Investigation on the growth, structural, nonlinear optical, electric and dielectric properties of L-tartaric acid-nicotinamide single crystal

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ABSTRACT

An organic nonlinear optical single crystal of L-tartaric acid-nicotinamide (LTN) has been grown by slow evaporation of the saturated solution at constant temperature of 45 ^{0}C. The grown crystal is subjected to single crystal X-ray diffraction analysis to identify the space group and unit cell parameters. The crystalline quality of LTN has been investigated by high-resolution X-ray diffractometry (HRXRD). The powder SHG study demonstrates the phase matching characteristics of the materials. The laser induced damage threshold data indicate the moderate quality of the developed sample to with stand laser radiation. The dielectric response of the sample is studied as a function of frequency and temperature. The ac conductivity properties of the sample are also reported.

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INTRODUCTION

The search and design of highly efficient non-linear optical (NLO) crystals for visible and ultraviolet (UV) region are extremely important for laser processing. High-quality organic NLO crystals must possess sufficient large NLO coefficient, transparency in UV region, high laser damage threshold power and easy growth with large dimension [1]. Organic materials attract much interest to physicists, chemists and material scientist because of their superior performance such as large NLO coefficient, and ultra-fast nonlinear response than their inorganic counterparts.

In this connection, the study of the molecular packing and hydrogen bonding in L-tartaric acid and its derivatives is relevant to the development of approaches in crystal engineering, especially, related to the field of nonlinear optics [2]. The history of tartaric acid has long been associated with the most important discovery in the field of stereochemistry. It is a naturally occurring dicarboxylic acid. Its industrial applications are broad and include pharmaceutical and

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dental materials, ceramics, paints, electrochemical coating and piezoelectronics devices [3]. Salts of tartaric acid with amines, amides and amino acids are long been studied for their structural, spectroscopic properties and NLO activities [2]. In complexes of organic bases with L-tartaric acid, one or two protons can be transferred from the carboxylic groups of tartaric acid to form the monovalent (semi-tartrate) or divalent (tartrate) anions, respectively [2]. In these systems, by linking the organic molecules through hydrogen bonds, we can obtain systems with NLO and strong mechanical property. Typical representatives for such systems are; L-tartaric acid-nicotinamide, D-tartaric acid nicotinamide, urea-(d)tartaric acid (UDT), L-lysine-L-tartaric acid, L-histidinium-L-tartrate hemihydrates, 2-amino-5-nitropyridinium monohydrogen L-tartrate, P-nitroaniline-L-tartaric acid and 2,4,6-triamino-1,3,5-triazin-1,3-ium tartrate monohrdrate [1-5].
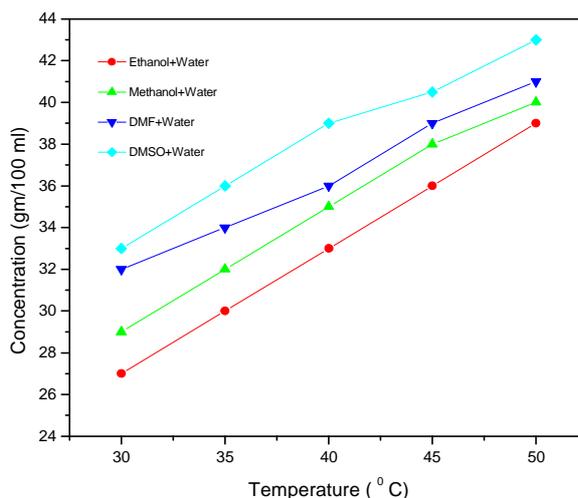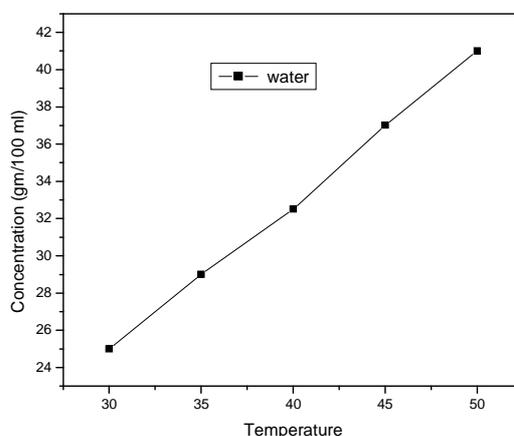
Organic adduct of L-tartaric acid-nicotinamide (LTN) (2HOOC HC(OH)HC(OH)COO$^-$-2C$_5$H$_4$NH$^+$CONH$_2$.H$_2$O) is a novel NLO crystal material, with molecular formula C$_{20}$H$_{26}$N$_4$O$_{15}$. The crystal structure of LTN is built from organic-organic complexes in which the high optical nonlinearity of organic adduct is very advantageous compared with inorganic compounds [1]. The transmission range (280-1900 nm) and intense SHG signals from the crystal being better than KDP have been reported [6]. Shen et al have made a systematic investigation on the growth of LTN crystal by slow cooling technique [1]. The crystal structure was solved and the result indicated that LTN crystallizes in the monoclinic system in the space group P2$_1$ [1]. The unit cell is composed of four L-tartaric acid, four nicontinamide and two water molecules. Haja Hameed and Lan have studied the nucleation kinetics of LTN crystal [6].

