

## Field Dependence of Electrical Conductivity of Powder Compacts of $(KNO_3)_{1-x}Cu_x$ Mixtures

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*The field dependence of electrical conductivity of powder compacts of the mixtures  $(KNO_3)_{1-x}Cu_x$  ( $0.2 \leq X \leq 2 \text{ at.}\%$ ) has been investigated. The current-voltage characteristics at fixed temperatures in the range ( $\approx 30 \leq T \leq 160^\circ \text{C}$ ) were found non-linear. The calculated characteristic length (L) possessed values in the range  $\approx 10^{-5} \text{ cm}$  and proved significant dependence on the content of copper and the conditions of sintering. The significant role of the applied electric field was found to shorten the characteristic length.*

**Introduction:**

The compound is strongly dependent on pressure and temperature;  $\text{KNO}_3$  exists in seven different phases [1,2]. Under atmospheric pressure it exists in three phases depending upon temperature. The ambient phase II has the aragonite structure with four formula units in the orthorhombic primitive cell (space group  $\text{Pnmn} - \text{O}_{2h}^{16}$ ) [3]. Upon heating, phase II transforms at about  $103^\circ\text{C}$  to the high-temperature paraelectric phase, named phase I, which is trigonal, closely related to the calcite structure (space group  $\text{R3m} - \text{D}_{3d}^{16}$ ) [4]. When the crystal is cooled from  $180^\circ\text{C}$ , the inverse transition phase I – phase II does not occur directly, but the crystal changes first to another trigonal, but polar phase, commonly called phase III (space group  $\text{R3m} - \text{D}_{3v}^{16}$ ) [5]. Phase III is metastable at normal pressure, and the crystal transforms again to phase II at  $110^\circ\text{C}$  with cooling to the room temperature. Accordingly [6], phase III is ferroelectric with the polar axis along  $\langle 001 \rangle$  direction (c-axis). The transition temperature of this phase depends upon the history of the sample and the cooling process.

The ferroelectricity in  $\text{KNO}_3$  arises from the fact that the  $\text{NO}_3$  does not lie exactly midway between the adjacent  $\text{K}^+$  planes but are slightly displaced from the center of the unit cell in the c-direction by  $\delta = 0.055 \text{ nm}$  [5]. This displacement is positive in one stack and negative in the neighboring stack giving rise to an antiferroelectric structure with two primitive stack units ( $Z=4$ ) per unit cell [3]. In the ferroelectric rhombohedral structure the polarization is believed to be due to the in phase displacement of triangular  $\text{NO}_3$  ions along the trigonal axis [5]. Sawada et al., [7] have related the spontaneous polarization to the displacement  $\delta$ : assuming unit electric charge for the nitrate ion and using the measured  $\delta$ -value, the resultant spontaneous polarization is  $11 \mu\text{C}\cdot\text{cm}^{-2}$ , which compares very well with their experimental measurements [7]. Besides, Chen and Chernow [8] concluded that there is an ordering of permanent dipoles at the transition I-III.

Wyncke and Brehat [9] proved the possibility of using the  $\text{KNO}_3$  phase III as a thermal detector using the pyroelectric properties of this ferroelectric phase. However, ferroelectrics exhibit the strongest pyroelectric effect and IR sensors using them offer a number of advantages over competing technologies using semiconductors [10].

In this paper, a trail has been made to study the effect of Cu dispersion on the electrical conduction behaviour of the  $\text{KNO}_3$  matrix. Besides, the effects of the temperature of measurements, both temperature and time of sintering and the applied electric field intensity are all taken into consideration.

**Experimental:**

Samples in tablet form of  $(\text{KNO}_3)_{1-x}\text{Cu}_x$  powder mixtures with  $(0.2 \leq X \leq 2 \text{ at.}\%)$  were prepared in a way that they possess almost the same density  $2.12 \pm 0.13 \text{ gm cm}^{-3}$  and thickness  $2.5 \pm 0.12 \text{ mm}$  at the green state as described elsewhere [11]. The contact electrodes were made of graphite. The current-voltage characteristics at different ambient temperatures in the range from room temperature up to  $160^\circ\text{C}$  were measured using a conventional series current circuit. The electrical field across the sample could be changed from 0 up to  $2620 \text{ Vcm}^{-1}$  to test the possibility of field enhancement of conductivity. All measurements were carried out under moderate vacuum ( $\sim 10^{-3} \text{ mmHg}$ ). Isothermal sintering was carried out for different periods of time under the same evacuation. By using temperature controller (Heraeus Type TRK), the fluctuations in the temperatures of both sintering and measurement did not exceed  $\pm 0.5^\circ\text{C}$ .

