AC Conductivity and Dielectric studies of Nickel Selenate Hexahydrate Single Crystal

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ABSTRACT

AC electrical conductivity and dielectric studies are carried out in $NiSeO_4.6H_2O$ single crystal. The crystal has been grown by the method of slow evaporation at constant temperature. Measurements are taken for both a and c axes in the temperature range 301 K – 403 K. Activation energies for both axes are calculated for heating and cooling runs. The broad conductivity anomaly observed around 320 K can be attributed as a possible polymorphous transformation occurring in the crystal.

Keywords:Electrical conductivity, Dielectric, Single crystal, Nickel Selenate

I. INTRODUCTION

Nickel selenate hexahydrate ($NiSeO_4.6H_2O$) crystallizes in the tetragonal crystal system with unit cell parameters a = 6.914 Å, c = 18.420 Å and $\alpha = \beta = \gamma = 90^0$. It exists in the non-centro symmetric crystal class with space group D_4^4- $P4_12_12$. From the works of Snyman et al. [1] it has been known that these crystals are isomorphous with $NiSO_4.6H_2O$ and have axial ratio a: c = 1: 1.8364 = 1.2596 cos 45°. They calculated the density of the crystal at 25°C, assuming 4 molecules per unit cell as equal to 2.336 g/cm^3 which is in agreement with the pycnometric value of 2.314 g/cm^3. $NiSeO_4.6H_2O$ single crystals gain much importance since they exhibits optical activity. Toshiko et al. [2] measured the absorption, circular dichroism (CD) and optical rotatory dispersion (ORD) of these crystals in the 200 – 1500 mμ region at room temperature and 77 K. There appear three CD bands, which correspond, to the three main absorption bands, and they are ascribed to the transitions from the $^3A_2$ ground state to the $^3T_2$, $_a{}^3T_1$ and $_b{}^3T_1$ excited states in order of increasing energy. The concomitant ORD curve exhibits anomalous dispersion anti symmetric about the center of each CD band. Nabar et al. [3] using TG, DTG and DTA proposed a mechanism for the thermal dehydration of $NiSeO_4.6H_2O$ in which no intermediate hydrates (penta, tetra, or dihydrate) were found. In their scheme, $NiSeO_4.6H_2O$ transforms directly to $NiSeO_4.H_2O$ at 573 K and decomposes further into $NiSeO_4$ at 783 K. Stoilova et al.[4] reported that $NiSeO_4.6H_2O$ is stable up to 353 K and transforms into $NiSeO_4$ in six dehydration stages. According to them the transformation of $NiSeO_4.6H_2O$ direct into $NiSeO_4.H_2O$ is due to the experimental conditions i.e. the sample mass and heating rate. They proposed a different mechanism for the thermal dehydration of these crystals in which intermediate hydrates are also present and reported that $NiSeO_4.6H_2O$ transforms into $NiSeO_4.5H_2O$, $NiSeO_4.4H_2O$, $NiSeO_4.2H_2O$, $NiSeO_4.H_2O$, $NiSeO_4.0.5H_2O$, and $NiSeO_4$ at 381 K, 393 K, 429 K, 453 K, 553 K, and 633 K respectively. In a different work Stoilova et al. [5] investigated the vibrational behaviour of the S-O stretching modes $\square_3$ and $\square_1$ of the matrix isolated SO_4^{2-} guest ions isomorphously incorporated in selenate matrices of different crystal structure types which includes $NiSeO_4.6H_2O$ also. In a previous paper the authors reported the results of the ac electrical conductivity and dielectric studies of this crystal below room temperature where the Cole-Cole and Power law parameters are calculated [6]. In this paper we report the results of the ac electrical conductivity and dielectric studies of this crystal above room temperature.

