

Effect of the Metal Oxides Additives on the Electrical Properties of β -Eucryptite Ceramics

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The dc electrical conductivity and thermally stimulated discharge current (TSDC) studies have been made on pure and modified β -eucryptite with TiO_2 , Fe_2O_3 and CuO in the temperature range 303 – 423 K . The calculated values of activation energy and ionic transference number from dc electrical conduction indicate the presence of ionic character in the investigated samples. The global TSDC spectra studies point to a superposition of dipole orientation and space charge effects. With the aid of the thermal sampling technique, the complex spectrum could be resolved into its elementary processes. The compensation effects is observed to be valid and the values of the compensation temperature and time are found to be 356 K and 1.18 sec respectively.

1. Introduction:

Lithium aluminosilicate has been widely used in the glass and ceramic industry for decades as a lithia-bearing flux and low expansion filler in white ware bodies [1-4]. It is widely known to possess a low coefficient of thermal expansion, relatively good strength, good thermal shock properties [5,6]. Also it has attractive application for ionic conductivity purposes [7] and as a humidity sensor [8].

Polarization effects due to ionic motion in insulators have been studied over many years, by considering the change of the electrical current with time in a sample subjected to dc electric field [9] at a fixed temperature. The technique of thermally stimulated depolarization currents (TSDC) has proved to be most useful in studying the electrical properties of materials, and their variations when the material is subjected to treatments which lead to

configurational changes [10-12]. Besides, using the thermal sampling (TS) technique it is possible to decompose a complex relaxation mechanism into its individual or elementary components allowing the analysis of fine structure of TSDC spectra [13-15].

The present work aims to throw light on the influence of the additive metal oxides on the insulating characteristics of β -eucryptite ceramic, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Thus, a systematic investigation on dc conductivity, TSDC and TS techniques are done in the temperature range 303 – 423 K. The compensation behavior is also studied.

2. Experimental:

β -eucryptite ceramic in the powder form with the formula $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ was prepared by using pure Li_2CO_3 (99.5%) as source of Li_2O , local quartz (from upper Egypt), and pure Kaolin from Montcataire S. E. A Milano as source of both Al_2O_3 and SiO_2 . Three types of metal oxides CuO , Fe_2O_3 and TiO_2 as modifiers were added with percentage 0.05 mole to β -eucryptite. Batches were wet mixed, dried, calcined at 1393 K with heating rate 10 deg/min. Final product was grounded. The obtained sample in the form of disks of 0.3 cm thickness and 1.0 cm in diameter were shaped using semidry pressing technique (80 Kg/cm²) and vitrified in an electric furnace. Detailed preparation technique was reported elsewhere [16].

Differential scanning calorimetry (DSC) measurement was carried out on β -eucryptite modified by Fe_2O_3 from room temperature up to 573 K with heating rate of 10 deg/min.

The electrical measurements of the samples were done on sandwich configuration of the samples using a sample holder of brass electrodes, and the currents was measured using Keithley electrometer model 616.

The global TSDC spectra were done first by heating the sample to a specific polarization temperature of 373 K and by applying electric field strength $E_p = 4.0$ kV/cm for a polarizing period of $t_p = 2$ h. After polarization, the sample was cooled to the room temperature while the field is on. Then, the field was switched off and the sample was shorted for 15 min to remove frictional and stray charge [17], if any.

The TS technique was carried out as the sample was subjected to an electric field, E_p , at temperature, T_p , for a time, t_p , (15 min. was taken as poling time). The sample was rapidly cooled to the lowest desired temperature, T_d , where in our case $T_p - T_d = 10$ deg. After removing the electric field the sample was short-circuited. Then the sample was cooled down to room

temperature and subsequently warmed up by a heating rate of 2 deg/min. while the current is measured.

3. Results and discussion:

3.1. D.C. electrical conductivity

The temperature – dependence of the electrical conductivities σ_{dc} of pure β -eucryptite and modified by CuO , Fe_2O_3 and TiO_2 ceramic powder samples are shown in Fig. (1). It can be seen that the general trend of the conductivity-temperature curves are similar. From these plots, it is seen that all the samples show two regions with changing of slope at different temperatures which are attributed to change in conductivity mechanism [18]. A discontinuous region II, is observed for pure and modified β -eucryptite which may be due to structural changes by weakening of bonds and/or the increase in lattice vibrations [19] vibrations. This is consistent with the diffuse phase transition found in differential scanning calorimetry (DSC), for β -eucryptite modified by Fe_2O_3 shown in Fig. (2). During sintering, the interaction between the various modifiers (Cu^{2+} , Fe^{3+} , and Ti^{4+} ions) and ceramic lattice creates chemical defects and modifies the stress distribution.