The aim of the present work is to make a systematic investigation to grow bulk size single crystal of L-tartaric nicotinamide by slow solvent evaporation method and study its physicochemical properties. In order to improve the growth kinetics, solubility studies have been carried out in different solvents. The structural property of the grown crystal was investigated by single crystal XRD and High resolution X-ray diffractometry (HRXRD). To the best of our knowledge, the phase matching, laser damage threshold measurement and *ac* conductivity studies are reported for the first time.

MATERIALS AND METHODS

2.1 Determination of solubility

AR grade (Merck) L-tartaric acid (purity 99.9 %) and nicotinamide (purity 99.9 %) were bought commercially and used as purchased. A systematic study was under taken to determine the solubility of LTN salt in different solvents including deionized water, pure polar organic and inorganic solvents like methanol, ethanol, mixture of N, N-dimethyl formamide (DMF), DMSO and water, mixture of ethanol and water. Though the solubility (Fig. 1a) of L-tartaric acid nicotinamide salt is reasonably good, the solutions prepared with alcohols, DMF, DMSO and their mixtures with water have yielded very small size crystals which are predominantly in needle form with visible inclusions. The solubility study confirmed that the deionized water is the best solvent for crystallizing good quality single crystals. The solubility of L-tartaric acid nicotinamide in water at different temperatures (30, 35, 40, 45 and 50 ºC) is shown in Fig. 1b. L-tartaric acid nicotinamide has a positive solubility coefficient in water solvent since its solubility increases with the temperature.

Fig. 1a Solubility curve of LTN with different solvents

Fig. 1b. Solubility curve of LTN with water

2.2 Growth of LTN crystal

L-tartaric acid nicotinamide was synthesized by dissolving L-tartaric acid (225 g, 1.5 mol) in deionized water that contained nicotinamide (183 g, 1.5 mol). The prepared solution was stirred magnetically for 2-3 hours and then heated up to 45 °C to form saturated solution. The solution was transferred into a Petri dish and then allowed to dry so as to collect the salt. The synthesized product was further purified by repeated recrystallization (typically 3-4 times) to improve the purity. Based on the solubility data, the obtained salt of L-tartaric acid nicotinamide was dissolved in deionized water to carry out the growth experiment. The saturated solution was prepared at 45 °C, and covered with perforated lid and then it was housed in a constant temperature bath controlled with an accuracy of 0.01 °C. Within a week time crystal seeds with perfect shape and transparency were formed by spontaneous nucleation. Optically clear, defect free crystals with perfect shapes were chosen as the seeds and used for the growth experiment. The seed crystal was tied with nylon thread and then submerged into the supersaturated solution kept in the beaker. The solvent was allowed to evaporate at a constant temperature of 45 °C. After a growth period of 30 days, the crystal was harvested. The photograph of the crystal is shown in Fig. 2.

Fig.2 Photograph of as grown LTN crystal

RESULTS AND DISCUSSION

1.1   Single Crystal XRD

The structure of LTN was solved by the direct method and refined by the full matrix least–squares fit technique employing the SHELXL program. The single crystal XRD data indicates that the sample belongs to monoclinic structure with a space group of $P2_1$. The lattice parameter values are a = 7.655(1) Å; b = 15.491(3) Å; c = 10.507(5) Å and β = 103.00 ˚ (2) are in good agreement with the reported values [1]. The unit cell is composed of four L-tartaric acid, four nicotinamide and two water molecules.

