Synthesis and Characterization of Pure and Lithium nitrate doped Sodium bromate Single Crystals

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Abstract —The lithium nitrate doped sodium bromate crystal is grown by slow evaporation solution growth technique at room temperature. The grown crystal was subjected to XRD, UV, FTIR, SEM, TG/DTA, Microhardness, Dielectric and SHG analysis. Characterization studies reveal that the grown crystal forms cubic system with space group $P2_13$. The crystal possesses less absorption in the UV-Visible region. The presence of various functional groups has been identified from FTIR studies with their vibrating frequencies. The second harmonic generation efficiency was also determined. The electrical and mechanical property was studied by dielectric measurement and microhardness.

KEYWORDS – XRD,UV,FTIR,SEM,TG/DTA, Microhardness, Dielectric, SHG.

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1 INTRODUCTION

Materials answering for high optical linearity are a potential area which has attracted many experimental researchers. Pure inorganic NLO material, sodium bromate doped lithium nitrate are of hydrogen bonded materials which possess piezoelectric optic and nonlinear optical properties with excellent mechanical and thermal properties [1,2]. Pure and lithium nitrate doped sodium bromate crystals were grown and characterized and it was found that sodium bromate increased the second harmonic generation (SHG) efficiency and it was dependent on doping [3]. The thermal stability,dielectric properties, SHG efficiency and the percentage optical transmission of grown crystals is reported.

2 EXPERIMENT

2.1 Materials used and Solubility

AR grade sodium bromate salt was purchased from Zigma-Aldrich Company, Hydrabad and re-crystallization was carried out to improve the purity. The solubility of the re-crystallized sodium bromate salt in double distilled water was measured at different temperatures by gravimetrical method as explained. The same procedure was followed to determine the solubility of 0.5 mol% of lithium nitrate sodium bromate samples in double distilled water.

The solubility curves of pure and doped sodium bromate samples are shown in figures. From the solubility curves it is seen that the solubility of the samples increases with increase in temperature and hence the samples have positive temperature coefficient of solubility.
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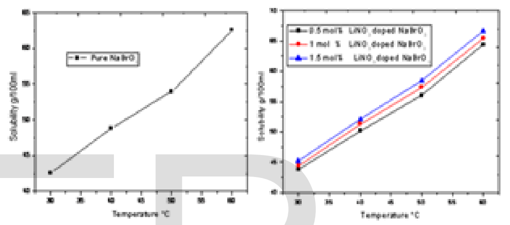

Figure :1
Solubility curves of Pure and lithium nitrate doped sodium bromate

2.2 Growth of pure and doped sodium bromate crystals

Using the solubility data, 100 ml of saturated solution of the re-crystallized salt of sodium bromate was prepared at 30°C and stirred well for about 2 hours. Then the solution was filtered and it was taken in a beaker for crystallization. Seed crystals were obtained in a period of 10 days and the grown seed crystals are shown in the photograph.

Figure: 2 Seed crystals of sodium bromate

Saturated solution of sodium bromate was prepared using the re-crystallized salt at 30°C by constant stirring for 2 hours using the predetermined solubility data. The solution was then filtered into a breaker. Good quality seed crystals were selected and were placed at the bottom of the beakers containing the solutions. The beakers were covered with perforated papers and the growth experiment was carried out in the room temperature.The solvent gradually evaporates leading to supersaturation and the excess of the solute was deposited on the seed crystals and the crystals grew into big-sized crystals. The grown crystals are shown in figure. The grown crystals were found to be transparent and colorless. The crystals were found to be triangular morphology and well faceted. It seems

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that the transparency of doped crystals is more compared to undoped sodium bromate crystal.

The morphology of the pure sodium bromate crystal is found to be triangular with pyramidal morphology with less transparent.