Electrical conduction in materials depends on the concentration of charge carriers and their mobility in polycrystalline materials. Several factors such as coordination number of modifier ions, character of the neighbouring oxygen ligands or the state of the polarisability of oxygen anions, whether the modifier metal ion behaves as a network former or a network modifier and valence state of the modifier metal ion are considered to affect the conductivity of the modified β -eucryptite ceramic samples. The additive enters the ceramic lattice network by breaking up the random network (bonds) thus introducing coordinated defects in the network [20]. These bonding defects give rise to electron state within the band gap of the material and these will therefore be localized in that region. The increase of the conductivity on increasing temperature may be attributed to the liberation of more charge carriers from traps or to a greater mobility through the ceramic lattice network. In the low temperature region, the conductivity is more affected by the addition of metal oxides to β -eucryptite ceramics in the order $\sigma(\text{TiO}_2) > \sigma(\text{Fe}_2\text{O}_3) > \sigma(\text{CuO})$. This can be attributed to the decrease of the radii of the additive ions in the order $\text{Ti}^{4+} < \text{Fe}^{3+} < \text{Cu}^{2+}$ [12], since the mean ion spacing decreases with the increasing radius of cations and this raises remarkably the hopping probability.

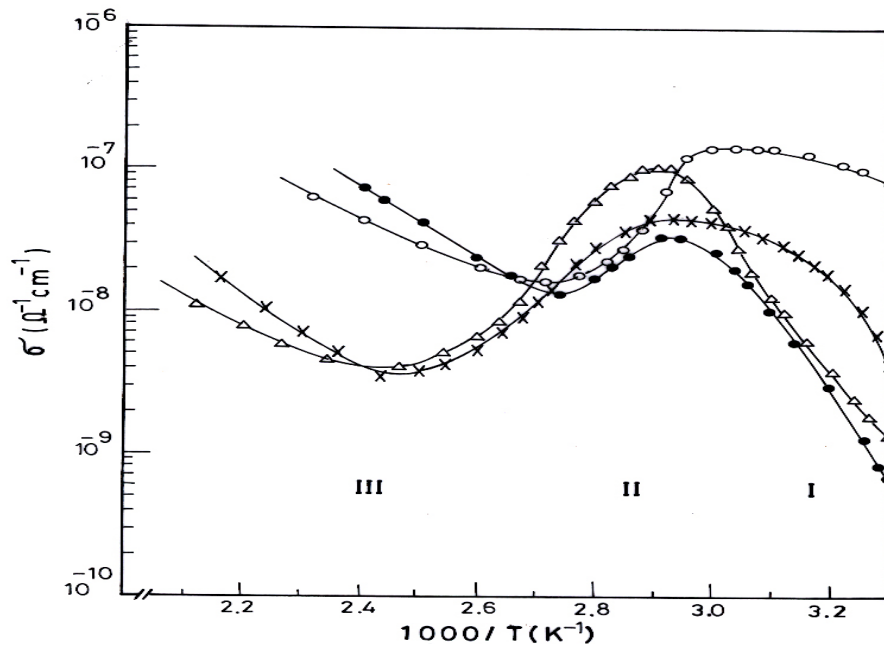


Fig.(1): Reciprocal temperature dependence of dc electrical conductivity under electric field $E=67V/cm$ for pure β -eucryptite (\bullet) and modified by Fe_2O_3 (\times); CuO (Δ) and TiO_2 (\circ) ceramic samples.