3.2 High resolution X-ray diffraction studies

The crystalline perfection of the grown single crystal was characterized by HRXRD (rocking curve study) by employing a multicrystal X-ray diffractometer developed at NPL, India [7] and description of the apparatus. The rocking or diffraction curve was recorded for the LTN sample by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle. The detector was kept at the same angular position $2\theta_B$ with wide opening for its slit, the so-called ω scan.

Before recording the diffraction curve, in order to remove the non-crystallized solute atoms remaining on the surface of the crystal and to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchants of water and acetone mixture in 1:2 volume ratio. Fig. 3 shows the high-resolution diffraction curve (DC) recorded for LTN specimen using (0 1 0) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer. It is to be noticed that the FWHM is 13 arc s and thus the crystal shows very good crystalline quality. The absence of additional peak indicates that the grown crystal does not contain any internal structural grain boundaries and the FWHM value is close to the theoretical expected value of perfect crystal according to the plane wave dynamical theory of X-ray diffraction [8].
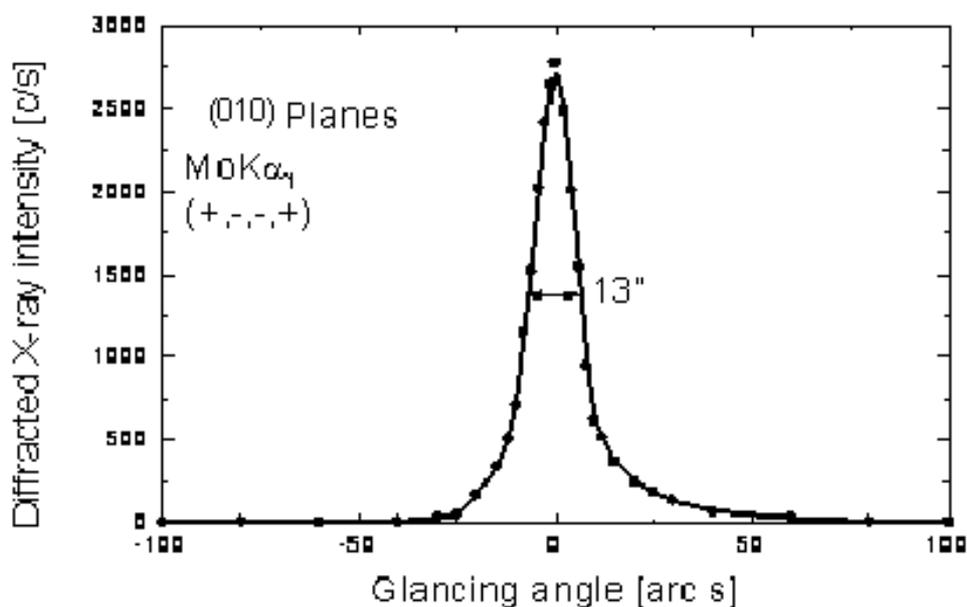
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Fig. 3 High-resolution diffraction curve recorded for LTN single crystal

3.3 Phase matching studies

The Kurtz and Perry powder technique is the most widely accepted technique for confirming the SHG from potentially useful SONLO materials [9]. In addition to identifying the materials with non-centrosymmetric crystal structures, it is also used as a screening technique to identify the materials with the capability for phase matching. The SHG efficiency from the NLO material can be measured as a function of particle size. If the measured output from the sample increases with particle size, then the sample is said to possess phase matching behaviour.