**Results and Discussion:**

Whatever the amount of copper in the compact, the temperature of measurements (within the considered range) and the conditions of sintering were, the current-voltage characteristics were in general non-linear. Besides, the corresponding double logarithmic relations between the current density (J) and the applied electric field (E) were linear even when the applied electric field strength was extended up to  $2620 \text{ Vcm}^{-1}$ . One example for  $\ln J - \ln E$  plots at different ambient temperatures and at two ranges of field, from 551 to  $1517 \text{ Vcm}^{-1}$  and 1517 to  $2620 \text{ Vcm}^{-1}$ , is illustrated in Fig. (1-a&b). All the plots on this figure are corresponding to green compacts (as-prepared samples) with 2at.%Cu.

The validity of the linear double logarithmic relations between J and E for all the considered mixtures at all the considered temperatures and conditions of sintering proved that, the field dependence of the series current density can be described by the following empirical power equation.

$$J = CE^n \quad (1)$$

For conciseness, values for (n) corresponding to plots on Fig. (1) were only recorded in Table (1). As it is seen, the power n possesses values either slightly smaller or almost equal to unity or higher than unity, indicating the possibility of field inhibition, ohmic behavior and field enhancement of the d.c electrical conductivity  $\sigma$ , respectively:

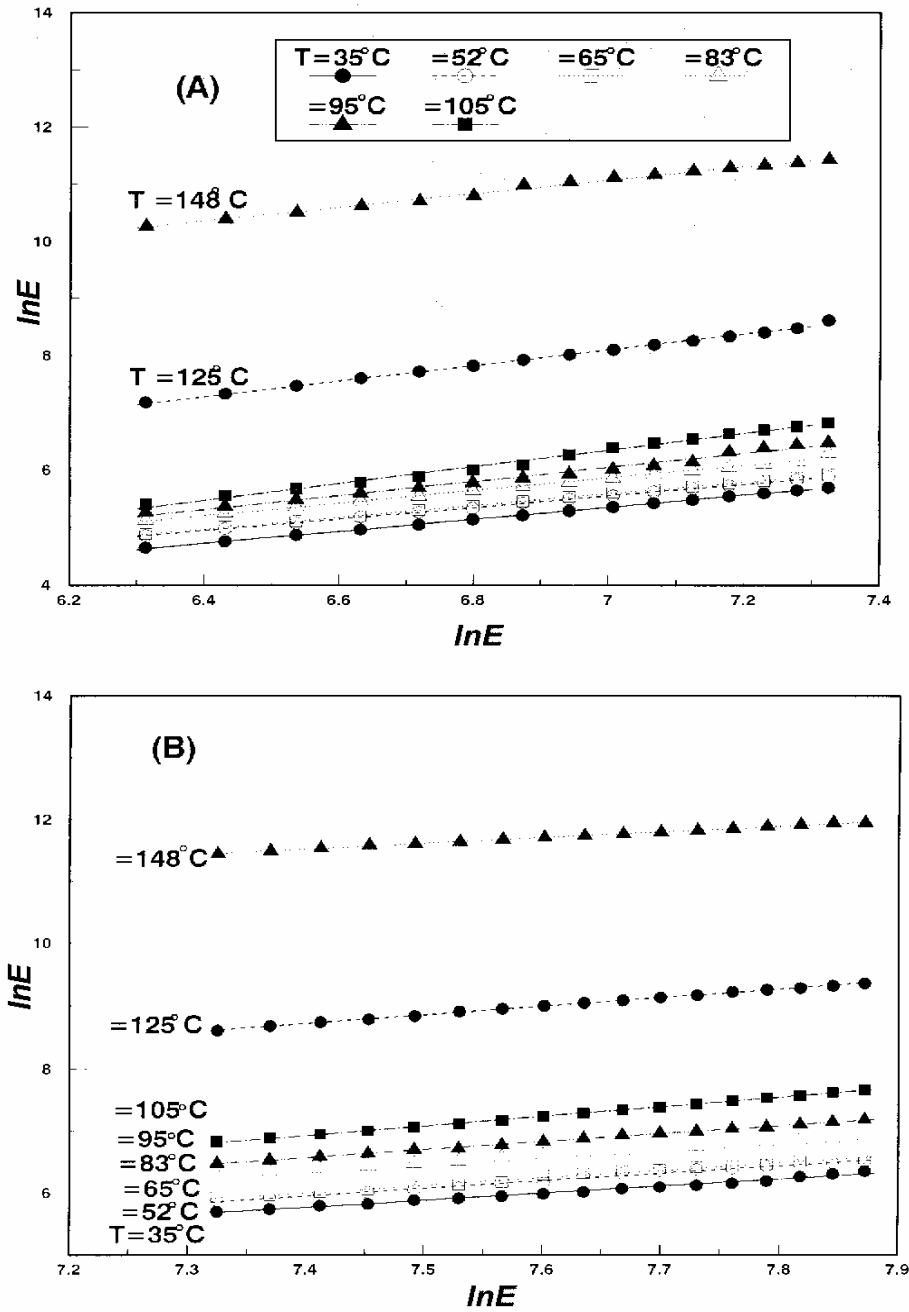
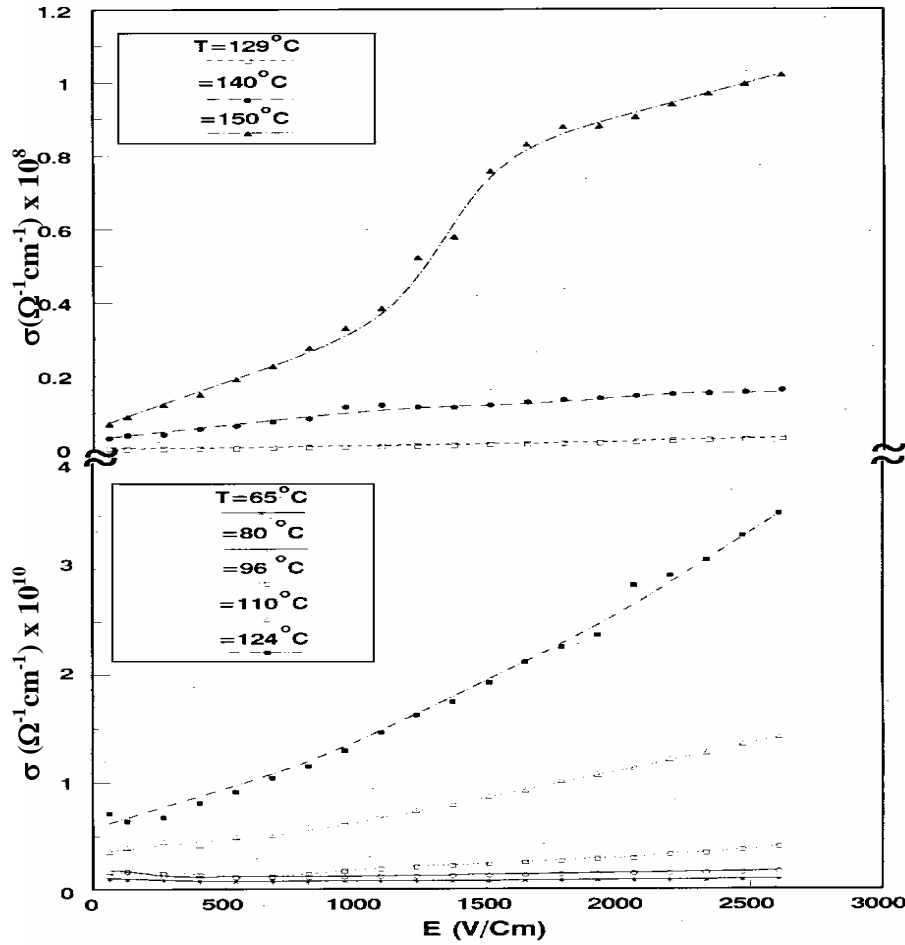


Fig. (1): The  $\ln J$ - $\ln E$  plots at different temperatures for green compact with 2 at.% Cu. A)  $E = 551$ - $1517$  V/cm B)  $E = 1517$ - $2620$  V/cm

**Table (1):** Variation of the power (n) with the ambient temperature ( $T_{am}$ ) and the range of E for green compacts with 2 at.% Cu.

$T_{am}$ °C	n ( $550 \leq E \leq 1517 \text{ Vcm}^{-1}$ )	n ( $550 \leq E \leq 2620 \text{ Vcm}^{-1}$ )
35	0.045	1.1595
54	1.009	1.229
65	1.022	1.22
83	1.092	1.15
95	0.22	1.3
105	1.495	1.55
125	1.366	1.36
148	1.191	0.94



**Fig. (2)** Dependence of dc electrical conductivity on the applied electric field for compacts with 2 at. % Cu sintered for 10 min at 170°C.