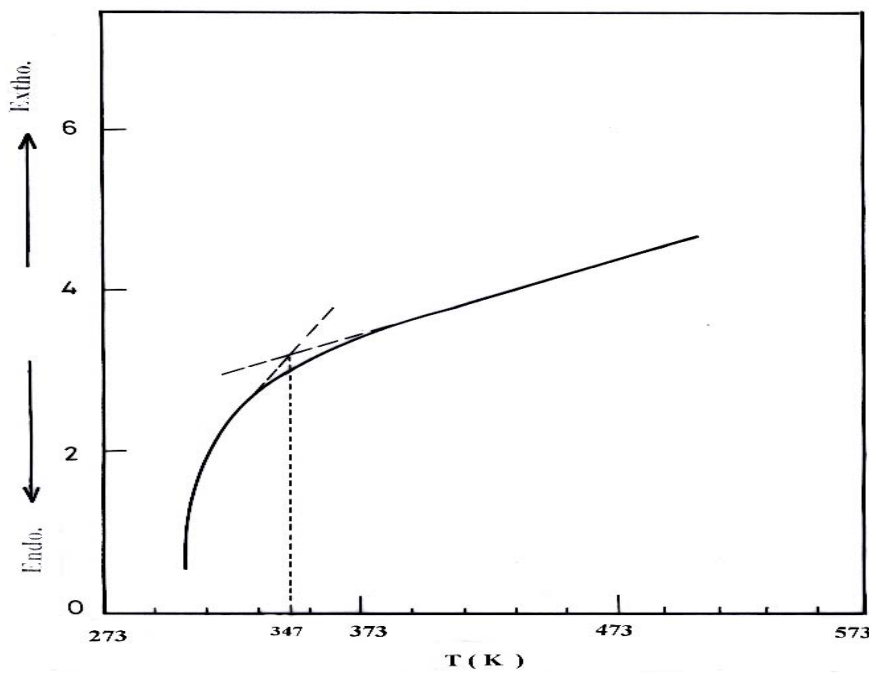


Fig.(2): DSC thermogram of β -eucryptite modified by Fe_2O_3 ceramic sample.

In addition, Li^+ ions are considered solely to be the mobile ones on account of their lower atomic mass unit (6.9) compared to Al^{3+} (26.08) or Si^{4+} (28.08) although of its large size compared to others (radii of atoms 1.586, 1.312, 1.068 Å for Li, Al and Si, respectively) [11,21].

The activation of conduction can be estimated using the relation

$$\sigma = \sigma_0 e^{-\Delta E / kT} \quad (1)$$

where σ_0 is constant, ΔE is the thermal activation energy and k is Boltzmann's constant. The activation energies evaluated for pure and modified β -eucryptite samples are listed in Table (1). It is clear from the values of activation energy and the change of conductivity with temperature in the low temperature region I that the electronic contribution is the predominant process. Thus, thermally activated electronic conduction is represented as a result of ions hopping between thermally created defect pairs or between a relatively high number of available vacant sites disposed at random in ceramic lattice [22]. However, at high temperature region III the conduction mechanism in the samples under investigation may be due to a combined electronic and ionic processes [23,24].

Table (1): Values of activation energy as calculated from dc conductivity measurements

Sample	Activation energy (eV)	
	Region I*	Region III**
Pure β -eucryptite powder ceramic	1.20	0.58
β -eucryptite modified by CuO ceramic	1.04	0.35
β -eucryptite modified by Fe_2O_3 ceramic	0.80	0.54
β -eucryptite modified by TiO_2 ceramic	0.77	0.32

*low-temperature region

** High- temperature region

The total dc conductivity $(\sigma_{dc})_{total}$, of a compound is given by $(\sigma_{dc})_{total} = \sigma_{ion} + \sigma_e$, where σ_{ion} and σ_e are the conductivities due to ion and electron/hole transport respectively. The ionic and electronic transfer number (t_{ion} and t_e) are a measure of extent of ionic and electronic contribution in the total conduction mechanism, where t_{ion} and t_e are defined as [25],

$$t_{ion} = \frac{\sigma_{ion}}{(\sigma_{dc})_{total}} = \frac{I_{ion}}{I_T} \quad (2)$$

$$t_e = \frac{\sigma_e}{(\sigma_{dc})_{total}} = \frac{I_e}{I_T} \quad (3)$$

where I_{ion} , I_e and I_T are the ionic, electronic and total current respectively. The instantaneous value of current at a fixed temperature gives $(\sigma_{dc})_{total}$ and the final stabilized value of it gives σ_e [25,26]. The variation of the current through pure and modified β -eucryptite with time at constant temperature (323 K), and field, $E=83V/cm$, is shown in Fig. (3). It is observed that the passing current decreases with increase of heating time reaching, stabilization after 25min. It is found that t_{ion} has a relatively high values 0.56, 0.96, 0.84 and 0.68 for pure, TiO_2 , Fe_2O_3 and CuO modifier in β -eucryptite respectively. Thus, t_{ion} indicate that the ionic character in the samples under investigation, is dominated.