In the present study, the SHG efficiency of the grown crystal was measured by the standard Kurtz and Perry powder technique using a fundamental beam of a Q–switched Nd:YAG laser with a wavelength of 1064 nm. For quantitative work, single crystal of LTN was powdered and then graded by the use of standard sieves to desired range of particle sizes (from 50 to 150 microns). To make relevant comparison with known SHG materials, KDP was also powdered and sieved into the same particle size range. The average particle sizes in the range <53 µ, 53-100 µ, 100-150 µ and >150 µ were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter to ensure uniform packing. The input energy incident on the capillary tube was selected to be 3.2 mJ, an energy level optimized not to cause any chemical decomposition of the sample. The SHG radiations (i.e.) 532 nm green light was emitted and collected by a photomultiplier tube (PMT-Philips Photonics-model 8563) after being monochromated (monochromator-model Triax-550) to collect only the 532 nm radiation. The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052B). The SHG output in each case was measured as the average of a few pulses to eliminate slight variations of input power. In the present work, the dependence of second harmonic intensity on the average particle size was measured and discussed. The plot of SHG output with average particle size for LTN is shown in Fig. 4. It reveals that approximately a linear increase in the second harmonic intensity with increasing particle size. This behaviour is due to the existence of a phase matching direction in LTN sample. For large particle sizes (particle size more than average coherence length), above 150 microns, the second harmonic intensity is essentially independent of particle size [10]. Thus, the striking difference in particle size dependence enables one to distinguish phase-matchable materials on the basis of second-harmonic measurements in powders and the present measurements confirm that the crystals of

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LTN have excellent phase matching properties. Similar behaviour was observed in LAFB [11] and EDMP crystals [12].
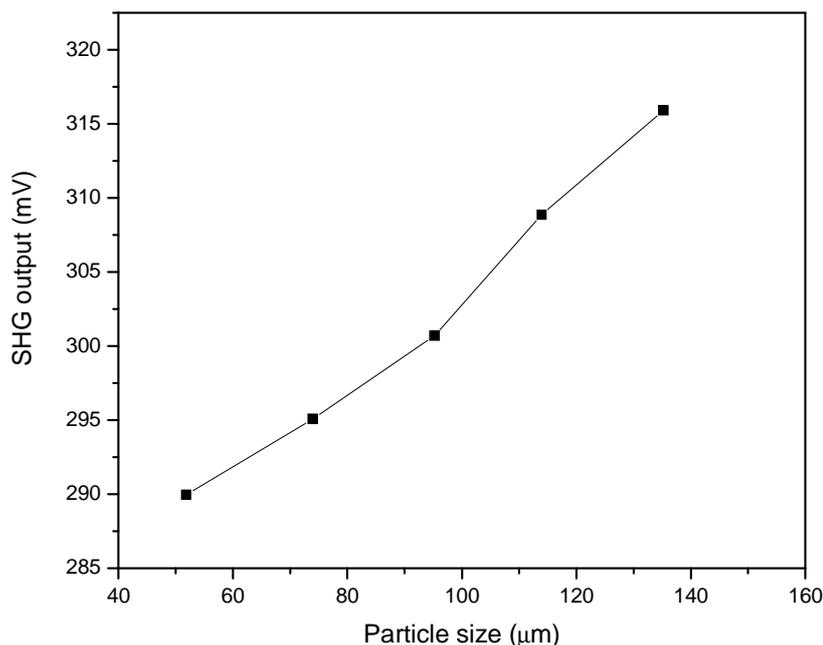

Fig. 4 Phase matching curve of LTN crystal

3.4 Laser damage threshold measurement

The laser damage threshold of the LTN crystal was measured using a Q-switched Nd:YAG laser which generates pulses at 1064 nm fundamental radiation. The grown crystal was cut and polished into a rectangular slab of area   4 x 5 mm^2 and then the laser damage threshold was measured. The laser beam of 1 Hz with pulse duration of 25 ps was focused by a lens on to the surface of the crystal. The damage was observed and the energy of the laser beam was measured by the power meter. The laser damage threshold value is calculated from the laser energy divided by focused area. The laser damage threshold of LTN crystal is found to be 6.9 GW/cm^2 at 1064 nm. Interestingly, the laser induced surface damage threshold study of LTN crystal indicates that the material possesses much higher laser damage threshold than the already commercially available NLO amino acid crystals of L-Prolinium tartrate (5.9 GW/cm^2) and L-Arginine phosphate (10.0 GW/cm^2) as well as crystals like L-Alaninium maleate (4.9 GW/cm^2) and L-Tartaric acid (5.4 GW/cm^2) [13].