The power law dependence of J on E described by eqn. (1) has led to plot, the direct dependence of dc electrical conductivity on the applied electric field. As an illustrating example, results corresponding to compacts of the mixture containing 2 at. % Cu after being sintered at 170°C for 10 min are presented in Fig. (2). In the considered range, 65 ≤ T ≤ 150°C, the results proved the possibility of field enhancement of the electrical conductivity.

Accordingly [12], such behaviour can be described by the eqn.

$$\sigma = \sigma(0,T) \exp\left(\frac{ea(T)E}{kT}\right) \dots\dots\dots(2)$$

where e is the electronic charge, k is Boltzmann’s constant and T is the temperature in Kelvin. Thus, the ln σ vs E plots are expected to be linear. The zero field conductivity σ (0, T) and the temperature dependent characteristic length a (T) (The length of hopping between the grains) could be calculated. To test the validity of Eqn. (2), results on Fig. (2) were replotted in terms of ln σ on Fig. (3a & b). The plots on Fig. (3a & b) cover the whole range of E >500 Vcm<sup>-1</sup>. The range for E below 500 Vcm<sup>-1</sup> was discounted because the field enhancement of σ was either very weak or could not be observed at all. Table (2) contains two values for σ (0, T) obtained from the extrapolations to E = 0 for both ranges of E and also two values for (T) obtained from the slopes corresponding to the two ranges of E at each particular ambient temperatures. As a matter of conciseness, results for the mixture 2 at. % Cu sintered at 170°C for 10 min were only considered in Table (2).

**Table (2):** Variation of σ (0, T) and a (T) with temperature. x = 2 at. %, T<sub>s</sub> = 170°C and t<sub>s</sub> = 10 min.

T <sub>am</sub> °C	500 ≤ E ≤ 1517 V cm <sup>-1</sup>		1517 ≤ E ≤ 2620 V cm <sup>-1</sup>	
	σ (0, T) 10 <sup>-10</sup> Ω <sup>-1</sup> cm <sup>-1</sup>	A(T) 10 <sup>-5</sup> Cm	σ (0,T ) 10 <sup>-10</sup> Ω <sup>-1</sup> cm <sup>-1</sup>	A (T) 10 <sup>-5</sup> Cm
35.5	0.079	0.187	0.072	0.035
80	0.11	0.205	0.11	0.0608
96	0.08	2.45	0.127	0.138
110	0.35	1.96	0.44	0.144
129	0.51	2.81	0.63	0.225
140	5.46	2.15	8.61	0.0908
150	8.64	5.1	53.81	0.091

Results in this table lead to the following conclusions: i) Except for T = 96°C and at 500 ≤ 1517 Vcm<sup>-1</sup> the values for σ (0,T) extracted from the extrapolations of both ranges of E increased with evaluating T. ii) The general trend was also that, values for σ (0, T) corresponding to the higher range of E

are higher than those corresponding to the low range of E, especially in the range  $T_s \geq 96^\circ\text{C}$ . iii) At all the considered temperatures, the values for a (T) reduced drastically (more than one order of magnitude) with transition from the lower to higher range of E. iv) Up to a certain ambient temperature which was relatively higher for the higher range of E, a (T) increased sequentially with increasing T.

