were found to be very nearly linear. So, the conductivity values can be fitted to the relation

$$\sigma_{ac} = \sigma_o \exp(-E_{ac}/KT)$$

where σ_{ac} is the activation energy, k is the Boltzmann constant, T is the absolute temperature and σ_o is the parameter depending on the material. Activation energies were estimated using the slopes of the above line plots [E=-(slope) k ×1000]. The dielectric conductivity was observed to increase with frequency and the dielectric conductivity was no change with temperature. The relaxation time (τ) was determined from cole - cole plots of the type shown Fig. 11. From the intercepts on the x-axis corresponding to zero frequency, resistance and corresponding conductance were determined at various temperatures. A shift in the peak is observed for increasing temperature. The relaxation time (τ) is calculated using the cole-cole plots by the relation

$$\tau = \tfrac{1}{2} \pi f_p$$

Where f_p is the value of frequency for maximum peak position of cole – cole plot. The analysis of cole – cole plots indicates a slight increase in the relaxation times as the temperature increases.

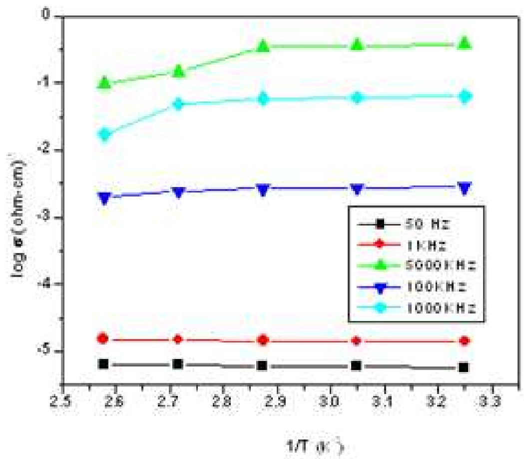

Fig. 10. Effect of temperature on Electrical conductivity of Na_2SbBF_8 at different frequency

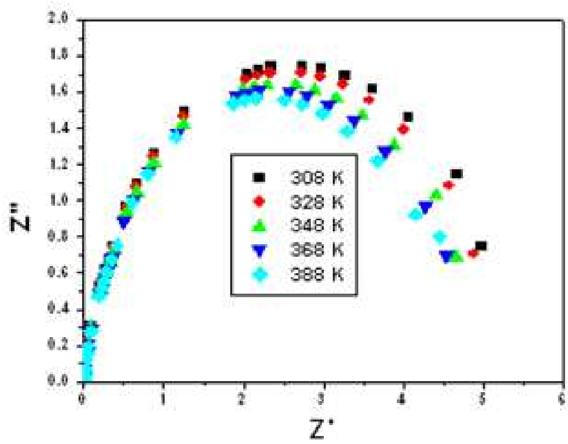

Fig. 11. The cole-cole plots for Na_2SbBF_8 single crystal

Conclusion

From the above results we conclude that optically clear Na_2SbBF_8 single crystals of dimensions upto 22 x 20 x 8 mm^3 in a period of two months can be grown by slow evaporation technique. These crystals are having good optical quality and transparency. The micro- hardness study shows that when the load is increased, the hardness number is increased. The work-hardening coefficient (n) for Na_2SbBF_8, crystal is found to be greater than 2. The dielectric studies of Na_2SbBF_8 reveal that at different temperature dielectric constant (ε_r) decreases with increase frequency up to 10 KHz beyond which they attain a constant value From the result of various dielectric measurement is observed that there is decrease in the rate of ε_r, tan δ, σ_{ac} with frequency and constant with temperature. The UV–Vis–NIR spectrum shows that the crystal is optically transparent with strong absorption at 250 nm. The lower cut-off wavelength is about 800 nm, above which the transparency conveniently extends to 2500 nm. The optical band gap was found to be 2.46 eV. The relaxation time is determined from cole-cole plot.

References

[1] A. Bensalah, K. Shimamura, K. Nakano, T. Fujita and T. Fukuda, *J. Crystal. Growth*, **2001**, 231, 143.
[2] J. G. Bergman, D. S. Chemla, R. Fourcade and G. Mascherba, *J. Solid state Chem*, **1978**, 23, 187.
[3] L. M. Avkhutskii, R.L. Davidovich, L.A. Zemnukhova, P. S. Urbonavicius and J. Grigas, *Phys. Stat. Solidi (b)*, **1983**, 116, 483.
[4] J. Benet Charles and F. D. Gnanam, *Cryst. Res. Tech*., **1994**, 29,707.
[5] M.B.Ducorant ,B.Bonnet, R.Fourcade, and G.Mascherba, *Bull.Soc.Chim*, **1975**, 8, 1471.
[6] S.E.Gugasyan, V.P.Gorkov, L.A Sodokhina, F.Kh.Chibirov and V.S. Shpinel Zh. *Strukt.Khim*., **1975**, 16, 207.
[7] Yu. Ya. Kharitonov , R. L. Davidovich, V.I. Kostin, L. A. Zemnukhova and V. I. Sergienko ,Russ. *J. Inorg. Chem*, **1972**, 17, 682.
[8] F.B.Kalinchenko, M.P.Borzenkova and A.V.Novoselova, Russ. *J.Inorg.Chem*.,**1982**, 27, 1653.
[9] M.P.Borzenkova, F.V.Kalinchenko, A.V.Novoselova, A.K.Fvanovshits and N.I. Sorokin, *Russ. J.Inorg Chem*., **1984**, 29, 405.
[10] J.Benet Charles, Studies on growth and characterization of sodium fluoroantimonate single crystal ,Ph.D thesis ,Anna University ,(Madras, India ***1992)***.
[11] J.Benet Charles, *Materials Chemistry and Physics* **1996**, 45, 189.
[12] J.Benet Charles and F.D.Gnanam, *Materials Chemistry and Physics*, **1994**, 38, 63.
[13] J. Benet Charles and F. D. Gnanam, *J. matter. Sci. Letts*, **1990**, 9, 165
[14] J. Benet Charles and F. D. Gnanam, *Cryst. Res. Tech*., **1990**, 12, 1451
[15] J. Benet Charles, K. Sivakumar and F. D. Gnanam, *Cryst. Res. Tech.*, **1990**, 11, 1259.
[16] E.M. Onitsch, *Mikroskopie* **1950**, 95, 12.
[17] K. Sangwal, *Mater. Chem. Phys*. **2000**, 63, 145.
[18] B.W. Mott, Microindentation Hardness Testing, Butterworths, London, **1956**.
[19] D. Tabor, The Hardness of Materials, Oxford University Press, Oxford, **1951**.