

# Dielectric Properties of LiKSO<sub>4</sub> Doped with CaF<sub>2</sub>

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*The ac conductivity of polycrystalline LiKSO<sub>4</sub> doped with different concentrations of CaF<sub>2</sub> was measured at different frequencies and temperatures. The analysis of the obtained results shows that the correlated barrier hopping is the conduction mechanism. The distribution parameter calculated from the Cole-Cole diagram indicates that the dielectric dispersion is of poly-type. Moreover its value decreases with increasing CaF<sub>2</sub> percentage leading to the conclusion that the barrier height for some relaxation mechanisms is increased.*

## 1. Introduction:

Lithium potassium sulfate (LKS) is the object of great interest due to the complexity and richness of its sequence of phase transitions, an unusual case for an inorganic crystal with a simple chemical formula [1]. A set of phase transitions has been proposed for LKS including ferroelastic [2, 3], incommensurate [4, 5] and superionic phases [6]. However there is controversy concerning symmetries, phase transition temperatures, and even the existence of some of these phases. It seems clear that the sequence of phase transitions of LKS is strongly dependent on crystal growth conditions, on the thermal cycle, and on the presence of defects in the as-grown crystals.

Dielectric properties of single crystals LKS have been studied by other authors; in the temperature range from 290 to 800K [7, 8]. The aim of the present work is to study the dielectric behavior of polycrystalline LKS doped with different concentrations of CaF<sub>2</sub> in the temperature range from 673 to 733K.

## 2. Experimental:

LKS matrix was prepared by mixing high purity  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in equimolar ratio thoroughly. It was ground in an agate mortar to obtain a fine homogeneous mixture, and then heated at 1173 K in a ceramic crucible for four hours. The obtained LKS matrix was allowed to cool to room temperature and then mixed with different concentrations of  $\text{CaF}_2$  (0.1, 0.2, 0.5, 1, and 2% by weight) and were heated at 1223K for one hour.

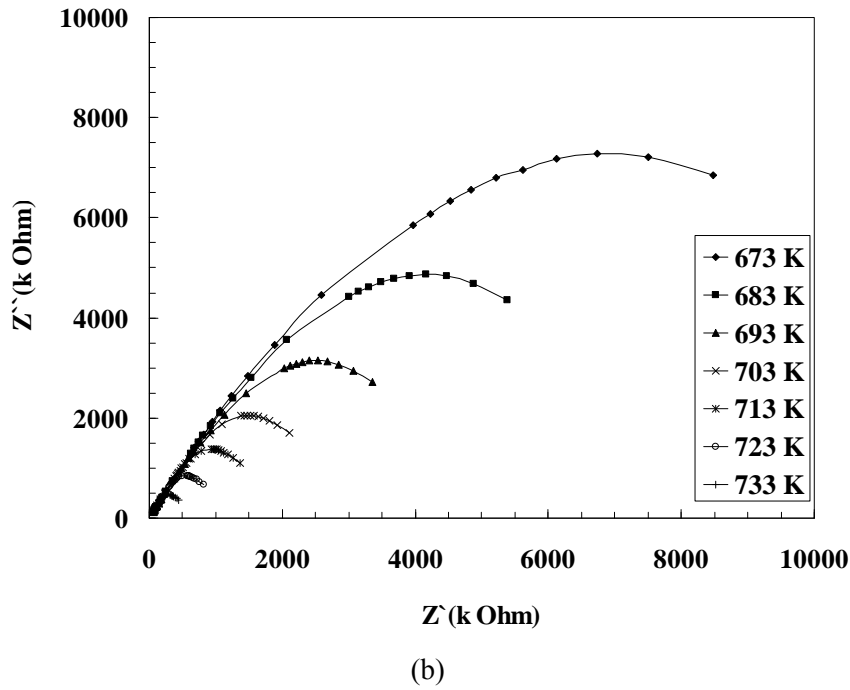
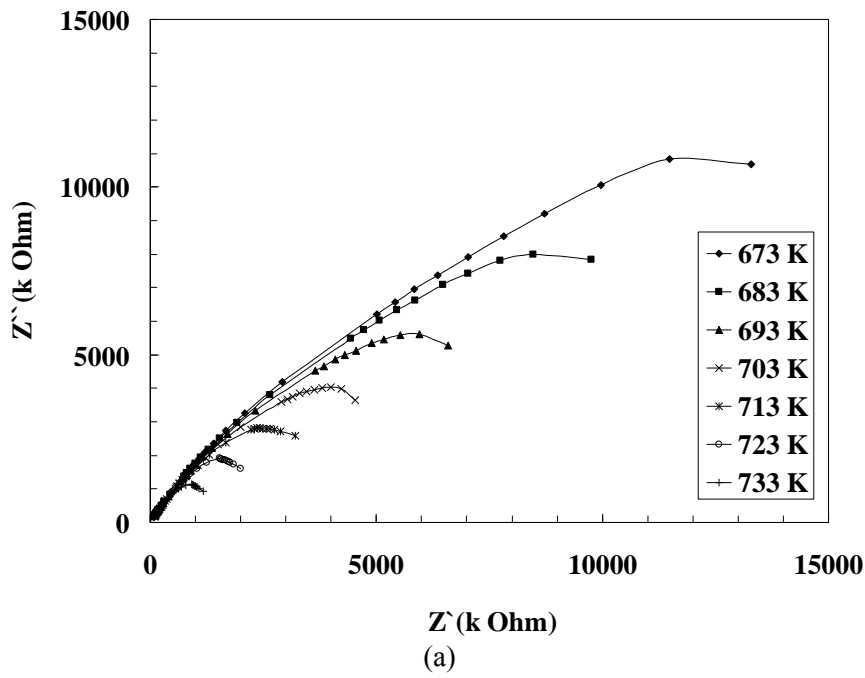
The doped samples were pressed to form discs of diameter 10 mm and thickness 1.2 mm. Silver electrodes were deposited on the polished sample surfaces by thermal evaporation. The dielectric measurements were carried out at different frequencies (from 0.1 – 100 KHz), and temperatures (from 673-733 K) using a HIOKI 3532 LCR tester. The temperature was controlled by means of a Digi-Sence proportional temperature controller connected to a K-type thermocouple.