II. EXPERIMENTAL

Single crystals of $NiSeO_4.6H_2O$ has been grown by slow evaporation methods from an aqueous solution of nickel carbonate ($NiCO_3$) and selenic acid (H_2SeO_4) in stoichiometric quantities at 313 K. H_2SeO_4 is obtained by refluxing H_2SeO_3 with H_2O_2 for several hours. Green coloured transparent crystals of size 45mm×20mm×20mm are obtained after a period of 60 days. The crystal has been cut perpendicular to a and c axes using a slow speed diamond wheel saw (MTI Corp. USA) and polished well to obtain samples of required thickness. The prepared crystal is placed in a sample holder inside a conductivity cell, which uses graphite electrodes for electrical contact. The conductivity cell is placed inside a temperature controlled circulated bath (Julabo Labortechnik GmbH, model FP 50). AC electrical conductivity and dielectric measurements are carried out in both axes using an Impedance Analyzer (Hioki model 3532). Measurements are carried out in the temperature range 301 K – 403 K with average measuring intervals 1 K. Since the sample is a hydrated crystal the experiment is conducted in two steps. First the temperature is varied from 301 K – 353 K and the data from both the heating and cooling runs are recorded. Thereafter the conductivity measurements are taken by varying the temperature from 301 K – 403 K, this time allowing the crystal to pass through hydration temperatures.

III. RESULTS AND DISCUSSION

Figures 1 and 2 shows the variation of ac conductivity with temperature along a and c axes respectively. The conductivity values of $NiSeO_4.6H_2O$ single crystal are found to be of the order of $10^{-9}\square^{-1}cm^{-1}$ at 303 K for both axes. The conductivity curves show a decrease in values up to a temperature 320 K and thereafter it begins to increase. This slight increase continues up to the temperature range 380 K after which it increases drastically. Electrical conduction of the ionic conductors is essentially due to ionic motion. The conductivity includes both the ionic and electronic contribution such as $\square\ \square\ \Sigma\ [\square_i + \square_e] = \Sigma\ [n_i\square_i(Z_ie) + n\square_e e]$. When the electronic conductivity is negligible, the conductivity becomes purely ionic, hence $\square\ \square\ \square_i = n_i\square_i(Z_ie)$ where n_i, $\square_i$, (Z_ie) are the concentration, mobility and charge of the mobile species respectively. The extent of the observed disorder and the energy barriers associated with hopping between the interstitial sites can be calculated from the measured conductivity. Ordinary ionic conduction relies on the formation of lattice defects under the action of thermal excitation, thus creating vacancies through which ionic motion may proceed under the action of external electric fields. This leads to Arrhenius temperature dependence with an activation energy given by the energy of formation of a defect. The temperature dependence of the ionic conductivity is usually given by the Arrhenius equation $\square\ (T) = \square_0 \exp - (E_\square/k_BT)$ Where T is in Kelvin, k_B is the Boltzman constant, $\square_0$ is the pre-exponential factor, and $E_\square$ is the activation energy of the migration ion. Activation energies are calculated from the plots of log □ and 1000/T for both axes as well as heating and cooling runs. Its values are found to be 1.27eV for heating and 1.56 eV for cooling for a-axis. For c-axis E□ is found to be 0.979 eV for heating and 0.745 eV for cooling run. These values are found to be in good agreement with that of ionic conductors. The dielectric curves (figures 5, 6, 7, 8) for $NiSeO_4.6H_2O$ single crystal shows a change in nature around 320 K. This anomaly which is also observed for the conductivity curves can be attributed as a

