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Growth and physicochemical properties of pure and urea doped sodium pentaborate dihydrate single crystals

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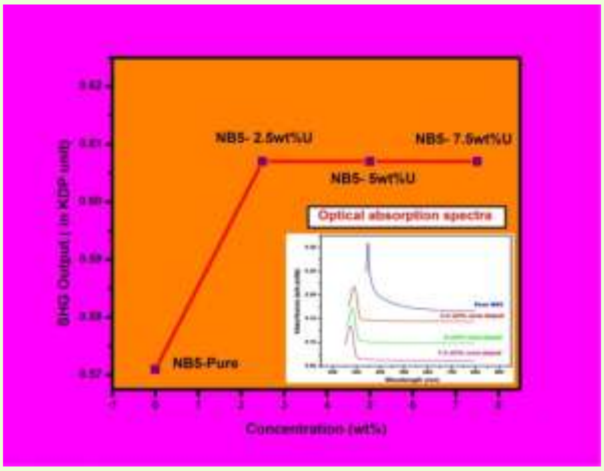
Abstract : Pure and urea doped sodium pentaborate dihydrate (NB5) single crystals were grown by the slow evaporation of solvent technique and characterized. The grown crystals (pure + 3 urea doped) were characterized structurally and chemically by carrying out X-ray diffraction (both single crystal and powder) and Fourier transform infrared and energy dispersive X-ray absorption spectral measurements. UV-Vis spectral and second harmonic generation (SHG) efficiency measurements were carried out to characterize the grown crystals optically. The electrical characterization was carried out by AC electrical measurements by the parallel plate capacitor method at various temperatures in the range 30 - 90 ^{o}C with different frequencies in the range 100 Hz - 1 MHz. Results obtained in the present study indicate that all the grown crystals belong to the monoclinic crystal system and exhibit a normal dielectric behavior. Moreover, urea doping is found to enhance the optical transmittance, window wavelength region and SHG efficiency of NB5 crystal.

Keywords : single crystals, doped crystals, crystal growth, optical properties, electrical properties.

Graphical abstract



1 Introduction

Research on borate crystals has been conducted for the past few decades and it remains strong to this date due to the commercial applications of these materials as laser hosts, non-linear optical elements and in UV optics [1-4]. There are several natural and synthetic borates used in different branches of industry. The borate crystal lattice is defined by the rigid polymer boron-oxygen skeleton that gives a series of unique properties and specific features to borate [5]. Sodium pentaborate dihydrate (NB5), $NaH_4B_5O_{10}.2H_2O$, is one such useful crystal in the borate family.

NB5 crystal belongs to the monoclinic crystal system with space group $P2_1/c$ and lattice parameters: a = 11.103, b = 16.437 and c = 13.564 Å and β = 112.85 ^{o} [6]. Forming hybrid materials is very much necessary for many emerging technologies. Certain impurity addition (doping), without any significant lattice distortion, is expected to tune significantly the physical properties of the un-doped crystal but depending on the impurity concentration.

Urea is a small molecular organic substance used in many practical applications. Doping with urea has been found to tune significantly the optical and electrical properties of certain important and useful crystals [7–11]. NB5 is a hydrogen bonded crystal, and if doped with urea the hydrogen bonding network is expected to get modified significantly. Consequently, doping with urea is expected to modify significantly the optical and electrical properties of NB5.

So, in the present study, pure and urea added (in 3 different concentrations, viz. 2.5, 5.0 and 7.5 wt%) NB5 single crystals were grown and characterized chemically, structurally, optically and electrically in order to understand the effect of urea doping on the structural, optical and dielectric properties of NB5 crystal. The details are reported herein.

2 Experimental details

2.1 Crystal growth

Analytical reagent (AR) grade sodium carbonate, boric acid and urea were used as the precursors for the preparation of single crystals. De-ionized water was used as the solvent.