Figure: 3 pure sodium bromate crystal

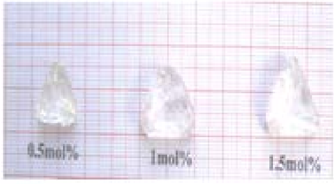


Figure:4 Lithium nitrate doped sodium bromate mixed crystals

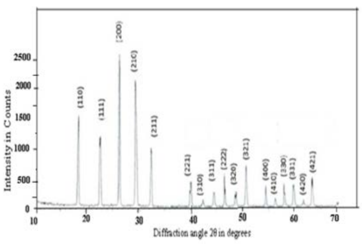
3 CHARACTERIZATION

The FTIR spectra were recorded on PERKIN ELMER FTIR spectrometer in the range from 400-4000cm^{-1}. Powder XRD study was carried out on PHILIPS X'PERT MPD system using Cu K_α radiation. The TG/DTA was performed on NETZSCH Geratebau GmbH from room temperature to 900°C at a heating rate of 10°C/min in nitrogen media. The dielectric characteristics of the samples were studied using Agilent 4274A LCR meter in the frequency range 200Hz to 1MHz. The UV-Vis spectra of pure and doped crystals were recorded using PERKIN ELMER LAMBDA-19 Spectrophotometer. For the measurement of SHG efficiency, the Kurtz Powder method was used by illuminating the powdered samples with fundamental (1064 nm) of a Q-Switched mode – locked Nd : YAG laser with input pulse of 2.7 mJ [4].

4 RESULTS AND DISCUSSION

4.1 Structural Studies

Structural studies for the pure and doped sodium bromate crystals were carried out by using powder X-ray diffractometry (PXRD). The recorded PXRD patterns of pure and doped sodium bromate crystals are shown in figures. The sharp peak indicates that the crystals posses good crystal crystallinity. The peaks observed on the X-ray diffraction patterns can be compared with the standard available JCPDS [5] for the confirmation of the structure. The lattice parameters of pure and sodium bromate crystals are tabulated .The lattice constants of pure sodium bromate crystal obtained in this work are found to be in good agreement with the reported values [6,7]. The lattice parameters and cell volume are altered when sodium bromate samples are doped with the lithium nitrate.



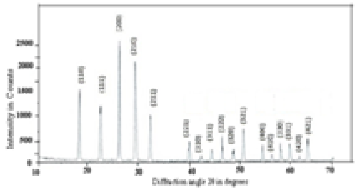


Figure:5 Powder XRD spectrum of pure sodium bromate single crystal

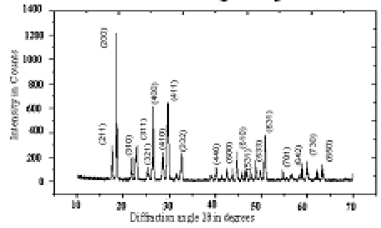


Figure:6 Powder XRD spectrum of lithium nitrate doped sodium bromate crystal

Table:1 Lattice parameters of pure and doped sodium bromate crystals

Sample	a=b=c (Å)	Unit cell volume V(Å)^3	α=β=γ degrees
Pure sodium bromate	6.7066	301.571	90
0.5 mol% $LiNO_3$ doped sodium bromate	6.7281	304.574	90

4.2 Hardness Studies

The hardness studies were carried out for pure and lithium nitrate doped sodium bromate crystals with the loads ranging from 25 to 100 g. The microhardness number (H_v) was calculated for the samples. Figures show the variation of microhardness number with the loads. It is observed that the hardness increases with increase of load. The hardness is found to be greater for pure sodium bromate single crystals. The value of microhardness number is found to be less on doping when compared to the undoped sodium bromate crystal. This is because of the entering of dopants into superfacial crystal lattice and forming defect centers generating weak lattice stress on the surface [**8,9**]. The plots of log P versus log d are almost straight lines shown in figures. The standard hardness for the samples was calculated using the equation $P = a d^n$. Here a is the standard hardness and n is the work hardening coefficient. The hardness is related to yield stress by the relation $H_v = 3\sigma_y$ where 'σ_y' is the yield stress. The first order elastic stiffness (C_{11}) has been evaluated for pure and doped sodium bromate crystals by using Wooster's empirical relation $C_{11} = (H_v)^{7/4}$ where H_v is microhardness number. The values of Vickers hardness number in (MPa) at different loads for pure and doped sodium bromate crystals are given in table. The values of yield stress, first order elastic stiffness constant at 100 g load, work hardening coefficient and standard hardness values for pure and doped sodium bromate crystals are provided in the table.