## 3. Results and Discussion:

The relation between the real ( $Z'$ ) and imaginary ( $Z''$ ) parts of the impedance was plotted for all prepared samples. Fig. (1) represents the  $Z''$ - $Z'$  for the pure LKS and 0.5% doped samples at different temperatures as representative data. Similar graphs were obtained for all other samples.

The behaviour of these Cole-Cole diagrams is characterized by semicircles originating from the origin with no overlap at all temperatures. This means that the surface resistance  $R_s$  is zero and the sample resistance could be composed mainly of the bulk resistance  $R_b$  in parallel with series capacitance  $C_s$ . Extrapolating the high-frequency limit of the semicircles intercepts the real axis  $Z'$  giving the value of  $R_b$  [9]. Ionic conductivity of the samples can be estimated using the sample geometry and the dc resistance at different temperatures.

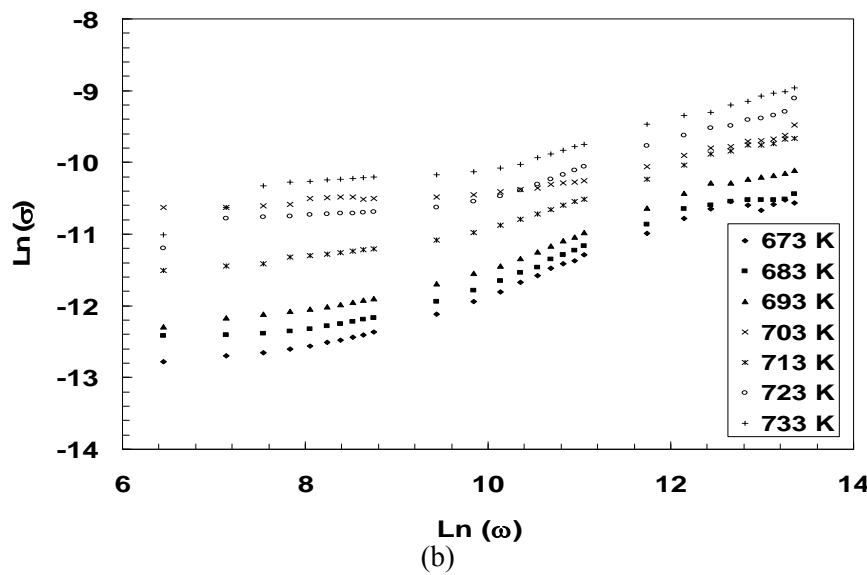
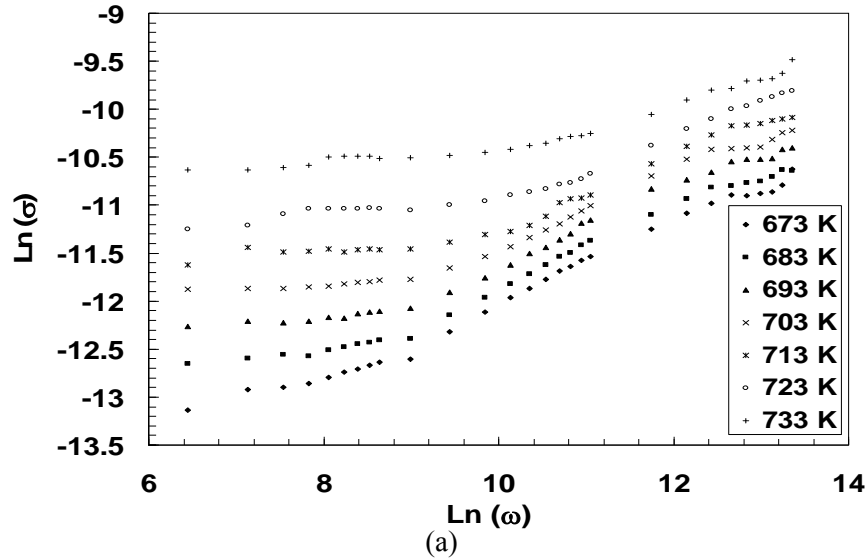
D.C. conductivity measurements for these samples were carried out previously [10]. The analysis of the  $\ln(\sigma_{dc}T)$  versus  $1000/T$  for all samples leads to the conclusion that defects due to  $\text{CaF}_2$  were inserted in the matrix of LKS as interstitial ions for low concentrations of  $\text{CaF}_2$ , while by increasing the concentration of  $\text{CaF}_2$  substitution mechanism dominates.



**Fig. (1):** Complex impedance diagram for pure LKS samples (a), and 0.5% CaF<sub>2</sub>

doped LKS (b) at different temperatures.

The dependence of the ac conductivity on the frequency is illustrated in Fig. (2) for pure LKS and 0.5% doped samples at various temperatures. Similar behavior was observed for the other samples with different concentrations. Figure (2) indicates the existence of three segments with different slopes. The slight kink appearing in most curves and more pronounced at high temperatures are the result of the overlap of the response of the barriers [11].



**Fig.(2):** Frequency dependence of a. c. conductivity for (a) pure LKS sample and (b) 0.5% doped sample at different temperatures.

The relation between the ac conductivity and the angular frequency is given by the relation  $\sigma(\omega) = A \omega^s$  [11], where A is a constant which depends on temperature and s is an exponent parameter. A linear fitting, at the high frequency segment, of  $\ln(\sigma)$  against  $\ln(\omega)$  curves yields straight lines from which the exponent parameter s was estimated. Fig. (3) shows the variation of the frequency exponent parameter s with temperature for pure LKS and doped 0.5% samples. It is clear that s takes values smaller than one; therefore the ac conduction mechanism is of the correlated barrier hopping type [12].