Sodium carbonate and boric acid, as required, were dissolved in de-ionized water at room temperature (32 ^oC) and stirred with a magnetic stirrer for 6 h continuously. The above solution was filtered by using a Whatman filter paper and taken in a beaker covered with porous paper. The above beaker with solution was kept in a dust free atmosphere for the product to form as crystals, due to free evaporation of solvent, according to the chemical reaction:

$$Na_2CO_3 + 10\ H_3BO_3 \rightarrow 2[NaH_4B_5O_{10}.2H_2O] + 9H_2O + CO_2 \uparrow$$

Good quality (without any crack or visible unwanted defect), transparent and colorless NB5 crystals up to a size of 8 x 6 x 5 mm^3 could be harvested in about 54 days.

In order to form the urea added NB5 crystals, the above process was repeated by adding the required amount of urea in the solution. Three different concentrations, viz. 2.5, 5.0 and 7.5 wt% of urea were considered in the present study. Good quality, transparent and colorless urea added NB5 crystals up to a size of 8x8x6 mm^3 could be harvested in about 23 days. It should be noted that urea doping (in the solution used for the crystal growth) leads to growth of considerable size crystals in a short time.

All the four crystals (pure + 3 doped) grown in the present study are found to be quite stable in the normal atmospheric condition and are now represented here as Pure NB5, 2.5 wt% urea doped, 5.0 wt% urea doped and 7.5 wt% urea doped respectively for the pure NB5, 2.5wt% urea added NB5, 5.0 wt% urea added NB5 and 7.5 wt% urea added NB5 crystals. A photograph of the grown crystals is shown in Figure 1.

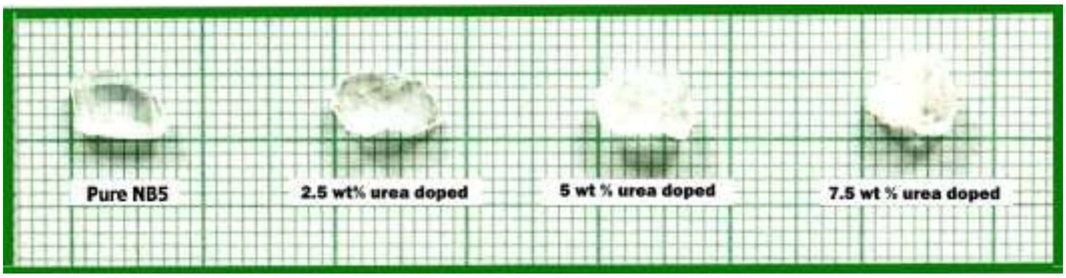


Fig. 1 Photograph of the grown crystals

2.2 Characterization

The lattice parameters were determined by the single crystal X-ray diffraction (SXRD) method using a Bruker Kappa Apex II diffractometer with MoK_α radiation (λ= 0.71073 Å). The crystallinity of the grown crystals was checked by collecting the X-ray powder diffraction (PXRD) data using an automated X-ray powder diffractometer (PANalytical) in the 2θ range 10-80 ^{o} with CuK_α radiation (λ = 1.5406 Å). The observed reflections were also indexed using the *2*θ (Bragg angle) and d (interplanar spacing) values.

Chemical analysis was carried out on the grown crystals by recording Fourier transform infrared (FTIR) spectra at room temperature by the KBr pellet method using a SHIMADZU spectrometer in the wavenumber range 400 – 4000 cm^{-1} and energy dispersive X-ray absorption (EDX) spectra using a scanning electron microscopic system (JEOL JSM-6390).

The optical (UV-Vis) absorption spectra were recorded in the wavelength range 190 – 790 nm using a JASCO UV spectrometer and the forbidden energy gaps (E_g) were determined from the cut-off (absorption edge) wavelengths (λ) using the relation: $E_g = hc/\lambda$, where h is the Planck's constant and c is the speed of light. Kurtz and Perry powder method [12] was adopted to determine the second harmonic generation (SHG) efficiency using a Nd-YAG Quanta ray laser (with fundamental radiation of wavelength 1064 nm). Potassium di-hydrogen phosphate (KDP) was used as the reference and the results were obtained in terms of KDP unit.