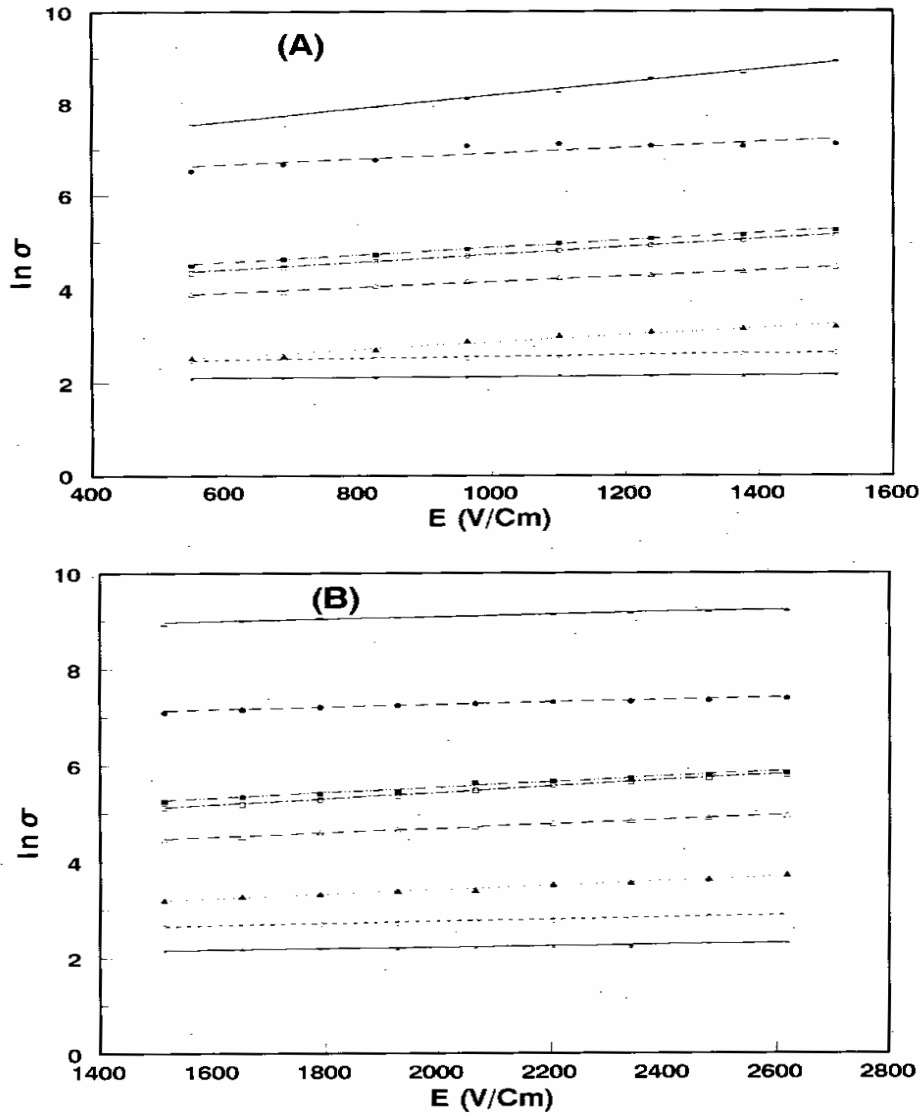


Fig. (3): The  $\ln \sigma - E$  plots at different temperatures for a powder compact with 2 at. % Cu sintered at  $170^\circ\text{C}$  for 10 mins.

Making use of the values for  $\sigma(0, T)$  and the modified model suggested by Grante et al. [11] which is described by the following equation

$$\sigma(E, T) = \sigma(0, T) \exp\left(\frac{eLE}{kT} \left(1 - \frac{T}{T_0}\right)\right) \dots\dots\dots(3)$$

In eqn. (3)  $\sigma(0, T)$  and  $E$  have the same significances as before,  $L$  is the characteristic length and  $T_0$  is a characteristic temperature. The relations between  $\ln(\sigma(E, T)/\sigma(0, T))$  and  $1/T$  were plotted. For the green compacts, Figure (4) shows that in the range  $551 \leq E \leq 1517 \text{ Vcm}^{-1}$ , the characteristic length  $L$  possesses minimum followed by maximum value at  $x = 0.8$  and  $1.4$  at. %, respectively.

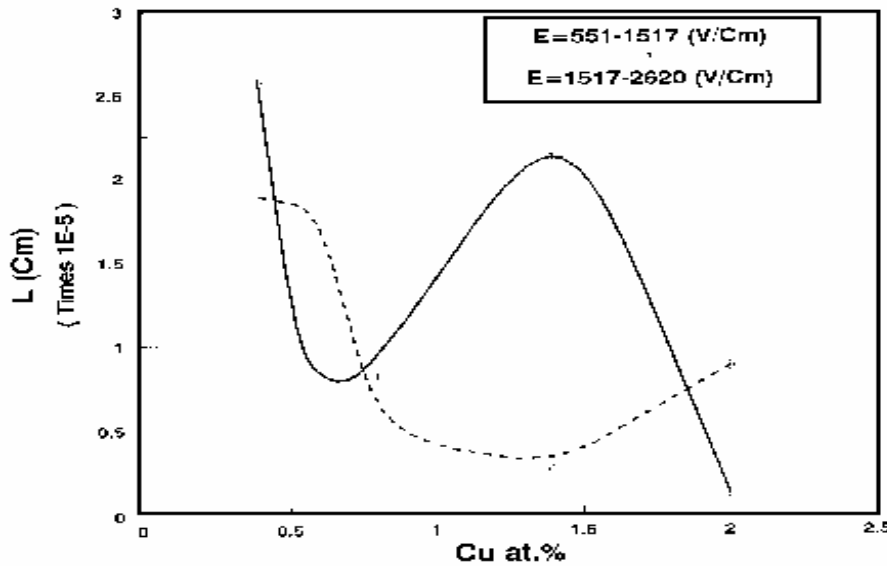


Fig. (4) Variation of  $L$  with the cu content for green powder compact.