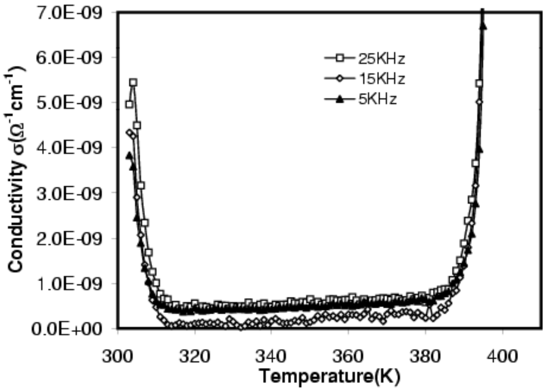

Figure 1 Plot of conductivity vs. temperature along a-axis

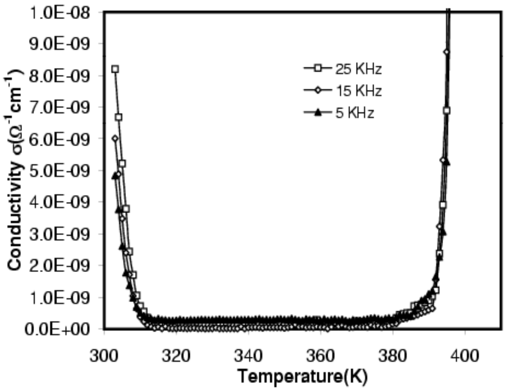

Figure 2 Plot of conductivity vs. temperature along c-axis

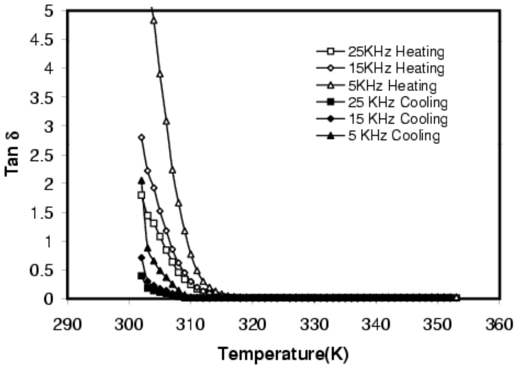

Figure 3 Plot of loss tangent vs. temperature along a-axis

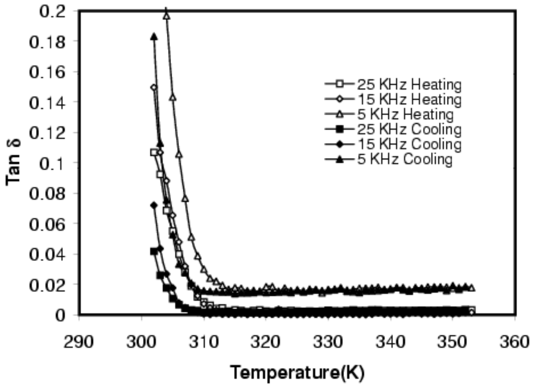

Figure 4 Plot of loss tangent vs. temperature along c-axis

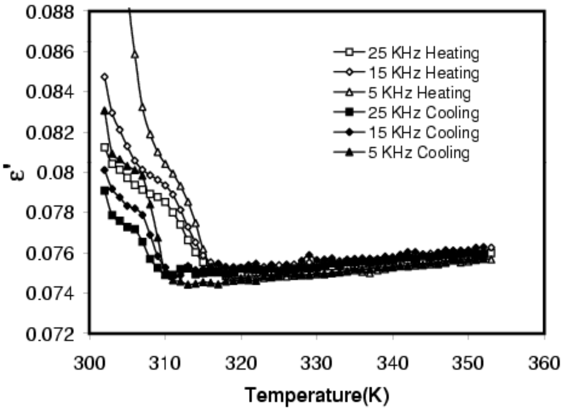

Figure 5 Plot of real part of dielectric constant vs. temperature along a-axis

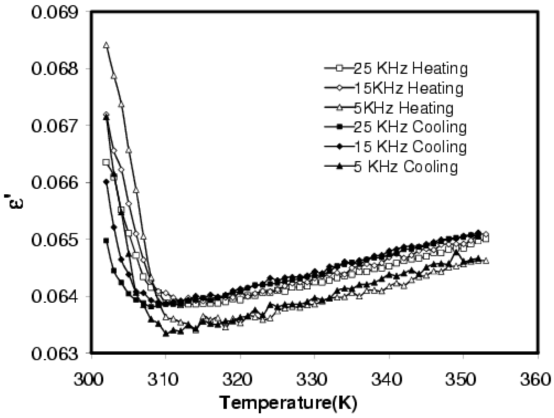

Figure 6 Plot of real part of dielectric constant vs. temperature along c-axis

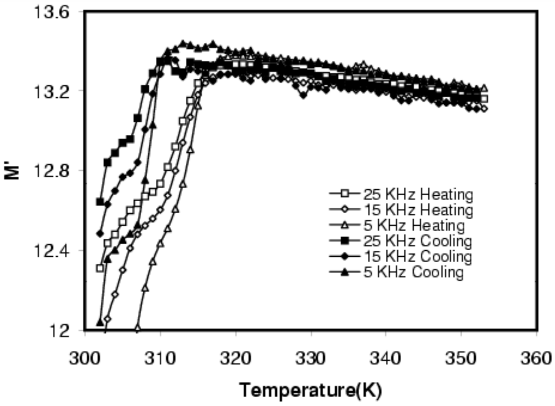

Figure 7 Plot of real part of dielectric modulus vs. temperature along a-axis

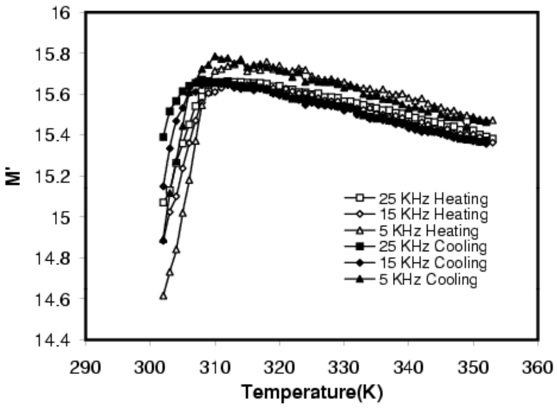

Figure 8 Plot of real part of dielectric modulus vs. temperature along c-axis

possible phase transition around that temperature. However the presence of any polymorphous transformations in the crystal needs further investigations. The large increase in conductivity values after 380 K can be attributed as the thermal dehydration occurring in the crystal. This has been found in very good agreement with the dehydration mechanism proposed by Stoilova et al [4] in which the transformation of $NiSeO_4.6H_2O$ to $NiSeO_4.5H_2O$ occurs at 381 K. Figures 3 and 4 show the variations of loss tangent with temperature along a and c axes respectively. The values of $\tan\delta$ are found to be very low approaching that of low-loss dielectrics. At 303 K its values are in between 0.5 and 5 along a axis for different