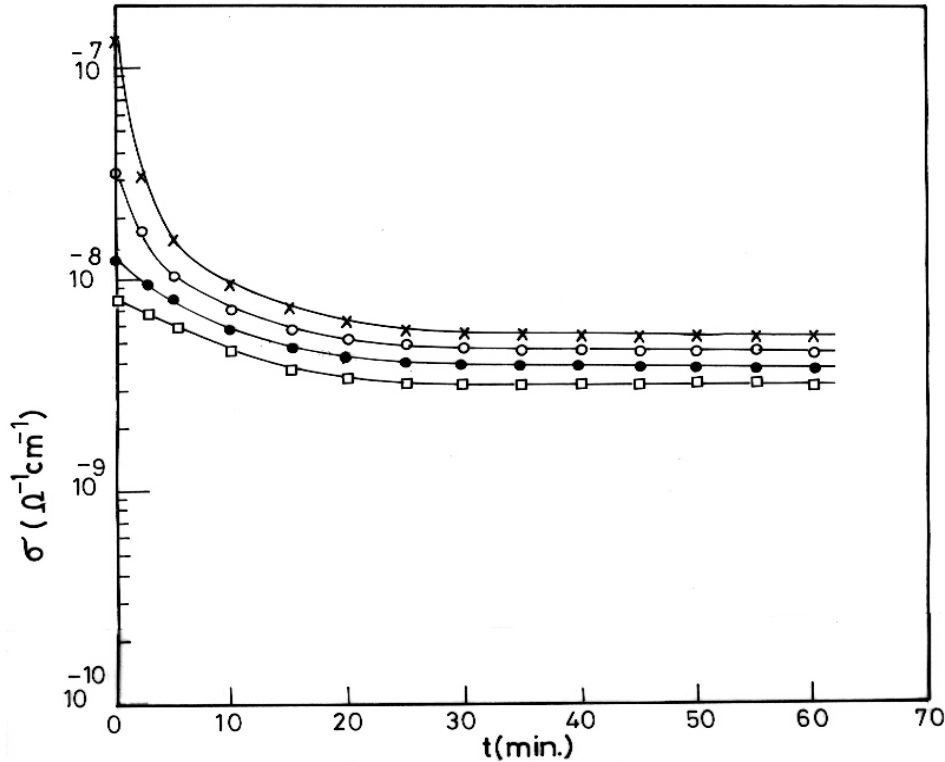


Fig.(3): Variation of current with time at constant temperature (323 K) and field (83V/cm) for pure β -eucryptite (\square) and modified by CuO (\bullet); Fe_2O_3 (\circ) and TiO_2 (\times) ceramic samples.

3.2. Global TSDC Spectra

The trapping and relaxation processes of the charges are intimately related to the physical and chemical properties of the material. Because of this, a study of these processes can provide useful information from the material science point of view [27,28]. During the polarization process, the charge carriers flow from insulator material to metal electrodes, to establish thermal

equilibrium, resulting into depletion-region in the insulator near the electrode [28]. The charge carrier in bulk, contribute to heterocharge while the barrier layers contribute to homocharge [11,29]. Both charges co-exist and are responsible for the electrical conductivity [12]

The thermally stimulated depolarization current is measured as a function of temperature for pure and modified β -eucryptite prepared under the same polarizing conditions ($E_p=4\text{kV/cm}$, $T_p=373\text{ K}$ and $t_p=2\text{h}$). The TSDC thermograms Fig. (4), are found to consist of single, broad pronounced peak, while for the modified β -eucryptite have in addition a shoulder in the high temperature side. It is to be pointed out that a TSDC peak is a consequence of depolarization process, and that the area bounded by the peak and the abscissa is proportional to the total relaxed charge due to the overall relaxation process. Thus the relaxation processes should be described by distribution of relaxation times with different activation energies for each element.