Whereas for the range  $1516 \leq E \leq 2620 \text{ Vcm}^{-1}$ ,  $L$  possessed minimum at  $x = 1.4$  at.%. Furthermore, for  $x \leq 0.8$  the effect of  $E$  is confused. However, for  $x > 0.8$  is characterized by significant role of  $E$ , where the latter inhibits much the value of  $L$ . Meanwhile, for both the considered ranges of  $E$ ,  $L$  decreased asymptotically with increasing the content of  $\text{Cu}$  up to the values at which minima attained. On the other hand, where the compacts were sintered at  $170^\circ\text{C}$  for either 5 or 10 minutes as shown in Fig. (5),  $L$  depends on  $x$  in a quite different manner. For  $t_s = 5$  min, despite the dependence of  $L$  on  $x$  seemed relatively weak, the general trend was that, the former decreases with increasing the latter up to  $x=0.8$  at. % for both ranges considered for  $E$ . Thereafter, for the relatively lower range of  $E$ ,  $L$  exhibited a peak at  $x = 1.4$  at. %. In contrast, for



the relatively higher range of E, L showed continuous increase with more enriching with Cu. In the other side, for  $t_s = 10$  mins, for both ranges of E, the behaviour seemed similar and L possessed permanent maximum at  $x = 1.4$  at.%. Such discrepancy between results plotted on Fig. (4&5) reveal beyond doubt the role of sintering on characteristic length.

