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1999 J. Phys.: Condens. Matter 11 713

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Phase transitions of K_2CrO_4 crystals

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Received 10 May 1998, in final form 3 September 1998

Abstract. The electrical conductivity measurements on single crystals of K_2CrO_4 have been carried out in the temperature range from 580 to 1070 K. The bulk ionic conductivity along the three principal crystallographic axes has been determined by means of complex impedance formalism. The ionic conductivity in the low-temperature phase β follows closely the classical Arrhenius law up to around 890 K ($\sim T_c - 50$ K). From 890 K, the slope of the conductivity curve increases up to T_c and it is attributed to the existence of a pretransitional region which may be a consequence of the significant rotational disorder of chromate ions below its phase transition. Unusual behaviour in the temperature dependence of the vibrational mode (ν_1) of chromate ions has been observed in roughly the same temperature range. The dielectric properties are similar to the prototype K_2SO_4 crystal and are discussed concerning an intermediate phase above T_c .

1. Introduction

Potassium chromate (K_2CrO_4) undergoes a structural phase transition at 942 K. The crystal structure of the room-temperature β -phase is orthorhombic, space group $Pm\bar{c}n$, with lattice constants $a = 7.663$, $b = 10.388$ and $c = 5.922$ (McGinnety 1972). The high-temperature α -phase is hexagonal, space group $P6_3/mmc$, with ortho-hexagonal constants $a = 8.22$, $b = 10.61$ and $c = 6.12$ Å at 953 K (Eysel 1973). A large number of K_2SO_4 -family crystals (e.g. Na_2SO_4 , LiKSO_4 and K_2SeO_4 etc) transform at high temperatures into the α - K_2SO_4 structure type in spite of the structural differences of their low-temperature modifications (Aleksandrov and Beznosikov 1991). K_2CrO_4 is isostructural with K_2SO_4 in its low- and high-temperature structures. Hence, the $\beta \leftrightarrow \alpha$ phase transition of K_2CrO_4 is regarded as similar to that of the prototype K_2SO_4 crystal.

The $\beta \rightarrow \alpha$ K_2SO_4 phase transition ($T_c = 860$ K) is of the order–disorder type with orientationally ordered SO_4^{2-} ions in the β -phase and disordered ones in the α -phase (Watanabe *et al* 1973, Natarajan and Secco 1975, Miyake *et al* 1981, Arnold *et al* 1981, Ishigame and Yamashita 1983, Kurtz 1992). At high temperatures (e.g. 1073 K), K_2SO_4 adopts an apex model orientation where one of the apices of the sulphate tetrahedra is pointing statistically up and down with respect to the hexagonal axis (van den Berg and Tuinstra 1978, Miyake *et al* 1980, Arnold *et al* 1981). When the temperature is closer to the phase transition, it is likely to adopt an edge model orientation, which consists of three superimposed split tetrahedra each with one edge parallel and one perpendicular to the hexagonal axis (Arnold *et al* 1981). The apex- and edge-models are also reported in Na_2SO_4 crystals (Eysel 1985, Naruse *et al* 1987). The α - K_2CrO_4 crystal can be regarded as having just the same dynamically disordered state of chromate ions as in the α - K_2SO_4 structure.

Ionic conductivity and dielectric constant values are related to intrinsic structural features and well reflect the structural changes. To investigate the $\beta \rightarrow \alpha$ phase transitions of K_2CrO_4

crystals, dielectric properties have been studied (Russell and Merlin 1986, Dissado and Haidar 1987, Merlin 1988) but with noticeable inconsistencies in the published reports including an appearance of a dipole glass phase above T_c . Ac conductivity measurements on two crystallographic axes of K_2CrO_4 at 1 kHz were also reported with suspicious low-temperature anomalies below T_c (Natarajan and Secco 1974). The conductivity measurements at a fixed frequency seem to be rather inadequate for separating interfacial and bulk conductivity, and thereby for the determination of activation energy. In this work, we report measurements of the bulk dc ionic conductivity along all three crystallographic axes of oriented single crystals of K_2CrO_4 by means of complex impedance measurements. The dielectric properties are also described to investigate whether the glassy phase above T_c exists or not.