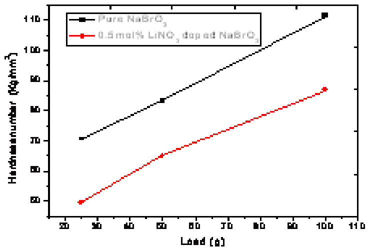


Figure:7 Variation of Vickers microhardness number with the applied load for pure and lithium nitrate doped sodium bromate crystals

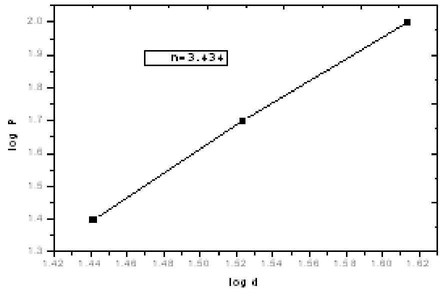


Figure:8 A plot of log P versus log d for pure sodium bromate crystal

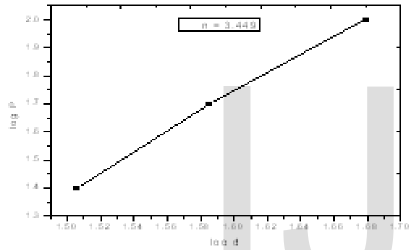


Figure:9 A plot of log P versus log d for lithium nitrate doped sodium bromate crystal

Table:2 Values of Vickers microindentation hardness in (MPa) at different loads for pure and doped sodium bromate crystals:

Load (N)	Pure sodium bromate (MPa)	0.5 mol% of $LiNO_3$ doped sodium bromate (MPa)
0.245	692.37	485.59
0.430	816.536	637.98
0.980	1092.7	851.13

Table:3 Yield stress, first order elastic stiffness constant at 100 g load and work hardening coefficient values for pure and doped sodium bromate samples

Samples	Yield Stress σ_y (MPa)	First Order Elastic Stiffness Constant C_{11}(MPa)	Work Hardening Coefficient n	Standard Hardness a (MPa)
Pure sodium bromate crystal	364.23	208130.05	3.434	197799.90
0.5 mol% of lithium nitrate doped sodium bromate crystal	283.71	134405.41	3.449	193297.43

.3 Fourier Transform Infrared (FTIR) Spectral studies

The FTIR spectra are useful to identify the molecular groups present in the samples and these spectra of doped sodium bromate crystals were recorded using Perkin-Elmer FTIR spectrometer by KBr pellet technique in the range 400-4000 cm^{-1}.

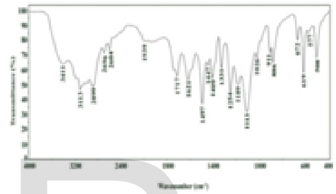


Figure:10 The FTIR spectrum of lithium nitrate doped $NaBrO_3$ crystal

4.4 Surface Features By Scanning Electron Microscopic (SEM) Studies

SEM studies were carried out for the samples at NIIST, Papanamcode, Trivandrum. SEM images of pure and lithium nitrate doped sodium bromate crystals are shown in figures. The surface of crystal was clearly seen at higher magnification in the micrographs. The particle grain size is observed to be about 10-50 μm. Microcrystallites were found on the surface.

