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Conductivity and dielectric relaxation phenomena in $(NH_4)_2SO_4$ single crystal

R.H. Chen [a,*], Yu-Chao Chen [a], C.S. Shern [a], T. Fukami [b]

[a] Department of Physics, National Taiwan Normal University, 88, Section 4 Ting-Chou Road, Taipei 11677, Taiwan
[b] Department of Physics and Earth Sciences, Faculty of Science, University of the Ryukyus, Okinawa 903-0213, Japan

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ABSTRACT

AC impedance measurements have been carried out on $(NH_4)_2SO_4$ single crystals for the temperatures from 300 to 473 K and frequency range between 100 Hz and 4 MHz. The results reveal two distinct relaxation processes in the sample crystal. One is the dipolar relaxation with a peak at frequency slightly higher than 4×10^6 Hz. The other is the charge carrier relaxation at lower frequencies. The frequency dependence of conductivity is described by the relation $\sigma(\omega)=B\omega^n$, and $n=1.32$ is obtained at temperatures below 413 K. This value drops to 0.2 and then decreases slightly with increasing temperature. The dipolar response of the $(NH_4)_2SO_4$ single crystal under an ac field is attributed to the reorientation of dipoles. The contribution of charge carriers is increasing substantially with increasing temperature at temperatures above 413 K. The temperature variation of conductivity relaxation peaks follows the Arrhenius relation. The obtained activation energy for migration of the mobile ions for $(NH_4)_2SO_4$ single crystal was 1.24 eV in the temperature range between 433 and 468 K in this intrinsic region. It is proposed that the NH_4^+ in the sample crystal has the contribution to the electrical conduction.

1. Introduction

Many crystals in the family of M_2XO_4($M=NH_4^+$, K^+, and X = S and Se) exhibit a series of structural phase transitions with the variation of the temperature. The crystal of K_2SO_4 is typical in this family and is crystallized with the so-called β-K_2SO_4 at room temperature. The crystal of β-K_2SO_4 in the room temperature phase is ferroelastic with the structure in the space group of *Pnam*. It transforms to the paraelastic phase, α-K_2SO_4 at 860 K. The ferroelastic domain structure of K_2SO_4 had been analyzed [1]. The space group of α-K_2SO_4 is then confirmed to be $P6_3/mmc$ [1]. The crystal of ammonium sulphate, $(NH_4)_2SO_4$ is isomorphous with β-K_2SO_4 at room temperature. It crystallizes with unit-cell dimensions $a=7.782$, $b=10.636$, and $c=5.993$ Å with the same space group as that of β-K_2SO_4 [2]. It has been reported that the $(NH_4)_2SO_4$ crystal undergoes a low-temperature phase transition at −50 °C [3,4]. The space group of low-temperature phase is $Pna2_1$ with $a=7.837(7)$, $b=10.61(1)$ and $c=5.967(6)$ Å [2]. The crystal structures of $(NH_4)_2SO_4$ crystal in these two phases have been extensively studied by neutron and X-ray diffraction methods [2,5].

$(NH_4)_2SO_4$ crystals had also shown ferroelastic twin structures with (011) and (031) twin planes in the room temperature phase [6]. The ferroelastic domain structures of the sample crystal were similar to those of K_2SO_4 crystal [1]. The existence of the high temperature paraelastic phase of the $(NH_4)_2SO_4$ crystal had been then suspected by Makita et al. [6]. The ratio of $b/c=1.775$ of $(NH_4)_2SO_4$ crystal is so close to $\sqrt{3}$ as in the case of K_2SO_4 single crystal, such that the hexagonal symmetry of crystal structure in high temperature phase (or prototypic phase) was also proposed [6]. However, Sawada et al. had found that $(NH_4)_2SO_4$ crystal decomposed into $(NH_4)HSO_4$ at 357 °C (= 630 K) and no phase transition took place [7].