2. Experiment

Yellowish, transparent crystals of β - K_2CrO_4 were grown from aqueous solution at 323 K by slow evaporation of the solvent. Crystals of bipyramidal shape grew with well developed (110) and (111) faces. We prepared from four to six samples of typical thickness 1 mm and area 6 mm² with evaporated gold contacts for each crystal axis study. The sample under investigation was mounted in an oven with platinum electrodes and most of the measurements were performed with heating and cooling rates of 0.5 K min⁻¹.

The electrical conductivity measurements were carried out in the temperature range 580–1070 K with average measuring intervals 0.5 K. The complex impedances were determined by means of a HP model 4192A LF impedance analyser. The signal applied across the samples was 200 mV. The complex impedance measured in the frequency range from 100 Hz to 10 MHz allowed us to obtain the dc conductivity of the bulk crystal by means of the usual impedance analysis.

The Raman spectrum was excited with 150 mW of 514.5 nm argon laser light. The Stokes Raman light scattered with back-scattering geometry was analysed with a Jovin–Yvon U1000 double monochromator.

3. Results and discussion

The temperature dependence of 10 kHz ac electrical conductivity for all three crystallographic axes of K_2CrO_4 is plotted in figure 1. The extrapolated onset temperature of the transition is 942.4 K on heating and 940.6 K on cooling, with the thermal hysteresis of 1.8 K. The T_c value measured is in good accord with that reported from accurate thermal analysis (Charsley *et al* 1993), in which the K_2CrO_4 crystal is known to be suitable as a temperature standard. Conductivity along the c -axis is highest. This can be understood from the crystallographic data. The unit cell area of the ab -plane is largest and therefore the K^+ ions along the c -axis are located in relatively open structure (McGinnety 1972). Suitable migration paths for K^+ ions can be placed along these open routes.

In K_2SO_4 crystals, several anomalies in the region of the phase transition were observed with different physical methods, where the sulphate ions are conjectured to be already in a dynamically disordered state before the transition (so-called pretransition phenomenon) (Kolontsova *et al* 1973, Miyake *et al* 1979, Zheludev *et al* 1989, Choi *et al* 1993). The same dynamics may hold in the isostructural K_2CrO_4 . To investigate the presence of pretransition phenomenon, bulk dc conductivities, extracted from the complex impedance plots, were analysed using the Arrhenius equation of the form