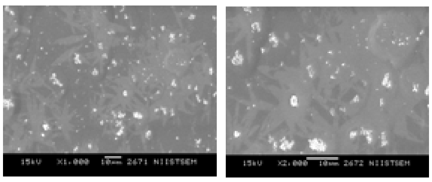


Figure:11 SEM images for the grown sodium bromate crystal

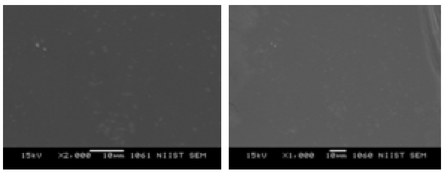


Figure:12 SEM images for the grown lithium nitrate doped sodium bromate crystal

4.5 TG/DTA Studies

The TG and DTA curves of pure sodium bromate single crystal are shown in figure. The decomposition begins at 310°C with

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2% weight loss and decomposes at 345 °C [10]. The DTA curve shows two endothermic peaks at 380°C and 750°C and one exothermic peak at 415°C. The peak at 380°C [11] gives the melting point of sodium bromate and the peak observed at 750 °C indicates the melting point of sodium bromide. The peak at 415°C represents the decomposition temperature of sodium bromate. The TG curve shows that the crystal is thermally stable upto 345°C and above this temperature it decomposes with the evolution of steam and oxygen. The decomposition equation is observed to be

$NaBrO_3 = NaBr + 3/2O_2$ [12]

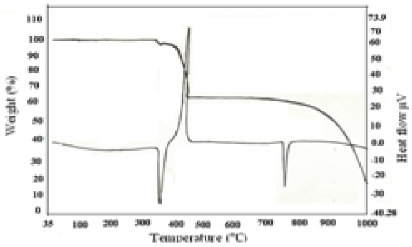

Figure:13 TG/DTA curves of pure sodium chlorate single crystal

TG and DTA thermograms of 0.5 mol% concentration of lithium nitrate doped sodium bromate single crystal are shown in figure . In this case, the initial mass of the sample is 11.656 mg. The value of decomposition temperature is observed as 360 °C. The crystal is stable without weight loss upto 360°C. The stability is increased when compared with the undoped crystal. The TG curve shows gradual mass loss without residue at 950 °C. The DTA curve shows three sharp peaks, two endothermic peaks at 360 °C and 745 °C and one exothermic peak at 430 °C and it corresponds to liberation of gaseous products and combustion of lithium ions. No weight loss is observed in TG above 980 °C which indicates the completion of decomposition process.

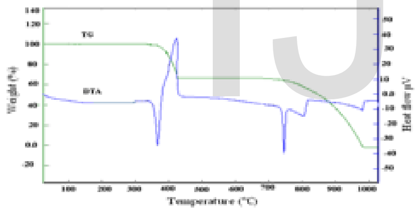

Figure:14 TG/DTA curves of lithium nitrate doped sodium bromate crystal

4.6 Nonlinear Optical (NLO) activity

NLO activity of the grown pure and doped sodium bromate crystals was checked by carrying out the second harmonic generation (SHG) studies. These crystals emit visible radiation and will have numerous device applications and frequency doubling [13,14]. The first known technique for confirming the SHG property is the Kurtz powder technique [15]. It is used to identify the non-centrosymmetric crystal structures. The SHG efficiency was determined for the pure and lithium nitrate doped sodium bromate single crystals using a Q-switched high energy Nd: YAG laser (QUANTA RAY). The Nd: YAG laser was used to generate about 0.68 mJ/pulse at 1064 nm fundamental radiation. The crystalline samples were ground into fine powder and packed into micro capillary tubes and mounted in the path of laser pulses. The second harmonic generation was confirmed by the emission of green light of wavelength 532 nm from the samples. The second harmonic generation efficiency obtained for the samples are given in table. It is noticed that lithium nitrate doped sodium bromate samples have high efficiency when compared to undoped crystal.

Table:4 SHG efficiency of pure and doped sodium bromate crystals

Sample	SHG output mJ	Efficiency
Pure sodium bromate	11.6	1
0.5 mol% of lithium nitrate doped sodium bromate	13.6	1.1724

4.7 Linear Optical studies

Linear optical studies for the samples were performed by recording UV-Vis-NIR transmission spectra using a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer in the range 190 nm to 1100 nm.