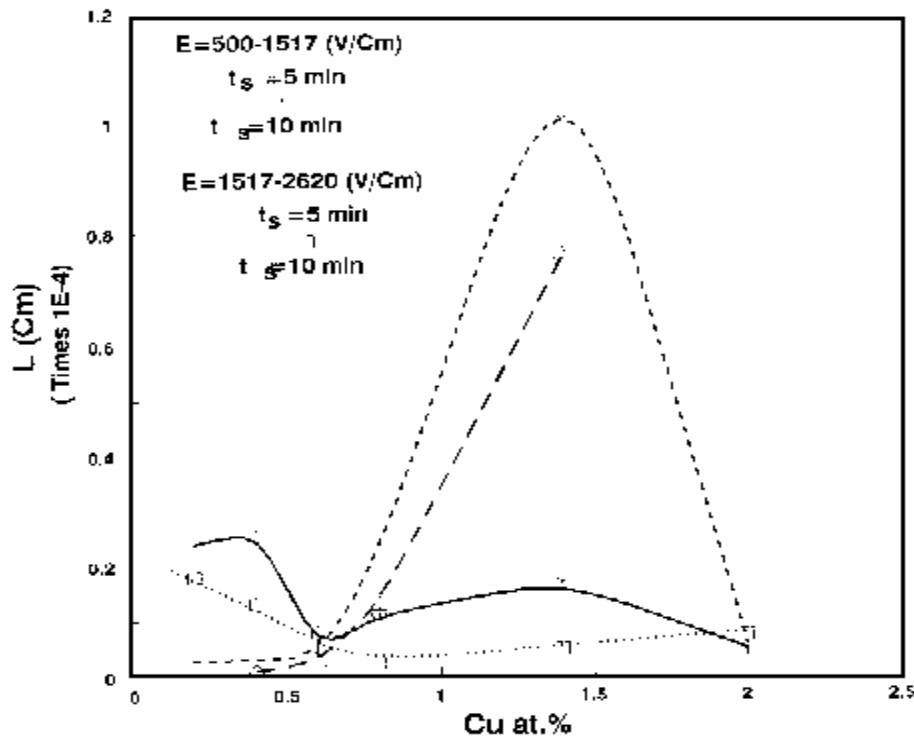
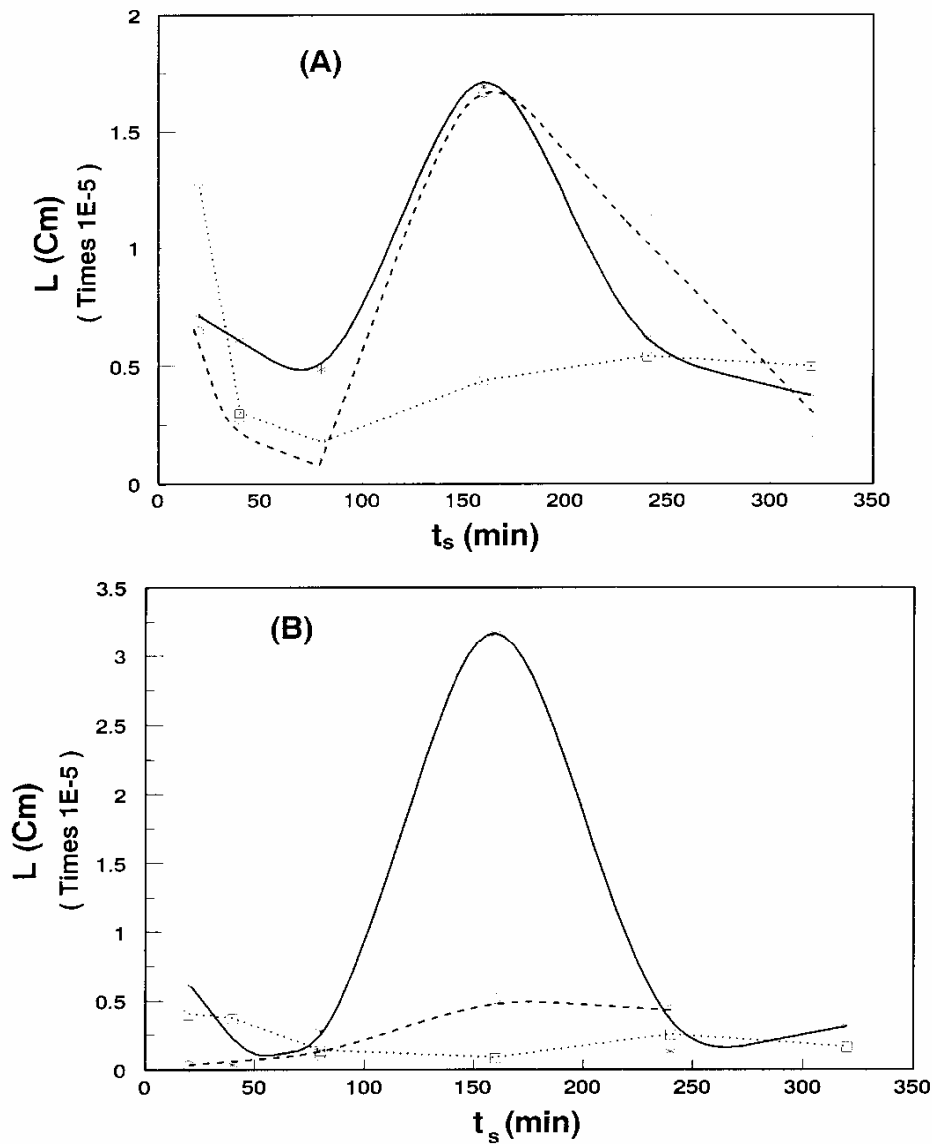


Fig. (5) Variation of L with the Cu content for mixed powder compact sintered at 170°C.

For the mixtures containing 0.4, 0.6 and 0.8 at. % Cu, the variation of L with the time of isothermal sintering at 170°C was as shown in Fig. (6a & b). For the relatively low field, Fig. (6-a), L possessed minimum value for the three mixtures at 80 mins. While for 0.4 and 0.6 at.% Cu, L passed through significant maximum at  $t_s = 160$  mins, it showed continuous increase with more prolongating of  $t_s$  for the third mixture. At the relatively high range of E for  $x = 0.6$  and 0.8 at. %, the general trend was that, L changes very slightly with  $t_s$  over the whole considered period of sintering. In contrast, for  $x = 0.4$  at. % the feature of change of L with  $t_s$  was almost similar to the case at the lower considered range of E.



**Fig. (6)** Dependence of  $L$  on the time of sintering at  $170^\circ\text{C}$   
 A)  $E=500-1517 \text{ (V/Cm)}$ . B)  $E=1517-2620 \text{ (V/Cm)}$ ,  
 $\text{Cu}=0.4 \text{ at.}\%$     $\text{Cu}=0.6 \text{ at.}\%$     $\text{Cu}=0.8 \text{ at.}\%$ .