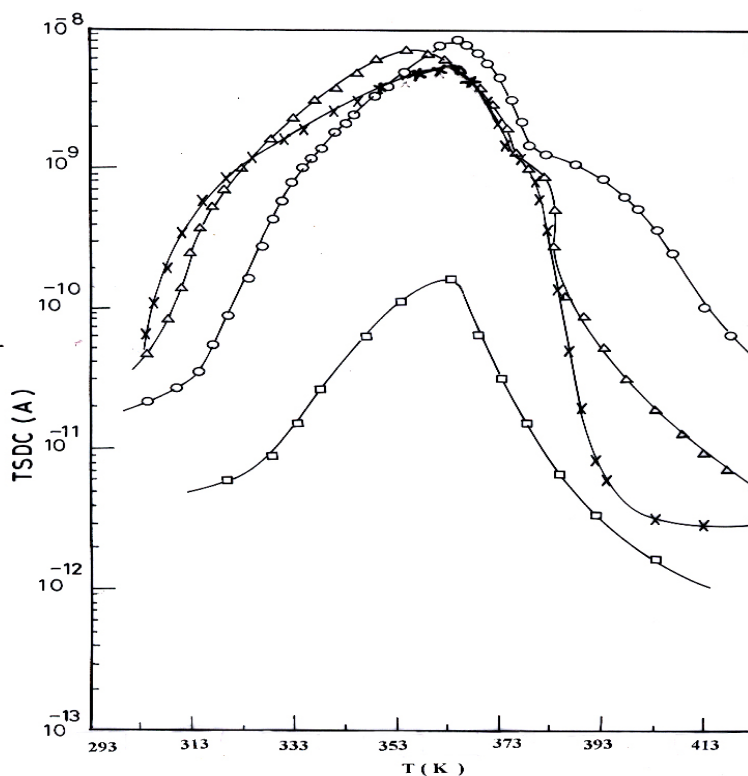


Fig.(4): TSDC thermogram of polarization field $E_p= 4\text{kV/cm}$, polarization temperature $T_p=373\text{ K}$, polarization time $t_p=2\text{h}$ for pure β -eucryptite (\square) and modified by CuO (Δ); TiO_2 (\circ) and Fe_2O_3 (\times) ceramic samples.

The broadening of the relaxation peak, in terms of the width at half maximum, for modified β -eucryptite samples are higher than pure one in the order $\text{TiO}_2 > \text{Fe}_2\text{O}_3 > \text{CuO}$. The increase in the width with the addition of metal oxides may result from the non-uniform nature of this process and a change in the distribution function of the associated relaxation times. Also, the height of current maximum, I_{max} , for the modified β -eucryptite samples are higher than pure one but in the order $\text{TiO}_2 > \text{CuO} > \text{Fe}_2\text{O}_3$. The location for temperature of the maximum intensity T_m , is nearly constant at about 363 ± 2 K for all samples except for CuO modifier is at 353 ± 2 K. From these behaviours we might conclude that there are more than one response in the experimental spectra and more than one competing thermally activated processes strongly overlapping in the hexagonal bipyramidal crystal structure of β -eucryptite [30]

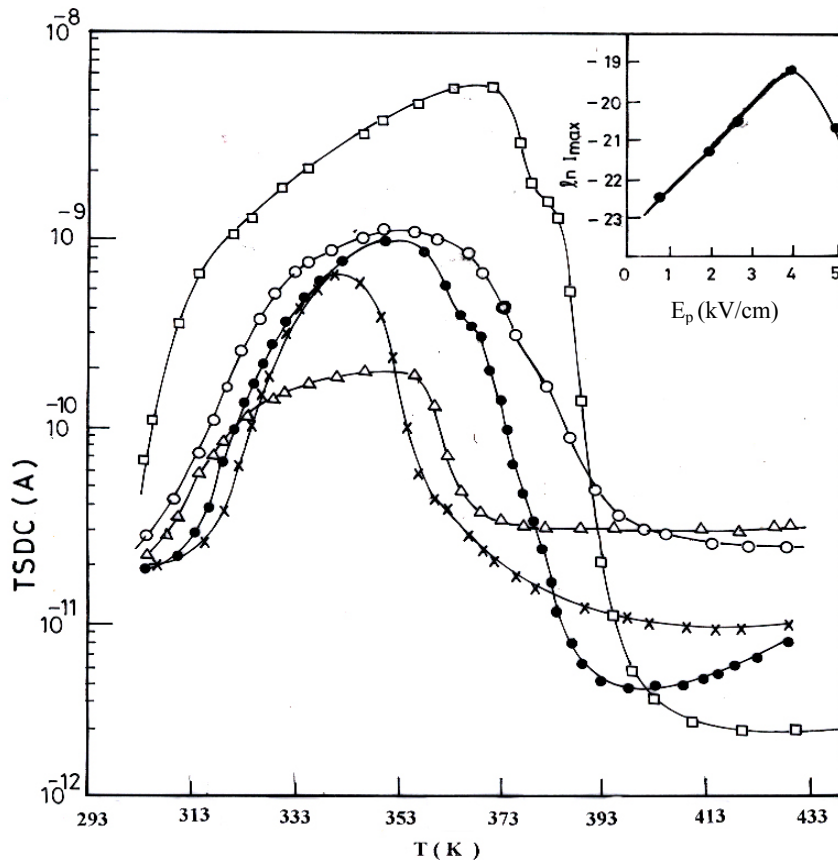


Fig.(5): Effect of polarization field $E_p = 1\text{ kV/cm}$ (Δ), 2 kV/cm (\times), 3 kV/cm (\circ); 4 kV/cm (\square) and 5 kV/cm (\bullet) for pure β -eucryptite modified by Fe_2O_3 ceramic sample at polarizing temperature $T_p = 373$ K and polarizing time $t_p = 2\text{ h}$.