The AC electrical (dielectric) measurements were carried out by the parallel plate capacitor method to an accuracy of ±2 % using an LCR meter (HIOKI-3532-50) along the direction perpendicular to the major area surface of the crystal at different temperatures in the range 30–90 ^{o}C with different frequencies in the range 100 Hz – 1 MHz. Crystals with good transparency and large surface defect-free size were selected for the dielectric measurement. The extended portions of the crystal were removed properly and the opposite faces were polished and coated with good quality silver paste to obtain a good conductive surface layer. The dimensions of the crystals were measured using a traveling microscope with least count 0.001 cm. The dielectric constant (ε_r) and AC electrical conductivity (σ_{ac}) were determined from the measured capacitance (C) and dielectric loss factor (tan δ) values using the relations:

$$\varepsilon_r = Cd/(\varepsilon_0 A) \qquad (1)$$

$$\sigma_{ac} = \varepsilon_r \varepsilon_0\, \omega \tan\delta \qquad (2)$$

Here, ε_0 is the permittivity of free space, d is the thickness of the crystal, A is the area of the crystal touching the electrode and ω (= 2πf, f is the frequency of the applied electric field) is the angular frequency.

The AC activation energies (E_{ac}) were determined by fitting the AC electrical conductivity data obtained into the Arrhenius relation for electrical conductivity [13- 15]:

$$\sigma_{ac} = \sigma_0 \exp(-E_{ac}/(kT)) \qquad (3)$$

Here, σ_o is the pre-exponential factor (a constant depending on the material having the electrical conductivity unit), k is the Boltzmann constant and T is the absolute temperature.

3 Results and Discussion

3.1 Lattice parameters and chemical nature

The lattice parameters obtained for all the four crystals grown in the present study are given in Table 1. The lattice parameters obtained for Pure NB5 crystal are found to be in close agreement with those reported in the literature for the un-doped NB5 crystal [6]. All the four grown crystals belong to the monoclinic system with space group $P2_1/c$. So, the material of the grown crystals is basically sodium pentaborate dihydrate. The a, b and c values (individual lattice edges) slightly change but the lattice volume does not change significantly due to urea addition which indicates that the urea molecules have entered into the NB5 crystal matrix but the urea addition (doping) does not distort the crystal structure of NB5 significantly.

Table 1 Lattice parameters obtained for the pure and urea doped NB5 crystals

Crystal	**a (Å)**	**b (Å)**	**c (Å)**	**α=γ =90°**	**V (Å^3)**
Pure NB5	11.114(4)	16.437(3)	13.580(2)	□□□□=111.94°	2299.70(6)
2.5 wt % urea doped	11.121(4)	16.447(4)	13.563(2)	□=111.99°	2299.93(6)
5.0 wt % urea doped	11.105(4)	16.451(3)	13.569(2)	□=112.04°	2298.11(6)
7.5 wt % urea doped	11.11(4)	16.45(2)	13.56(4)	□=112.03°	2298.61(4)

The PXRD patterns obtained in the present study are shown in Figure 2. Strong and sharp peaks observed in the PXRD patterns indicate that the grown crystals exhibit good crystallinity. Small changes in relative intensities and d values observed due to urea doping can be attributed to the presence of urea molecules in the host NB5 crystal matrix.