The UV-Vis-NIR transmission spectrum of pure sodium bromate is shown in figure. It is observed that it has good transmittance in the entire visible and near infrared regions. The transmittance value is found to be 99.5%. The UV cut-off wave length of pure sodium bromate crystal is found to be 278 nm. The band gap was calculated to be 4.468 eV.

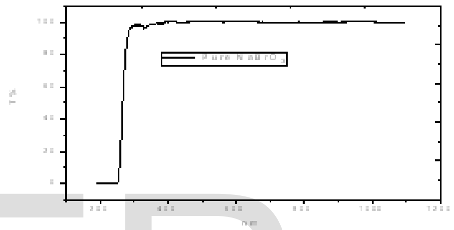

Figure:15 Transmittance spectrum of pure sodium bromate crystal

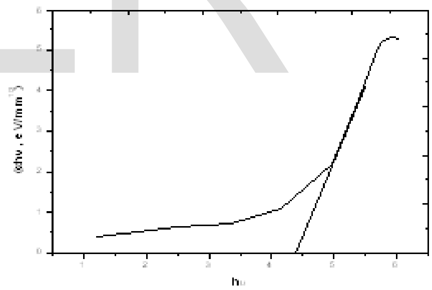

Figure: 16 Plot of hυ versus $(\alpha h\upsilon)^{1/2}$ of pure sodium bromate single crystal.

The optical absorption coefficient (α) was calculated from the transmittance curve using the relation $\alpha = 2.303(1/d) \log (1/T)$ where T is the transmittance and d is the thickness of the crystal. The plot of variation of $(\alpha h\upsilon)^{1/2}$ versus hυ of pure sodium bromate crystal is shown in figure. The band gap is indirect band gap and by extrapolation the linear part the value of band gap is found to be 4.46 eV. Since the crystal posses wide band gap it has large transmittance in the visible region.

The UV-Vis-NIR transmission spectra of pure and 0.5mol% of lithium nitrate doped sodium bromate samples are shown in figure. From the spectrum it is observed that it has good transparency and the transmittance value is found to be 99%. The cut off wavelength is observed at 330 nm and the excellent transmittance with no absorption takes place in the region 500 nm to 1100 nm. The transmittance is good in the entire visible and near infrared regions. The plot of variation of hυ versus $(\alpha h\upsilon)^{1/2}$ is shown in figure 4.54. It forms a straight line and can be observed as indirect band gap by extrapolating the straight line to α=0 axis and the optical band gap value is found to be 3.7 eV.

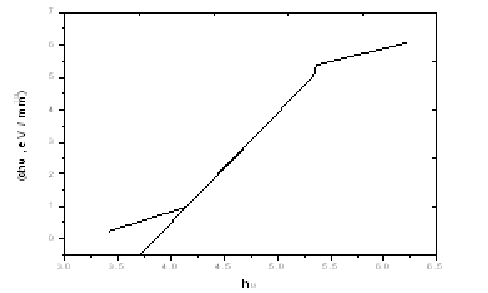

Figure:17 Plot of hυ versus $(\alpha h\upsilon)^{1/2}$ of lithium nitrate doped sodium bromate single crystal

4.8 Dielectric Properties

The dielectric properties such as dielectric constant, dielectric loss and electrical conductivity are the basic electrical properties of insulating solids. The capacitance and dielectric loss factor (tan δ) measurements were carried out for the pure and lithium nitrate doped sodium bromate single crystals using the parallel plate capacitor method at various temperatures ranging from 30 ^{o}C-100 ^{o}C. From the data, the dielectric constant, AC conductivity and activation energy were calculated. The obtained data of dielectric constant for pure and doped sodium bromate crystals are given in tables and the values are plotted with various frequencies and temperatures. The dielectric studies give useful information about structural change, defect behavior and transport phenomena of doped and mixed crystals. For all the samples, the value of dielectric constant increases with increase of temperature and the value of dielectric constant decreases with increase of frequency. The dielectric constant is due to the contribution of electronic, ionic, dipolar and space charge polarizations, which depend on frequencies. Higher space charge polarizability was found in the low frequency region. At low frequencies and high temperatures the space charge polarization is active. The magnitude of dielectric constant depends on degree polarization and the charge displacement in the crystal. The decrease in dielectric constant at higher frequencies is attributed to the absence of charge of polarization near the grain boundary [16]. From figures it is observed that the dielectric constant decreases with increase of frequency for pure sodium bromate single crystal. It is noticed that while adding dopant lithium nitrate to the sodium bromate crystal, the dielectric constant values are found to be lower than the component crystal.