$$\sigma T = A \exp(-E_\sigma/k_B T)$$

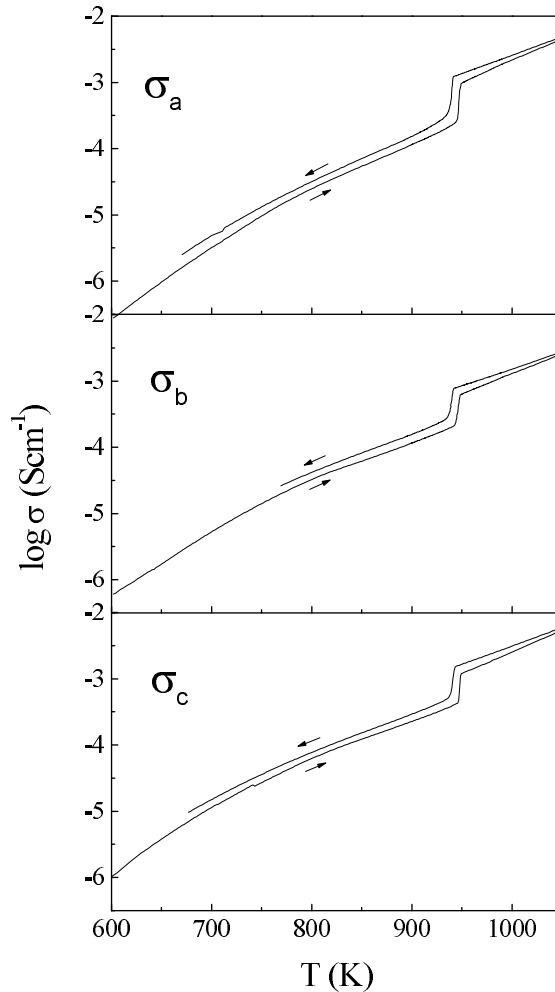


Figure 1. Temperature dependence of the 10 kHz ac electrical conductivity of K_2CrO_4 along a , b and c crystallographic axes measured on heating and cooling cycles.

where A is the pre-exponential factor and E_σ is the apparent activation energy for ion migration. Figure 2 shows Arrhenius plots from 770 K to 1000 K. Between 770 and 890 K, the conductivities of the β -phase are well represented by straight lines, following the Arrhenius law for all crystallographic directions, with activation energies of $E_a = 0.90$, $E_b = 0.79$ and $E_c = 0.80$ eV.

The discrepancy from the Arrhenius behaviour below T_c starts at around 890 K ($\sim T_c - 50$ K). In the range $T_c - 50$ K $< T < T_c$, the slope of the experimental curve increases steadily up to the transition temperature. The same type of conductivity variation is observed in K_2SO_4 crystals, in which the ionic conductivity deviates from the Arrhenius law roughly $T_c - 50$ K (Choi *et al* 1993). Kolontsova *et al* (1973) reported a pretransition of K_2SO_4 starting at around $T_c - 200$ K from x-ray observations. The pretransition is considered to be a preparatory stage caused by structural changes not associated directly with the formation of the new phase. Optical investigations of the $\alpha \leftrightarrow \beta$ phase transition of K_2SO_4 indicated the presence of

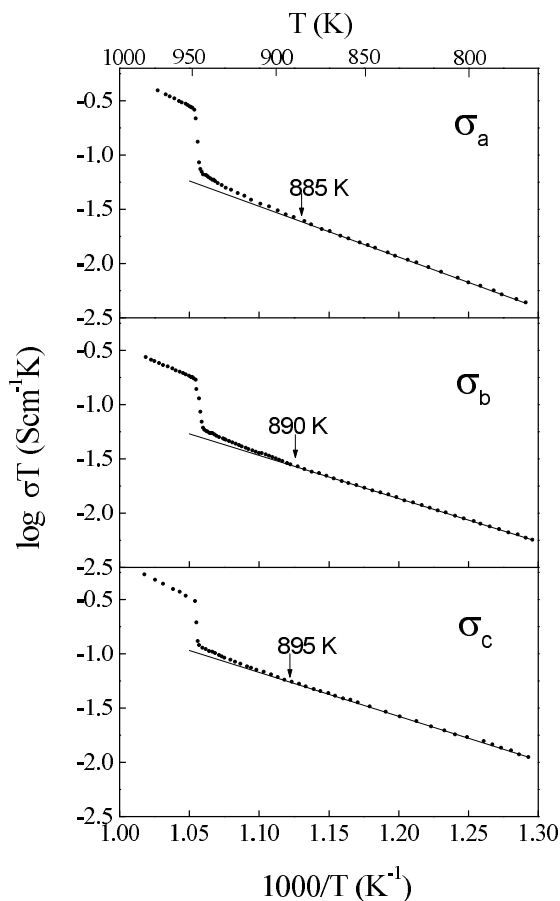


Figure 2. Arrhenius plots of dc ionic conductivity, extracted from impedance plots, of K_2CrO_4 along a -, b - and c -axes measured on heating cycle.

an intermediate phase existing in a narrow temperature range just below the phase transition (Miyake *et al* 1979, Zheludev *et al* 1989). Pimenta *et al* (1988) reported the same type of experimental conductivity curve in the LiKSO_4 crystal and attributed it to a consequence of the increasing disorder of the sulphate ions below the phase transition. Cazzanelli *et al* (1984, 1989) also pointed out, from their Raman scattering studies on Li_2SO_4 crystals, the possibility of the existence of a pretransitional region above 730 K ($\sim T_c - 120$ K) which seemed to be characterized by the onset of significant reorientational disorder of sulphate ions. In this regard, we can assume that the K_2CrO_4 shows the above-mentioned behaviour, significant rotational disorder of chromate ions below the transition temperature.