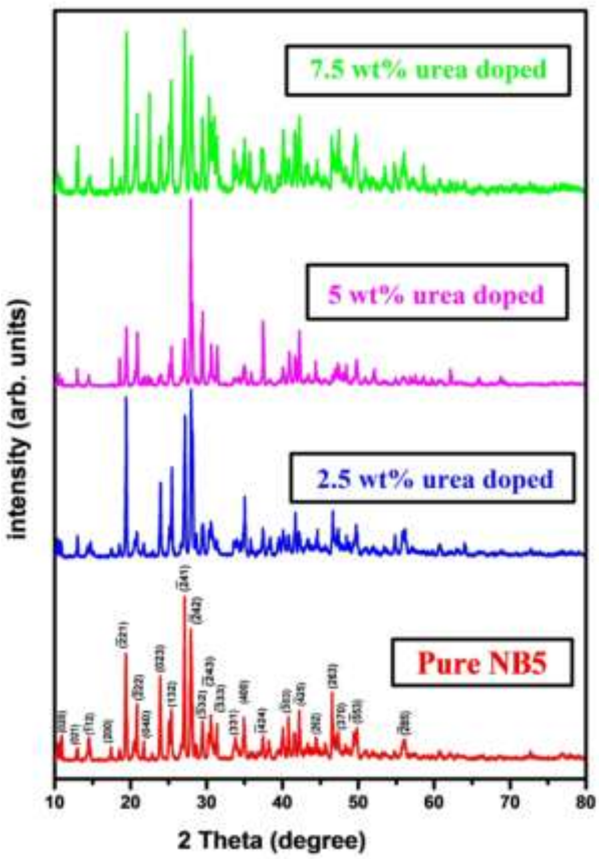


Fig. 2 PXRD patterns observed for the pure and urea doped NB5 crystals

The FTIR spectra observed in the present study are shown in Figure 3. The spectrum observed for Pure NB5 crystal is found to be in close agreement with that reported in the literature for the un-doped NB5 crystal [6]. The spectra observed in the present study for pure and urea doped crystals indicate that the material of the grown crystals is basically sodium pentaborate dihydrate. The peaks observed only for the urea added NB5 crystals at around 3322, 1662 and 1457 cm^{-1} can be assigned respectively to N-H asymmetric stretching, C=O stretching and N-C-N asymmetric stretching vibrations [16]. Thus, the FTIR spectral analysis also indicates the incorporation of urea (dopant) molecules into the NB5 crystal matrix.

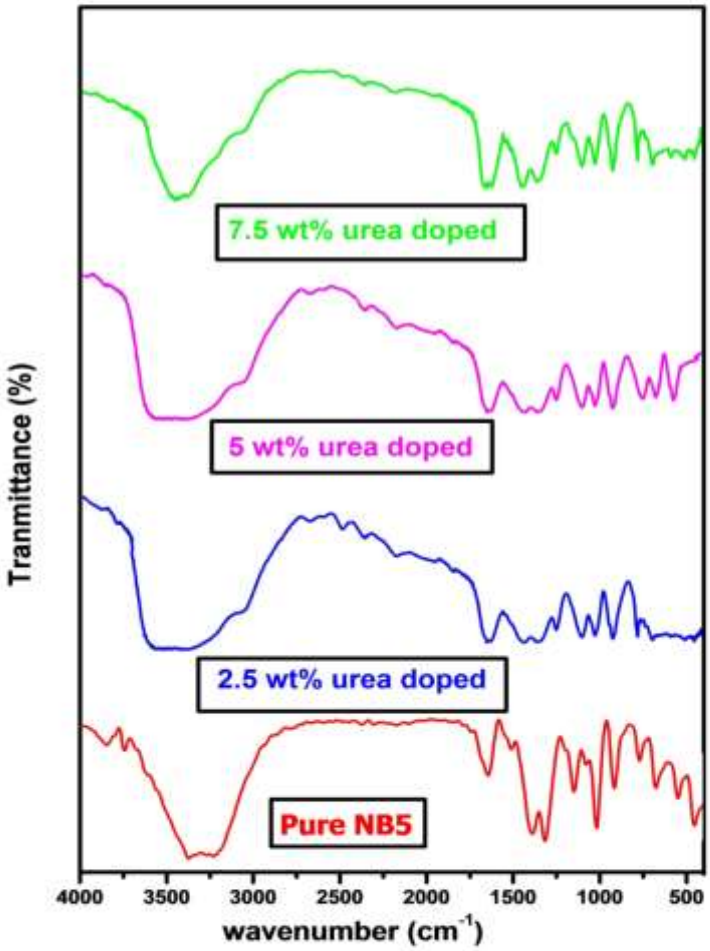


Fig. 3 FTIR spectra observed for the pure and urea doped NB5 crystals

Figure 4 shows the EDX spectra recorded in the present study. The EDX spectral analysis has verified the presence of Na, B and O atoms in all the four grown crystals. Also, observation of less intense peaks due to C and N atoms has confirmed the incorporation of urea molecules into the NB5 crystal matrix in the case of urea doped crystals.