3.5 Dielectric study

The dielectric study was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. Samples of known dimension were silver coated on the opposite faces and then placed between the two copper electrodes to form the parallel plate capacitor. Fig. 5 and 6 shows the variations of dielectric constant and the dielectric loss of LTN crystal. The dielectric measurements were carried out as a function of frequency at different temperatures (308 K, 328 K, 348 K and 368 K). It is evident from the plots that in both the samples the dielectric constant increases with temperature. The very high value of ε_r at lower frequencies may be due to the space charge polarization. It is further understood from Fig. 5 and 6 that the crystals have a reduced dielectric loss in the high frequency region, which indicates the lesser number of defects in the crystal and this parameter is of vital important for various nonlinear optical materials and their applications.
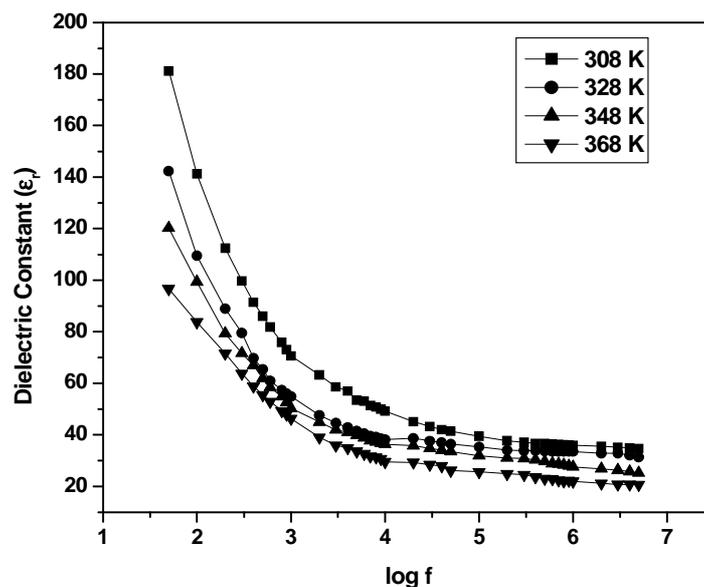
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Fig.5 Variation of dielectric constant with log frequency at different temperatures for LTN single crystal
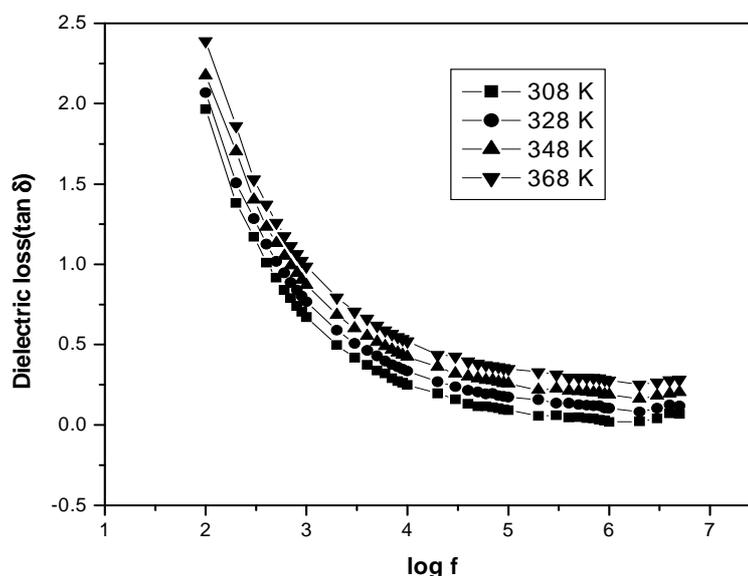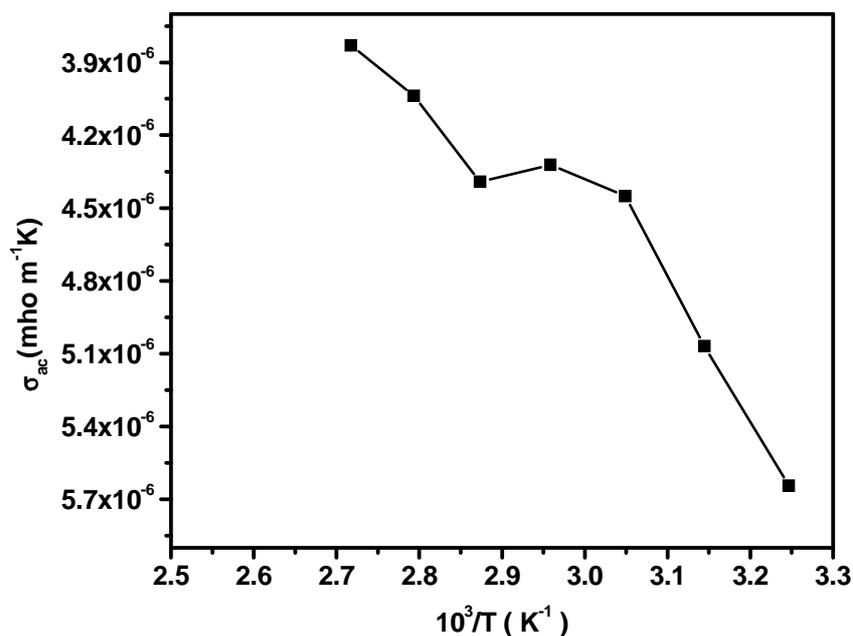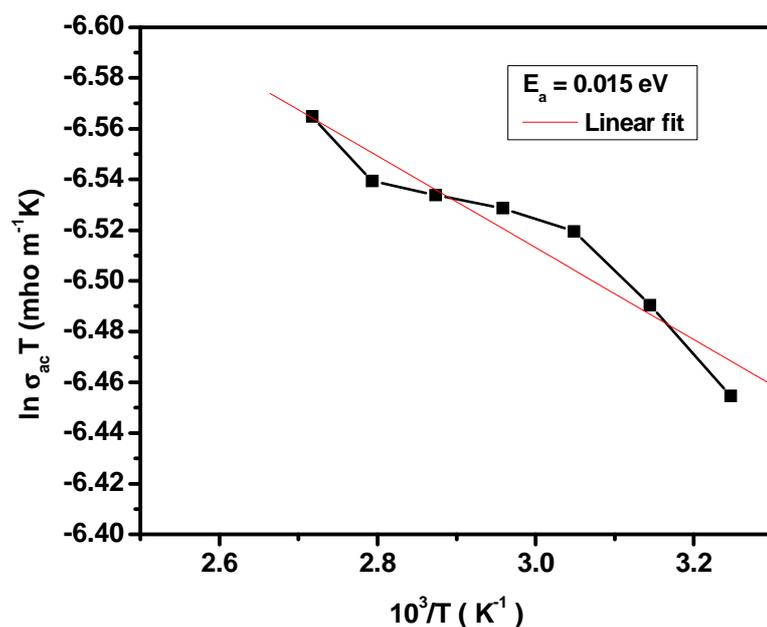