The dependence of the TSDC peak on the polarizing field, E_p , in the range 1-5 kV/cm is investigated only for β -eucryptite modified by Fe_2O_3 (see Fig. (5)). The inset of Fig. (5) indicate that the dependence of I_m on E_p shows clear deviation from linearity expected for uniform polarization. Therefore the origin of TSDC peak may be caused by metastable defects in crystalline system. These defects form dipoles in β -eucryptite modified by metal oxides. One can expect the formation of positively and negatively charged, non-bridging oxygen as well as triply bonded oxygen ions in the investigated samples. These dipoles share in the electrical polarization. In addition, a space charge may contribute to the electrical polarization depending upon the molecular packing within the samples under investigation. Since the packing of a modified ceramic might not be uniform as that of crystalline β -eucryptite, it is reasonable to expect dispersion due to molecular motions in the material. Physically, more complex behaviour of TSDC is obtained from a process involving space charge polarization, since generally the build-up release and equilibrium spatial distribution of the charges are strongly dependent on the applied voltage. When a carrier injection occurs, with or without subsequent trapping, one may predict a more or less complicated non-ohmic behaviour due to inefficient transport, potential-dependent injection or potential-dependent rate of detrapping [28, 31-33].

3.3. Thermal Sampling (TS) Spectra

The different discharge in the TSDC spectrum has been extensively studied by the thermal sampling technique, which allow us to polarize narrow segments of the whole thermocurrent spectrum and, thus, to separate the complex global peaks into its components. The application of the TS polarization technique results in quasi-non distributed peaks, so that interpretation of the resulting spectra is easier than the depolarization discharge which is obtained from conventionally polarized electret [13,14].

Seven representative TS spectra at polarizing temperature 323-383 K with a temperature window 10deg for β -eucryptite modified with Fe_2O_3 are shown in Fig. (6). It is evident that the peak intensities shown roughly trace out the shape of the global TSDC spectrum except TS spectra at $T_p=373 \pm 2$ and 383 ± 2 K. TS spectra are characterized by a linear relationship between the peak maximum temperature T_m , on the poling temperature T_p , as shown in the inset of Fig. (6). The slope of the line approaches unity, in a good agreement with the theoretical prediction for continuous distribution [34].

Fractional integration of each TS spectrum was performed using [34,35]:

$$\ln \tau(T) = \ln \left\{ \int_{T_0}^T J(T) dT \right\} - \ln J(T) \quad (4)$$

The relaxation times $\tau(T)$ are obtained by integrating the first half of the peak using Bucci method [36] and are plotted on an Arrhenius plot. In Equation (4) J is the depolarization current, T_0 is the initial temperature of the TS depolarization scan and T is the final temperature. Because the integration method is only an approximation, each TS spectrum is only integrated up to the maximum current. Relaxation times are typically analyzed using the Arrhenius equation [28]:

$$\tau(T) = \tau_0 e^{E_a/KT} \tag{5}$$

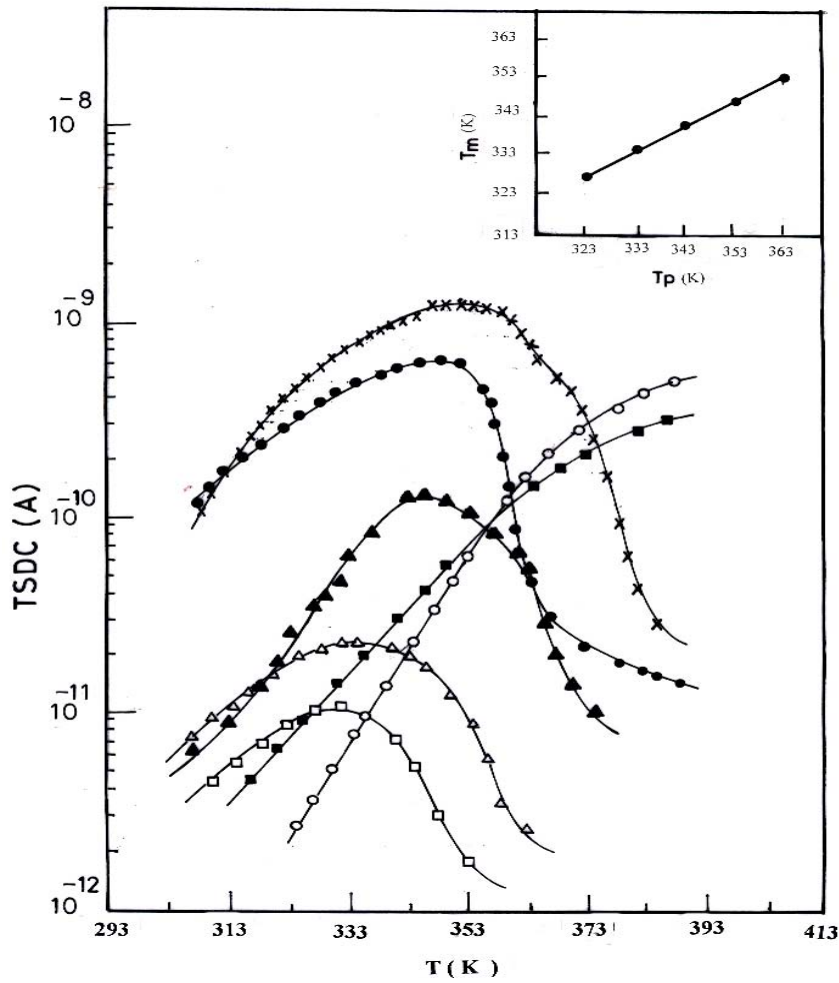


Fig.(6): TSDC of windowing polarized β -eucryptite modified by Fe_2O_3 ceramic sample, $t_p=15$ min. ; $E_p=4kV/cm$, T_p : 383 , 373 (0), 363 (X), 353 (●), 343 (▲), 333 (Δ) and 323 K (□).

Here τ_0 is the pre-exponential factor, E_a is the apparent activation energy, and k is the Boltzmann's constant. Each TS spectrum (except that found at $T_p = 373$ and 383 K) results in one Arrhenius line of relaxation times after numerical integration. Several representative Arrhenius lines thus obtained are shown in Fig. (7). Each line is characterized by nondependent parameters; its activation energy E_a , and the pre-exponential factor τ_0 , in the Arrhenius terminology. It is known that the relaxation lines such as these, there is an increase in slope (E_a is proportional to slope) as one approaches the phase transition. If the logarithm of the pre-exponential factor τ_0 varies linearly with the activation energy, one observes a compensation law.

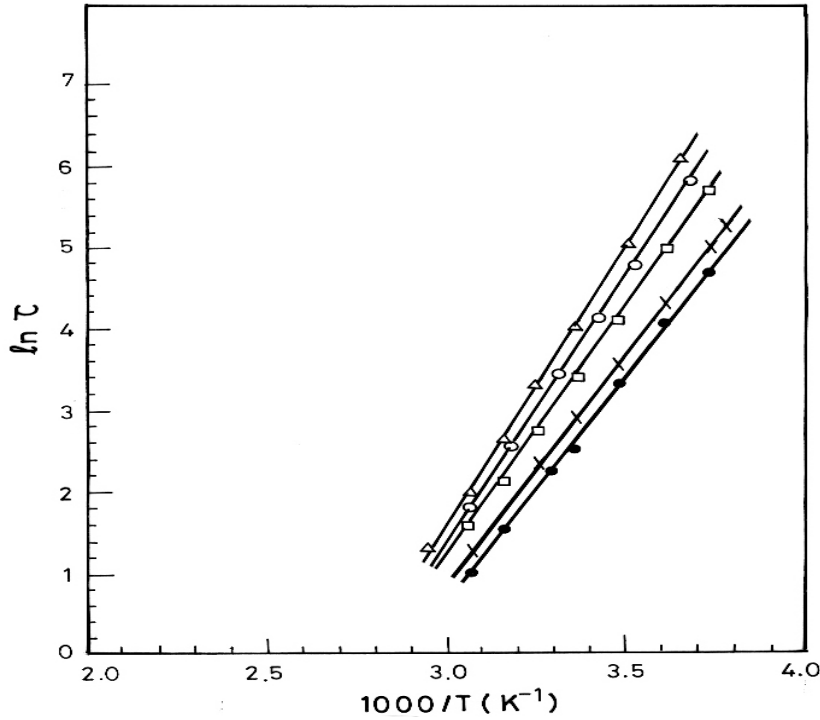


Fig.(7): Bucci lines ($\ln \tau$ Vs. $1000/T$) for pure β -eucryptite modified by Fe_2O_3 ceramic sample corresponding to the TS processes, T_p : 363(Δ); 353(0); 343 (\square); 333 (X) and 323 K (\bullet).