As an attempt to confirm the onset of rotational disorder of the chromate ions, the Raman spectra have been measured tracing the internal vibrations of chromate ions. The totally symmetric ν_1 mode of the CrO_4^{2-} ion is the most intense in the Raman spectrum of K_2CrO_4 and it is well separated from the other bands. Figure 3 shows that the ν_1 frequency decreases steadily with increasing temperature up to roughly about $T_c - 80$ K and then it shows an anomalous upward shift. It indicates that some kind of disordering of chromate ions occurs, varying the potassium–oxygen interaction and consequently increasing the frequency of the

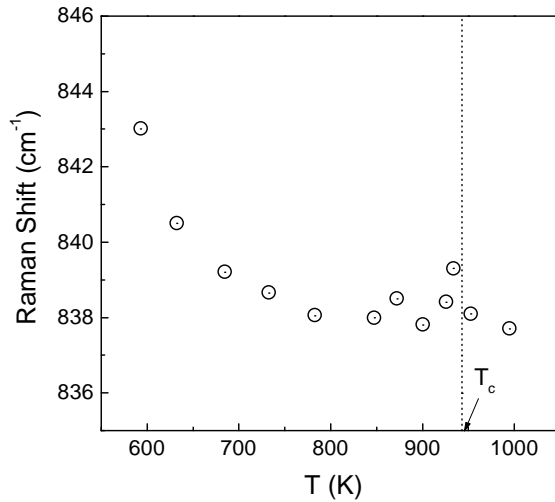


Figure 3. Temperature dependence of the frequency of the totally symmetric internal mode ν_1 of CrO_4^{2-} ions.

ν_1 mode. Although the observed shift is not significantly greater than the scatter in the data, it apparently shows that the unusual behaviour of CrO_4^{2-} internal vibration (ν_1) occurs in roughly the same temperature range as compared with the pretransitional departure of conductivity.

The mechanism of enhanced conductivity in the pretransitional region is considered to lie in strongly coupled rotation of chromate tetrahedra to the cations via the so-called paddle-wheel mechanism. The paddle-wheel mechanism was proposed to be operative in Li_2SO_4 -family crystals (e.g., Li_2SO_4 , $LiNaSO_4$, $LiAgSO_4$ etc), which undergo a first order phase transition to the high-temperature cubic phase, exhibiting very high cationic conductivity (Lunden 1988).

However, one can consider the other transport mechanism that may be responsible for the enhanced conductivity in the pretransitional region. In the case of K_2SO_4 crystals, the lattice parameters of the β -phase have been known to be expanded more than proportionally to T above ~ 620 K (Arnold *et al* 1980, Miyake and Iwai 1981). The excess expansion accounts for additional space needed to bring the ordered arrangement of tetrahedra into a rotational disorder condition (Kurtz 1992). The nonlinear thermal expansion below T_c has been also observed in β - K_2CrO_4 (Pistorius 1962). Hence the other possibility on the mechanism of the enhanced conductivity above the Arrhenius behaviour in K_2CrO_4 is that the more open lattice structure due to excess expansion may contribute to the cationic conductivity.