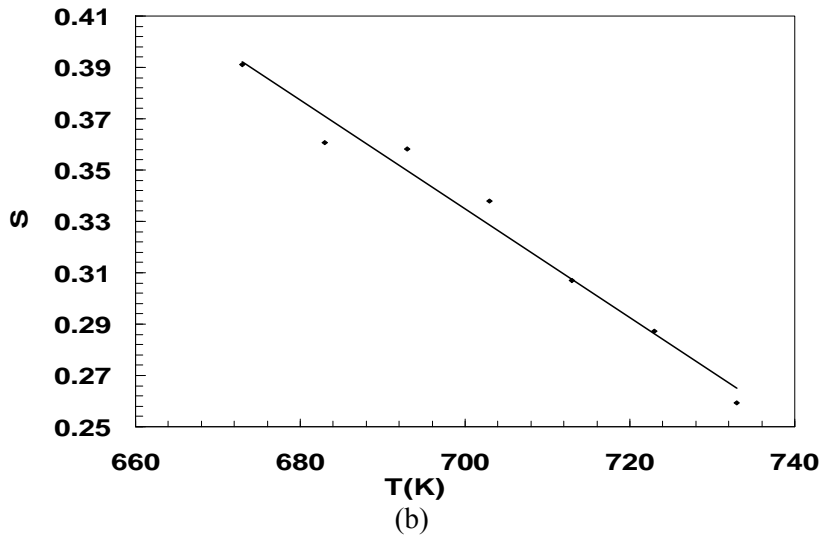
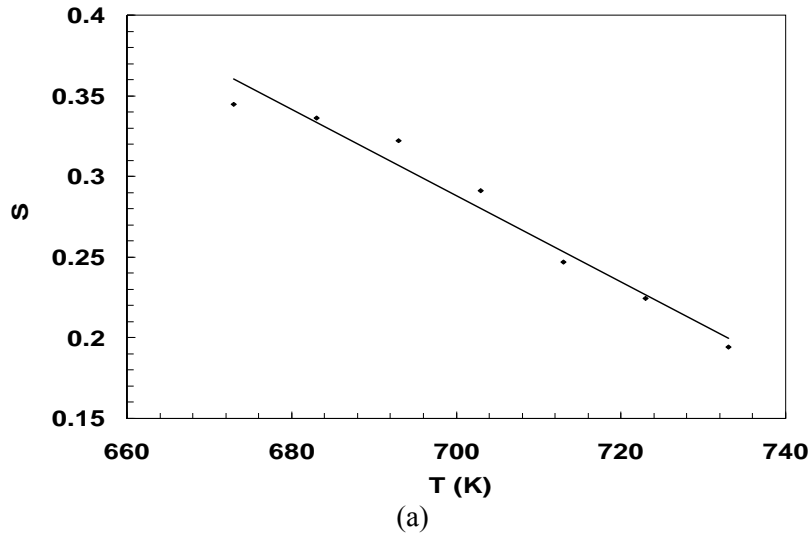
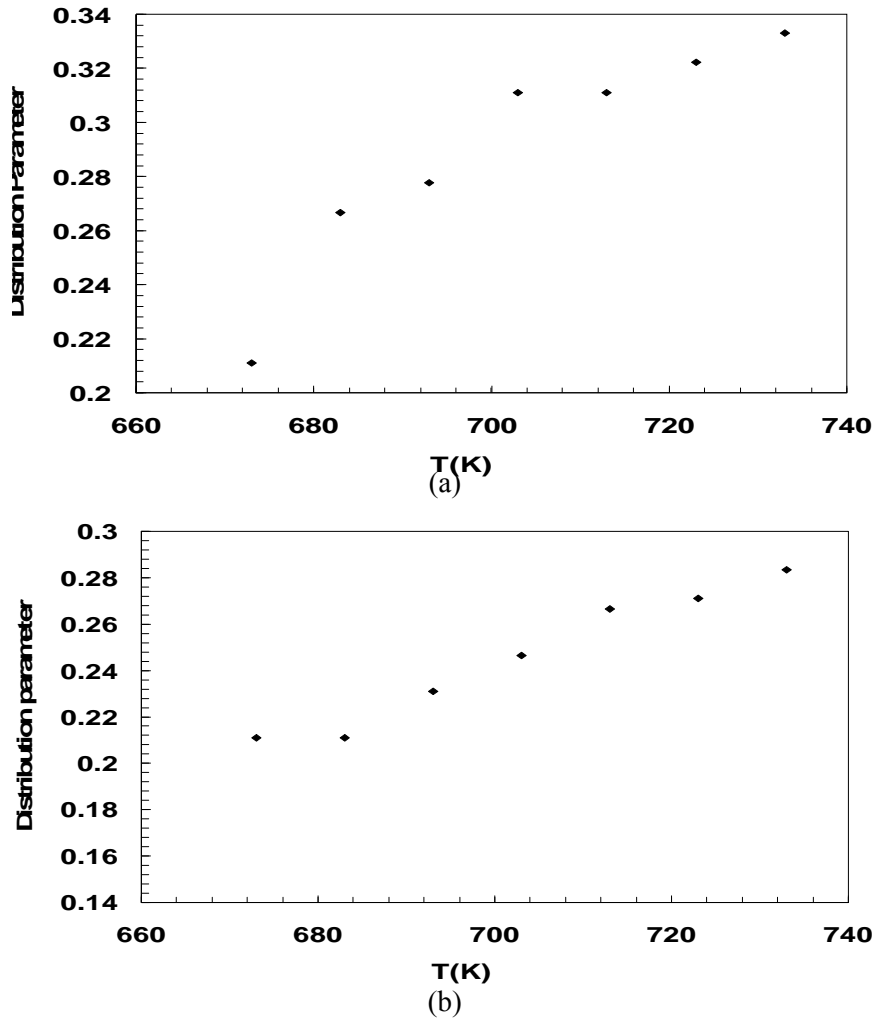


Fig. (3): Temperature dependence of the frequency exponent, s, for pure LKS sample (a) and 0.5% doped sample (b).