Fig. 6 Variation of dielectric loss with log frequency at different temperatures for LTN single crystal

3.4 *ac* conductivity

In order to understand the conduction behaviour of LTN crystals, electrical conductivity have been carried out at different temperatures ranging from 313 to 423 K. Profound changes which have occurred in the physical and chemical nature of the material essential gives information about its conductivity. The Plot of conductivity with temperature is shown in   Fig. 7, the conductivity is found to increase with temperature. The plot of *ln* $\sigma_{ac}T$ versus 1000/T is shown in Fig. 8. It is observed from the above studies that the grown LTN crystal exhibits low conductivity. The decrease in electrical conductivity with temperature may be due to the desorption of water molecules from the crystal lattice. On removal of water molecules, the crystal lattice slowly attains the perfect crystal symmetry which in turn reduces the electrical conductivity. The *ac* conductivity depends on the temperature and the activation energy for conduction is calculated from the slope of the Fig. 8. The activation energy of the sample is determined as 0.015 eV.

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Fig. 7 Variation of ac conductivity with 1000/T for LTN

Fig. 8 Plot of ln(σ_{ac})T versus 1000/T for LTN

CONCLUSION

An organic NLO crystal of L-tartaric acid nicotinamide of dimension 15 x 5 x 4 mm³ was successfully grown in a period of 30 days by low temperature technique. The rocking curve study confirms the good optical grade of the developed crystal. It is evident from single crystal XRD analysis that LTN crystallizes in monoclinic structure with P2$_1$ space group. The low value of dielectric constant and dielectric loss combined with moderate SHG efficiency make LTN a

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promising material for laser applications. The activation energy was determined from the plots for *ac* conductivity.

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