Dielectric constant data (ϵ') are determined from the complex impedance measurements using the relation

$$\epsilon^*(\omega) = 1/j\omega C_0 Z^*(\omega)$$

where C_0 is the vacuum capacitance of the cell and ω is the angular frequency ($\omega = 2\pi f$). Figure 4 shows the temperature dependence of the dielectric constants along the a -, b - and c -axes measured at frequencies of 10 kHz and 1 MHz in the heating process. The larger dielectric constant values observed in 10 kHz data than 1 MHz data may be associated with electrode polarization, since the electrode capacitance can be much larger than the sample capacitance at low frequencies (Macedo *et al* 1972). The transition temperatures derived from the dielectric constant data are in good accord with those derived from the conductivity data within $\pm 0.5^\circ C$.

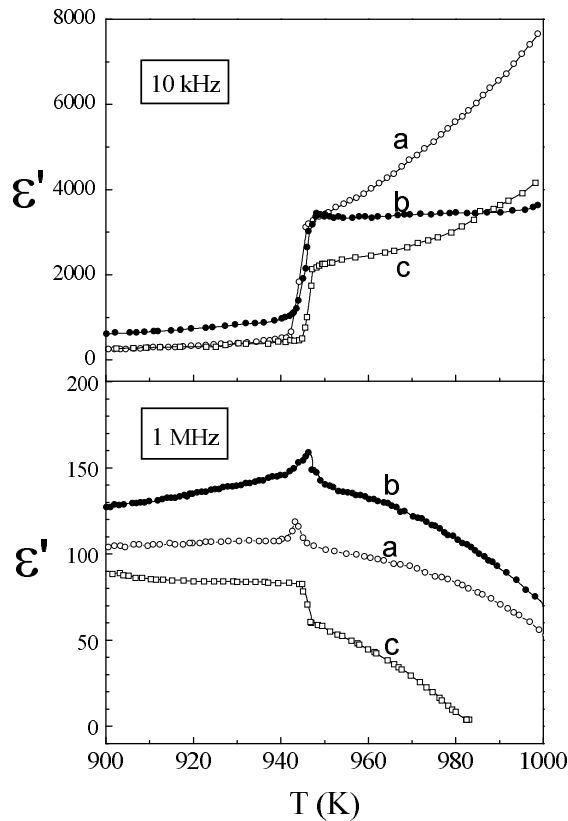


Figure 4. Temperature dependence of the real part of the dielectric constant of K_2CrO_4 along a -, b - and c -axes at 10 kHz and 1 MHz measured on heating cycle.

Russell and Merlin (1986) reported that the dielectric constant of the K_2CrO_4 crystal exhibits only a weak anomaly at T_c ; instead they observed a pronounced frequency dependent cusp at slightly higher temperatures. The cusp of ϵ was interpreted in terms of a possible dipole-glass state arising from randomness introduced by the presence of vacancies. Later, Dissado and Haidar (1987) reinvestigated the K_2CrO_4 system, and dielectric constant data, measured at frequencies between 10^{-2} and 10^4 Hz, were found to derive from a combination of bulk conductance and barrier capacitance, with a discontinuity marking the transition. They concluded that the existence of the dipole-glass state cannot be justified on the basis of the data given by Russell and Merlin. We found marked dielectric anomalies only at the transition point as shown in figure 4 and they are similar to those of the prototype K_2SO_4 crystal (Choi *et al* 1993). It shows no sign of the peak above T_c reported by Russell and Merlin, indicating no evidence for the existence of an intermediate dipole-glass state.

4. Conclusions

The study of the ionic conductivity of oriented single crystals of K_2CrO_4 by means of complex impedance formalism has revealed new information about its $\alpha \leftrightarrow \beta$ transitions. The ionic conductivity in the low-temperature phase β deviates from the classical Arrhenius law from

$T_c - 50$ K and it is attributed to a consequence of the onset of significant rotational disorder of chromate ions prior to the structural transition. The ν_1 internal vibration of chromate ions exhibits an anomalous upward shift in the same temperature range, indicating some kind of disordering of chromate ions occurs below T_c . The dielectric properties are very similar to the prototype K_2SO_4 crystal, showing no anomalous glass state above T_c .

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the RCDAMP at Pusan National University.

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