The thermal analysis of the $(NH_4)_2SO_4$ crystal had been studied by several groups. The measurements using DSC and thermal gravimetry (TG) had been carried out [8,9]. Some anomalies had been reported in the thermal measurements. An endothermic peak was found at 508 K just before the onset of the decomposition at 538.5 K [9]. A phase transition at 508 K was then proposed [9]. While Lee et al. had reported that the weight loss took place at 443 K and only a few weight percent was left after the measurement above 543 K [8]. Several complicated endothermic structures on heating above 633 K were also obtained, although this observation was not consistent with their own result of TG analysis [8].

The electrical properties for $(NH_4)_2SO_4$ crystal have also been studied by many researchers [8–14]. The dielectric constant increased rapidly at temperature above 403 K [13] or at 424 K [11] in the different reports. The anomalies had also been found in the conductivity measurements [8,9,12]. The temperatures of the anomaly were found at 403 K [8], 416 K [9], or 423 K [12]. The activation energies suddenly changed from 0.03 to 1.46 eV at 403 K [8], 0.64 to 1.11 eV at 416 [9], and 0.67 to 1.5 eV at 423 K [12] as reported respectively by those researchers. Another activation energy with 0.76 eV was obtained in the temperature range between 225 and 473 K [10]. The measurements were mostly performed at 1 kHz [8,9,11] or at dc [10,12]. The thermal

* Corresponding author. Tel.: +886 2 29346620; fax: +886 2 29326408.
E-mail address: rhchen@phy03.phy.ntnu.edu.tw (R.H. Chen).

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evolution of the dielectric properties for the $(NH_4)_2SO_4$ single crystal has no definite conclusion.

In this paper, we report the results of the ac impedance spectra of the $(NH_4)_2SO_4$ single crystal in the temperature rang between 300 and 473 K. We have made a comprehensive study of the temperature and frequency dependences of dielectric properties for the $(NH_4)_2SO_4$ single crystal.