frequencies. Along c axis its values are still lower and are found to be in between 0.02 and 0.2. Figures 5 and 6 show the variations of real part of dielectric constant with temperature along a and c axes respectively. The values of dielectric constant are also found to be very low (< 0.1). Figures 7 and 8 shows the dielectric modulus curves along a and c axes respectively. While the complex permittivity and susceptibility curves physically emphasis the parallel processes contributing to the real and imaginary components of polarization, the modulus curves emphasizes the series processes that may be acting in the material [7].

IV. CONCLUSIONS

$NiSeO_4.6H_2O$ single crystal. has been grown by the method of slow evaporation at constant temperature. AC electrical conductivity and dielectric studies are carried out in $NiSeO_4.6H_2O$ single crystal. The conductivity values of $NiSeO_4.6H_2O$ single crystal are found to be of the order of 10^{-9}□$^{-1}$cm^{-1} at 303 K for both axes. The values of dielectric constant and dielectric loss are also found to be very low. Measurements are taken for both a and c axes in the temperature range 301 K – 403 K. Activation energies Its values are found to be 1.27eV for heating and 1.56 eV for cooling for a-axis and 0.979 eV for heating and 0.745 eV for cooling run. These values are found to be in good agreement with that of ionic conductors. The dielectric curves show a change in nature around 320 K which is also observed for the conductivity curves can be attributed as a possible phase transition around that temperature.

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