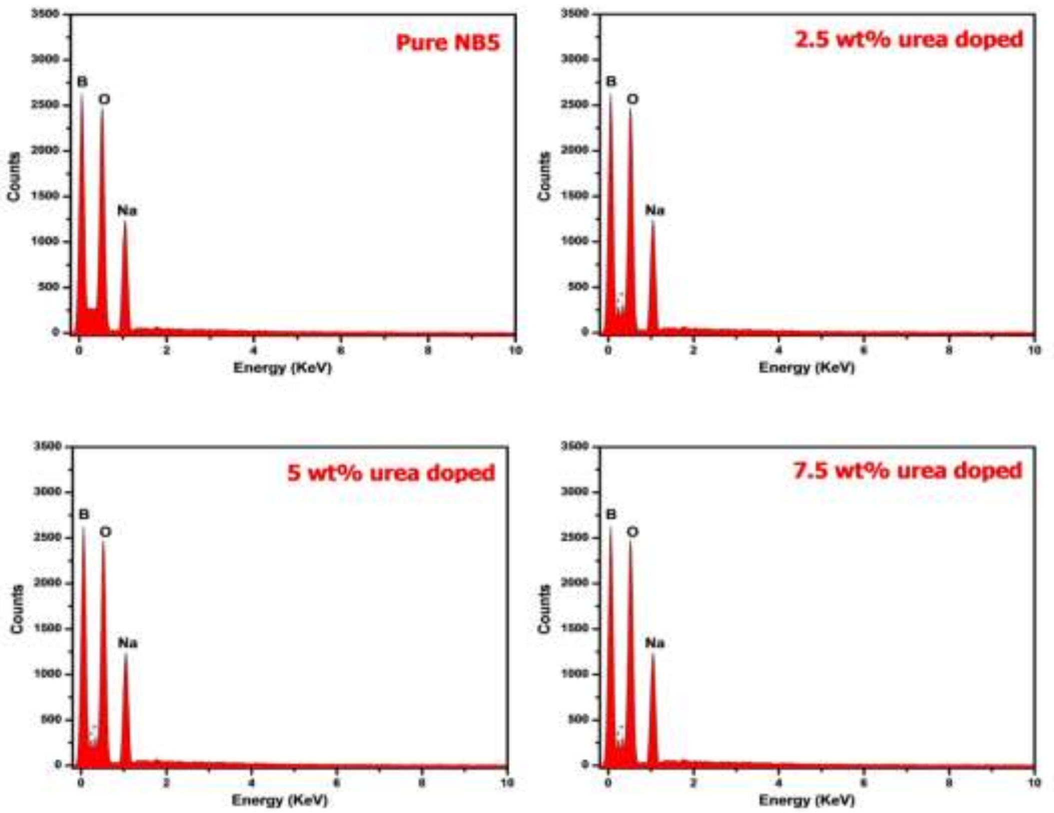


Fig. 4 EDX spectra observed for the pure and urea doped NB5 crystals

3.2 Optical properties

The UV-Vis absorption spectra recorded in the present study are shown in Figure 5. The optical absorption edge (cut-off) wavelengths and forbidden energy gaps observed are provided in Table 2. It is interesting to note that urea doping has reduced the optical absorption and cut-off wavelength significantly. This indicates that the optical transmittance and forbidden energy gap are increased due to urea doping. Moreover, this increase is in correspondence with the increase in concentration of urea doping.