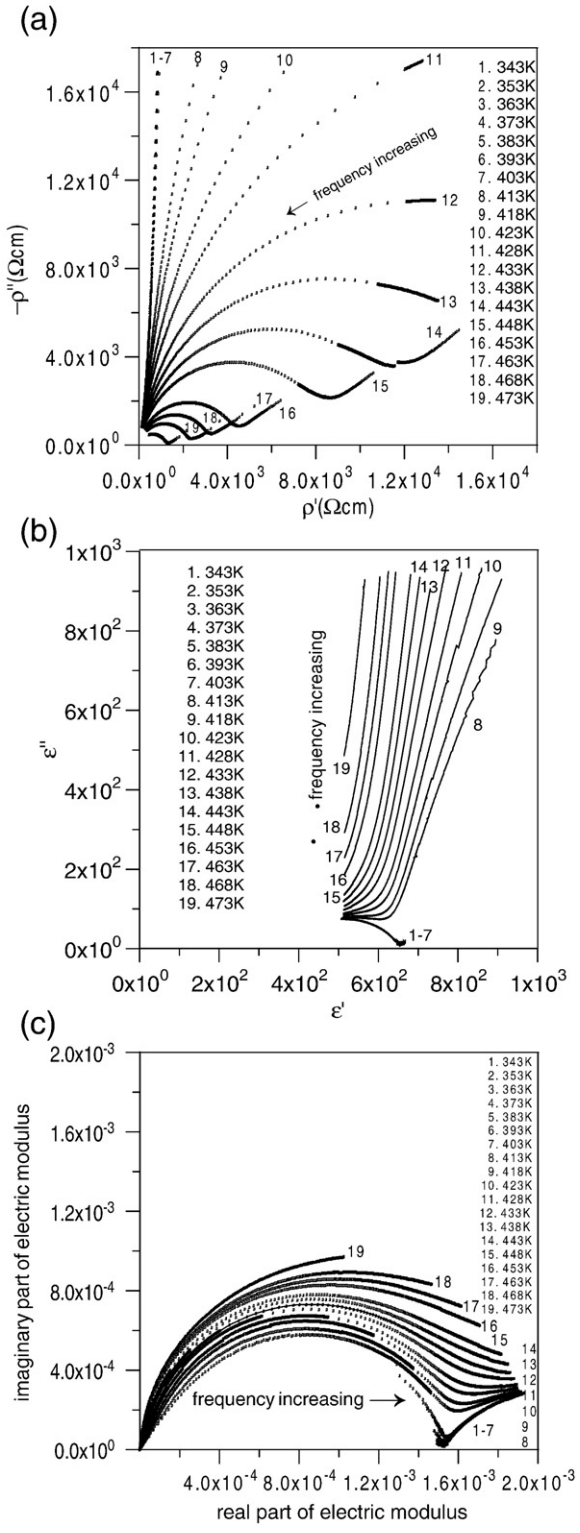

Fig. 1. The Cole–Cole plots of (a) resistivity, (b) dielectric constant, and (c) electric modulus for a $(NH_4)_2SO_4$ single crystal at various temperatures.

2. Experiment

Crystals of $(NH_4)_2SO_4$ were grown at room temperature by slow evaporation from aqueous solutions. Transparent plates with the dominant face of (100) were obtained. Three orientations of ferroelastic domains were observed under a polarizing microscope. The domain structures are similar to the ferroelastic domains of K_2SO_4 single crystal. Differential scanning calorimetry (DSC) measurements were performed on the crystals of $(NH_4)_2SO_4$ using a DSC-2920 instrument in the temperature range of 300–700 K. Three endothermic peaks were observed at 582.8, 619.6, and 653.5 K (not shown here). A transparent one-domain single crystal with the (100) plate was chosen to heat up under the polarizing microscope. The temperature of the sample was controlled using a heating stage THM600 (Linkam). The results showed that the crystals were very stable below 483 K. It also showed that partial decomposition on the very near surface had began at temperature above 503 K. Single domain crystal of $(NH_4)_2SO_4$ with 9 mm^2 and 0.81 mm thickness was used for the electrical impedance measurement. The sample crystal was pasted with silver plaster on the surface of (100) plate as electrodes. The impedance measurements of the specimen were carried out using a HP4194A impedance analyzer which was interfaced to a personal computer. The crystal was placed in a small oven with a quartz cover at ambient pressure. The temperature was controlled from 300 to 473 K with the stability within 0.5 K. The sample was left for 20 min at each temperature before the measurement. The measurements were performed in the frequency range from 100 Hz to 4 MHz, with an applied potential of 500 mV.

3. Results and discussion

3.1. Dielectric Cole–Cole plots

The complex impedance $Z^*(\omega)$ of a $(NH_4)_2SO_4$ crystal in an ac field (with frequency ω) was measured at the temperatures from room temperature to 473 K. In this temperature range, the sample crystal was in a stable form. The complex resistivity $\rho^*(\omega)$ of the sample crystal was then evaluated from the obtained complex impedance according to the following relations:

$$\rho^*(\omega) = \rho'(\omega) + i\rho''(\omega) = Z^*(\omega)\frac{A}{t}, \tag{1}$$

where A and t represent the electrode area and thickness of the sample, respectively. The complex dielectric constant was obtained by the relation:

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \frac{1}{i\omega\epsilon_0\rho^*(\omega)}, \tag{2}$$

where ϵ_0 is the dielectric constant of the vacuum. The complex electric modulus $M^*(\omega)$ is defined as:

$$M^*(\omega) = M'(\omega) + iM''(\omega) = \frac{1}{\epsilon^*(\omega)}. \tag{3}$$

Those dielectric parameters are usually used to analyze the dielectric properties of the sample.

The Cole–Cole plots of resistivity, $-\rho''$ versus ρ', for a $(NH_4)_2SO_4$ single crystal at several temperatures are shown in Fig. 1(a). Very large arcs (portion of the semicircles) were obtained for the temperatures below 443 K, since the resistivity of the sample crystal is very large at low temperatures. The variations of the plots with the frequency consist of a nearly semicircle and inclined spike (portion of the other semicircle) for the temperatures above 443 K. The results showed that the radius of the semicircle reduced as the temperature was raised. It was associated with the decreasing resistance of the sample crystal