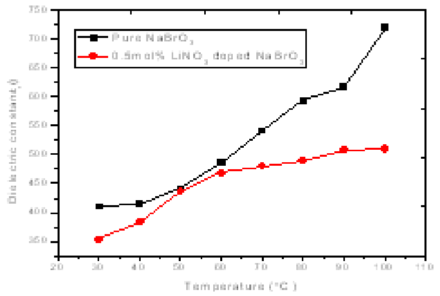

Figure:18Variation of dielectric constant with temperature at 1 kHz for pure and lithium nitrate doped sodium bromate crystals

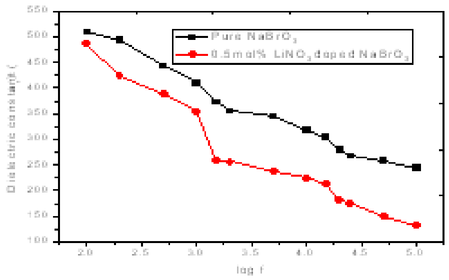

Figure:19 Variation of dielectric constant with various frequencies at 30 ^{o}C for pure and lithium nitrate doped sodium bromate crystals

Low dielectric loss materials are required for applications in radio frequency and microwave communications [17]. The values of dielectric loss obtained for the pure and lithium nitrate doped sodium bromate single crystals for various frequencies from100 Hz to 100 kHz at various temperatures are provided in table. The variations of dielectric loss with temperatures and frequencies are shown in figures. From figures it is observed that the dielectric loss decreases with increase of frequency. Also, it is noticed that the dielectric loss increases with increase of temperature. When the sodium bromate crystals are doped with dopants like lithium nitrate separately, it is found that the dielectric loss decreases and it is concluded that these crystals have better dielectric quality.

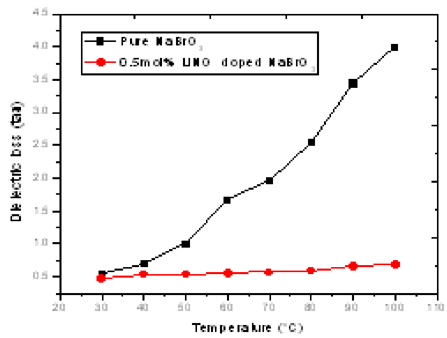

Figure:20 Temperature dependence of dielectric loss at 1 kHz for pure and lithium nitrate doped sodium bromate crystals

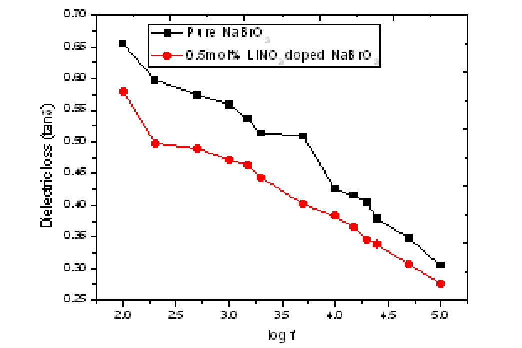

Figure:21 Frequency dependence of dielectric loss at 30°C for pure and lithium nitrate doped sodium bromate crystals

4.9 Conductivity and Activation Energy

AC electrical conductivity values were calculated for pure and lithium nitrate doped sodium bromate single crystals at different temperatures and frequencies. The variations of electrical conductivity with frequencies and temperatures for pure and doped sodium bromate single crystals are shown in figures. The AC conductivity is found to increase with increase of frequency for pure and a doped crystals. The AC conductivity is directly proportional to dielectric constant and dielectric loss and same behavior is noticed in AC conductivity for different kinds of polarizations namely space charge, electronic and ionic polarizations. When the temperature is increased the ionic distance will be increased and hence there is an increase of polarization so the conductivity increases for increase of frequency and temperature. The AC electrical conductivity values 'σ_{ac}' is given by the equation