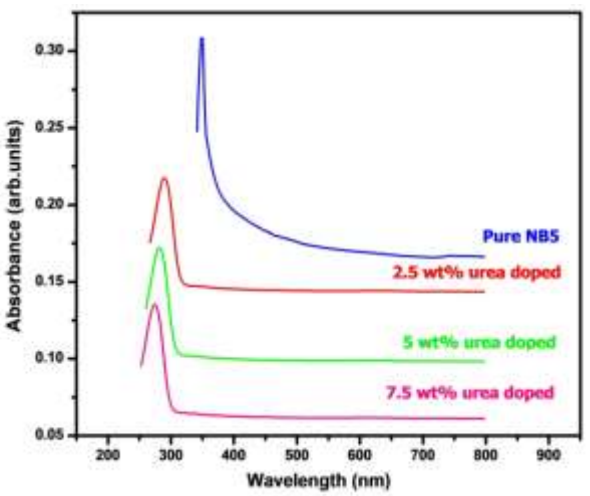


Fig. 5 Optical absorption spectra for the pure and urea doped NB5 crystals

In addition, the low value of absorbance in the entire visible range (large window wavelength range) shows the high optical transmission ability of the grown crystals. This result indicates that the crystals considered in the present study are expected to be useful for optoelectronic and SHG applications.

Table 2 Cut-off wavelengths, forbidden energy gaps and SHG efficiencies for the pure and urea doped NB5 crystals

Crystal	**Cut-off wavelength (nm)**	**Forbidden energy gap (eV)**	**SHG efficiency (KDP unit)**
Pure NB5	336	3.69	0.571
2.5 wt% urea doped	305	4.072	0.607
5.0 wt% urea doped	305	4.072	0.607
7.5 wt% urea doped	297	4.18	0.607

The SHG efficiencies observed in the present study are given in Table 2. It can be noted that the SHG efficiency also increases, though in a small quantity, in correspondence with the amount of urea doping. Thus, the results obtained in the present study indicates that the urea doping leads to significant improvement in the optical properties (optical transmittance, window wavelength range and SHG efficiency) of NB5 crystals and making them more useful in photonic devices than the pure NB5 crystal.

3.3 Electrical properties

The AC electrical (dielectric) parameters, viz. dielectric constants (ε_r) and dielectric loss factors (tanδ) observed in the present study are shown in Figure 6.

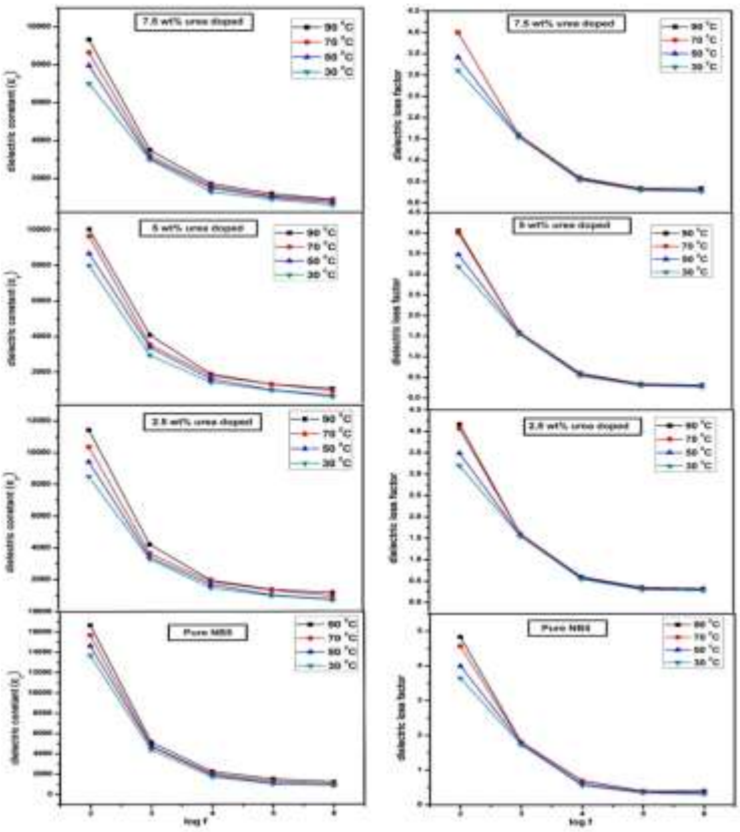


Fig. 6 Dielectric constants and dielectric loss factors observed for the pure and urea doped NB5 crystals

The ε_r and tanδ values are found to decrease with the increase in frequency and increase with the increase in temperature. The AC electrical conductivities (σ_{ac}) obtained in the present study are shown in Figure 7. The σ_{ac} values are found to increase with the increase in frequency as well as temperature. This is considered to be a normal dielectric behavior.