For compacts of the mixture containing  $0.4 \text{ at.}\%$   $\text{Cu}$  and for both ranges of  $E$ , despite the time of sintering was relatively short ( $t_s = 10 \text{ min}$ ), the effect of  $T_s$  on  $L$  was significant as shown in Fig. (7). The dependence of  $L$  on  $T_s$  seems almost similar in feature for both ranges of  $E$ . Besides, values for  $L$  corresponding to the high range of  $E$  were relatively smaller. Moreover, at the

lower range of  $E$ ,  $L$  has minimum values at both sintering temperatures 110 and 170°C. Besides, within the range  $130 \leq T_s \leq 150^\circ\text{C}$ ,  $L$  showed less sensitivity to the change in  $T_s$ , it seems as a stability region when those temperatures of sintering are considered as transition temperatures. At the higher range of  $E$ ,  $L$  possessed also minima at  $T_s = 110^\circ\text{C}$  and  $150^\circ\text{C}$  despite in the range of  $T_s \geq 120^\circ\text{C}$  the change of  $L$  with  $T_s$  seemed weak oscillatory in feature.

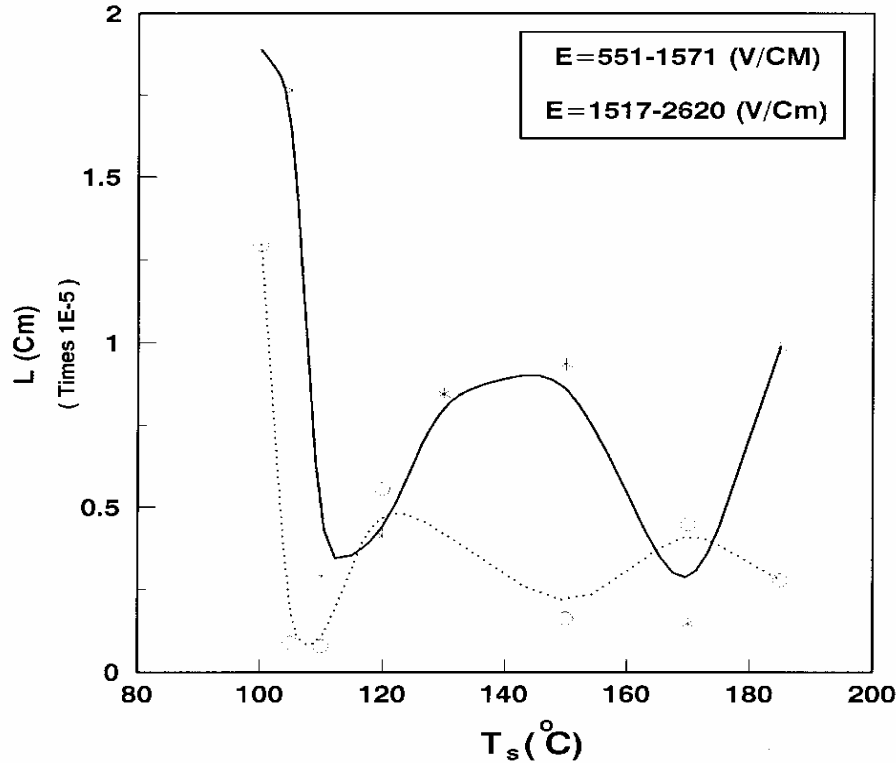


Fig. (7) Dependence of  $L$  on temperature of sintering at  $t = 10$  min for 4 at. % Cu.

### Conclusion:

- 1) Because of the granular structure of the powder compacts, all the current density- electric field characteristics seemed non-linear.
- 2) The content of copper in the compacts and both the time and temperature of sintering were found to have a significant influence on the calculated values of the characteristic length ( $L$ ). Besides, the relatively elevated range of  $E$  was characterized by relatively shorter values for  $L$ . This might reveal a possibility of enhancement of hopping process by the field.

However, values in the range  $10^{-5}$  cm were obtained for L which is about two orders of magnitude smaller than the original particle size in the compacts ( $2r < 60 \mu\text{m}$ ). In other words, it is about two orders of magnitude smaller than the distance between centers of two  $\text{KNO}_3$  particles. Considering that the particles of copper are homogeneously distributed in the  $\text{KNO}_3$  matrix, thus, L can be considered as 4 to 5 orders of magnitude smaller than the distance between two nearest copper particles. This makes hopping between copper sites less probable, and hopping of  $\text{NO}_3$  on the grain boundaries more probable. Besides, the discontinuous change of the electrical conductivity with the sequential change of copper content in the compacts whether green or sintered might confirm this conclusion.

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