The distribution parameter  $\alpha$  was calculated from Cole-Cole diagram (the diameter drawn through the center of the circular arc from the point  $\epsilon_\infty$  makes an angle  $\alpha\pi/2$  with the real axis) [11]. As it is known,  $\alpha$  is equal to zero when the dielectric dispersion has only one relaxation time, whereas for a distribution of relaxation times it varies between zero and one. The variation of  $\alpha$  with temperature for pure LKS and 0.5% CaF2 doped LKS samples is shown in Fig. (4). It is clear that the value of  $\alpha$  increases with increasing temperature. This indicates that the dielectric dispersion is of poly type [13]. The same behavior was observed for all other samples.



**Fig. (4):** Temperature dependence of distribution parameter for (a) pure LKS sample and (b) 0.5% doped sample.

As seen from Fig. (5),  $\alpha$  decreases with increasing  $\text{CaF}_2$  percentage, this could be attributed to the effect of both  $\text{Ca}^{2+}$  and  $\text{F}^-$  ions, which are most probably inserted at interstitial sites, acting as scattering centers. In other words the barrier height for some relaxation mechanisms is increased. Thus the probability of contribution of some relaxation times to  $\alpha$  decreases or even vanishes, which explains the decreasing of  $\alpha$  with increasing  $\text{CaF}_2$  content. Even when the doubly charged  $\text{Ca}^{2+}$  ions occupy substitution positions at high concentrations of  $\text{CaF}_2$ , the value of  $\alpha$  will be decreased due to the increase of the barrier height. Fig. (5) shows the distribution parameter  $\alpha$  versus  $\text{CaF}_2$  concentration.

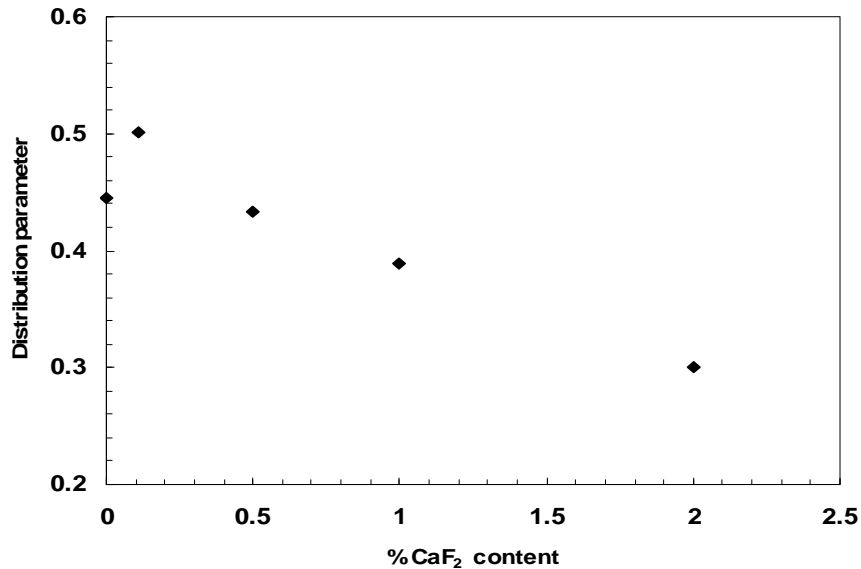


Fig. (5): Distribution parameter ( $\alpha$ ) variation with  $\text{CaF}_2$  percentage.

#### 4. Conclusion:

In the present work the dielectric properties of pure polycrystalline  $\text{LiKSO}_4$  as well as  $\text{CaF}_2$  doped samples were studied at temperatures in the range of (673-733 K). The Cole-Cole diagrams showed semicircles with centers below the abscissa axes which confirm the existence of a distribution of relaxation times. The value of the distribution parameter increases with increasing temperature indicating that the dielectric dispersion is of poly type. The a.c. conductivity for all samples showed strong temperature dependence and it was related to the correlated barrier hopping type mechanism. The dielectric dispersion was found to be influenced by the  $\text{CaF}_2$  dopant where the  $\text{Ca}^+$  and  $\text{F}^-$  ions are most probably inserted as interstitial ions.

**References:**

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