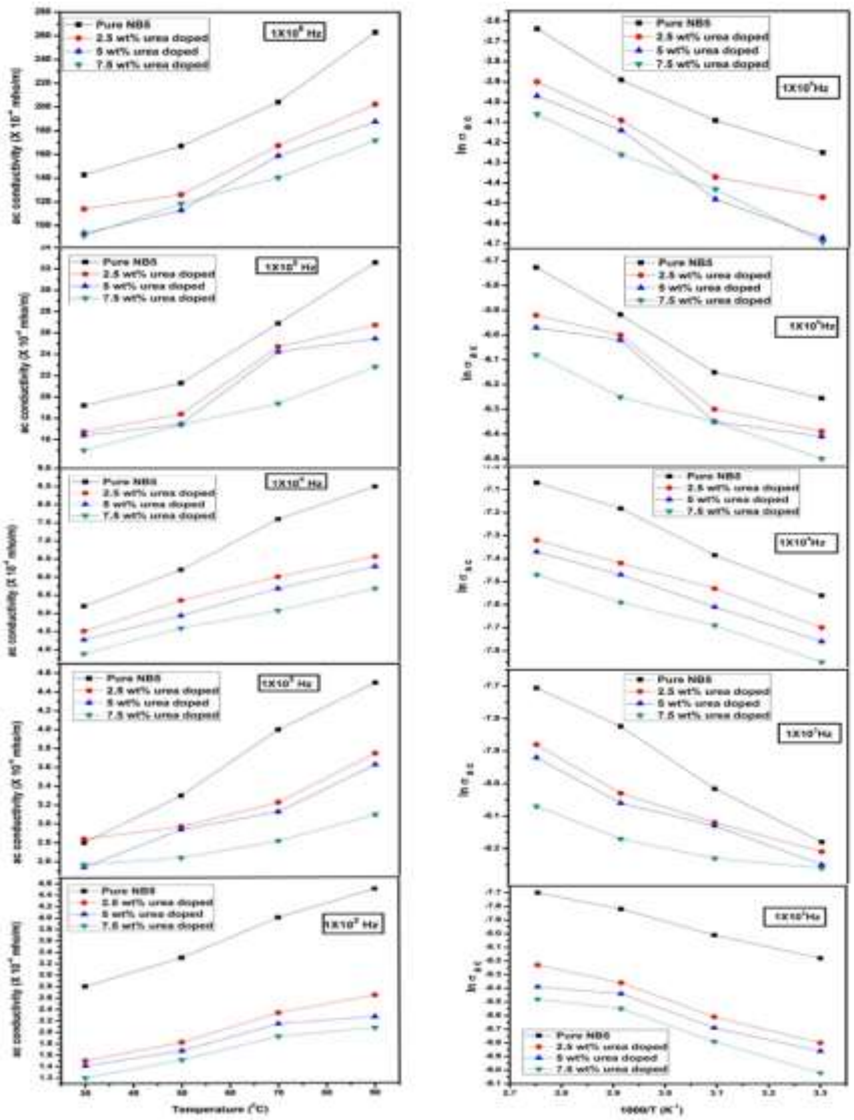


Fig. 7 AC electrical conductivities (σ_{ac}) and plots between ln σ_{ac} and 1000/T for the pure and urea doped NB5 crystals

The gradual and continuous decrease of ε_r as well as tanδ with the increase of frequency suggests that the pure and urea doped NB5 crystals considered, like any normal dielectric, may have domains of different sizes and varying relaxation times. The very high value of ϵ_r at low frequencies may be due to the presence of all the four polarizations, viz. space charge, orientation, electronic and ionic polarizations and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually [17]. At low frequencies, dipoles easily respond and align with the applied alternating electric field but as frequency increases dipoles cannot cope up with the pace of fast changing electric field and therefore dielectric constant decreases and become saturated at further higher frequencies [18]. The results obtained in the present study suggest that the dielectric constant and dielectric loss factor values are high at low frequencies and they decrease with increase in frequency and attain almost constant value beyond 10^5 Hz. Moreover, the dielectric parameters observed for the pure NB5 crystal in the present study are comparable to those reported for the un-doped NB5 crystal in the literature [6].