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

Where 'E_{ac}' is the activation energy, K_B is the Boltzmann's constant, 'T' is the absolute temperature and 'σ_o' is a constant depending upon the material. The activation energy for the pure and lithium nitrate doped sodium bromate single crystal were calculated from the slope of the plots of $\ln\sigma_{ac}$ against 1/T shown in figures. The calculated values of the activation energy (E_{ac}) are tabulated in table. From the table it is observed that activation energy decreases for impurity added in the lattice of sodium bromate crystal. Since charged carriers are more in the doped crystals, the activation energy is less and conductivity is more [18].

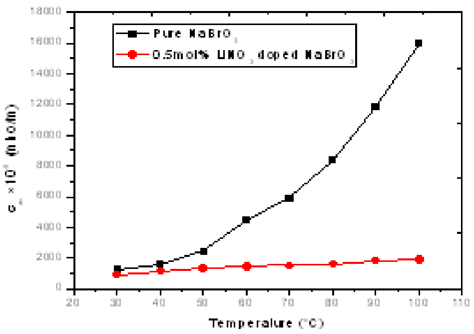

Figure:22 Variation of AC electrical conductivity with temperature at 1 kHz for pure and lithium nitrate doped sodium bromate crystals

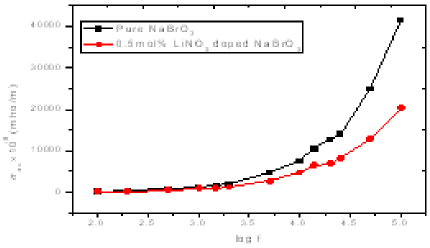

Figure:23 Variation of AC electrical conductivity with frequency at 30°C for pure and lithium nitrate doped sodium bromate crystals

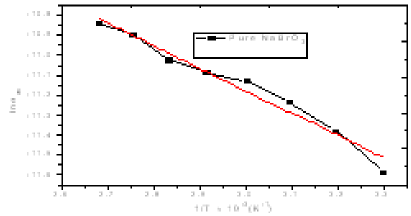

Figure:24 A plot of ln σ_{ac} versus 1/T for pure sodium bromate single crystal

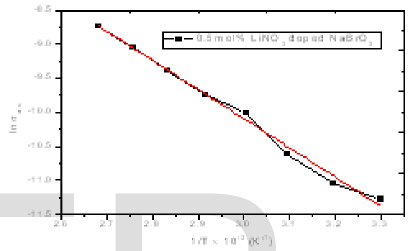

Figure:25 A plot of lnσ_{ac} versus 1/T for lithium nitrate doped sodium bromate single crystal

5 Conclusions

Sodium bromate NLO materials and they can be used as second harmonic generators of laser light. In the present investigation, the isomorphous crystals such as pure sodium bromate were grown. The solubility of pure and doped salts in double distilled water was determined.

The mechanical strength of the grown crystals of this work was studied by subjecting the crystals to microhardness measurements.The FTIR transmission spectra have been recorded in the range of 400-4000 cm^{-1} for all the grown crystals. The UV-Vis-NIR transmission spectra were recorded in the range 190–1100 nm for pure, mixed and doped crystals and from the results it is observed that the crystals were found to be transparent in the entire visible and near IR region. Pure sodium bromate crystal has a wide transmission with a transparency of 85%. The transparency was increased for lithium nitrate doped sodium bromate crystal with transparency 90%, respectively. The SHG efficiency of lithium nitrate doped sodium bromate crystals was found to be increased. The micrographs of pure and 0.5 mol% of lithium nitrate doped sodium bromate single crystals were presented and it is observed that surface of the crystals is smooth and clear Electrical properties were studied by dielectric measurements.

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