The plots between ln σ_{ac} and 1000/T (shown in Figure 7) are found to be nearly linear (slight deviation can be seen in few cases) which indicates that the AC electrical conductivity data obtained in the present study can be fitted into the Arrhenius relation (Eqn.3). The AC activation energies estimated in the present study are shown in Figure 8**.** The E_{ac} value is not found to vary systematically with frequency as well as with concentration of urea doping.

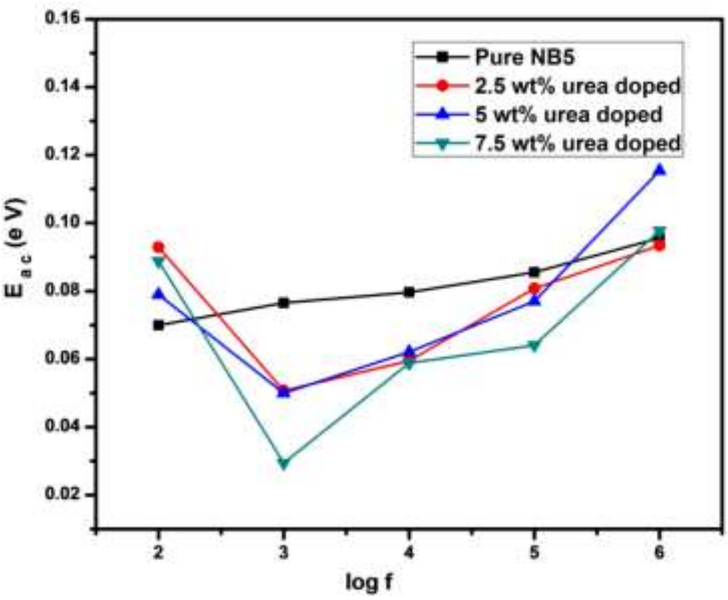


Fig. 8 AC activation energies (E_{ac}) for the pure and urea doped NB5 crystals

It can be noted that the urea doping leads to reduction of dielectric parameters. The NB5 crystals contain water molecules and are hydrogen bonded. In the case of urea added NB5 crystals, the urea molecules mainly occupy the interstitial sites which is expected to disturb the hydrogen bonding system in the host NB5 crystal matrix may be at random. The electrical conduction in NB5 crystals may be determined by the proton transport within the framework of hydrogen bonds as explained in the case of KDP (KH_2PO_4) and ADP ($NH_4H_2PO_4$) crystals [13]. The low activation energies observed indicate the presence of oxygen vacancies which is a dominating factor for the electrical conduction in pure and urea doped NB5 crystals grown in the present study. Thus, the results obtained indicate that the electrical properties of NB5 crystal could be tuned significantly by urea addition.

4 Conclusion

Optically transparent and colorless pure and urea added NB5 single crystals with good quality, considerable size and good crystallinity could be grown successfully at room temperature (32 °C) by the slow evaporation of solvent method. All the four crystals (pure + 3 urea added) grown belong to the monoclinic crystal system with space group $P2_1/c$. SXRD, PXRD, FTIR spectral and EDX spectral analyses indicate that the material of the grown crystals is found to be basically sodium pentaborate dihydrate and, in the case of urea doped NB5 crystals, the urea molecules have entered into the host NB5 crystal matrix. Results obtained through optical absorption and SHG efficiency measurements indicate that the urea addition leads to significant improvement in the optical properties (optical transmittance, window wavelength range and SHG efficiency) of NB5 single crystals and making them more useful in photonic devices than the pure NB5 crystal. Results obtained through dielectric measurements indicate that the AC electrical conductivity could be explained as due to the proton transport and the electrical properties of NB5 crystal could be tuned significantly by urea addition. The present study, in effect, indicates that urea addition significantly tunes the optical and electrical properties of NB5 crystal without distorting the crystal structure.

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