$$\tau_0 = \tau_c e^{-E_a/kT_c} \tag{6}$$

Where τ_c and T_c are known to represent compensation time and compensation temperature, respectively.

Then equation (5) can be expressed as:

$$\tau(T) = \tau_c \exp \left[\frac{E_a}{k} \left(\frac{1}{T} - \frac{1}{T_c} \right) \right] \tag{7}$$

The slope of the plot $\ln \tau_0$ versus E_a gives the reciprocal compensation parameter ($-1/kT_c$), and the intercept is related to the compensation time ($\ln \tau_c$). These values are found to be $\tau_c = 1.18$ sec and $T_c = 356$ K which transcribe the coupling characteristics between the different modes of relaxation as observed by individual activated processes in the set of Arrhenius lines. The most interesting outcome to be drawn from Fig. (8) is that all elementary processes for modified β -eucryptite by Fe_2O_3 can be ascribed to a dipolar polarization. On the other hand, the two exceptional cases done at polarizing temperatures 373 and 383 K may be attributed to space charge associated with the release of the trapped charge carriers and/or carrier injection. The fact that the dipolar mechanism is faster than space charge polarization mechanisms can be explained as follows: the dipole rotations are local motions and after these local interactions are formed in different ways in the ionic regions by enabling the separated charges "ions" to migrate through the intracuster regions and by means of thermal energy by increasing the temperature.

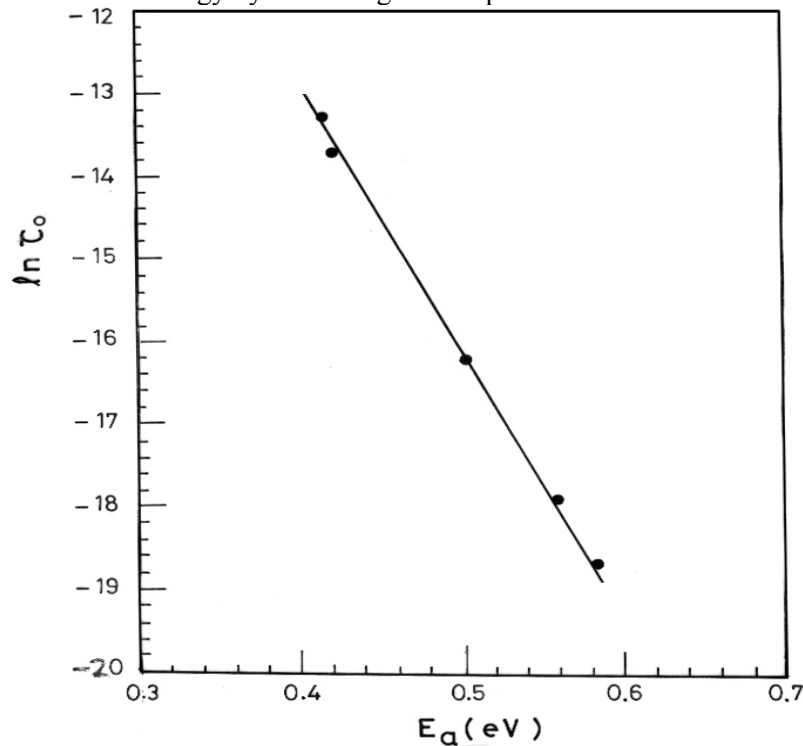


Fig.(8): Variation of the pre-exponential factor of relaxation time (τ_0) Vs. the activation energy (E_a) for the TSDC of β -eucryptite modified by Fe_2O_3 .

4. Conclusion:

Metal oxides have been shown to be suitable additives for β -eucryptite ceramic, leading to significant improvements of electrical conductivity and thermal stimulated depolarization current. The addition of any modifier (TiO_2 , Fe_2O_3 , and CuO) in β -eucryptite ceramic network increases both σ_{ac} and TSDC with temperature. The origin of observed TSDC peaks in all samples is related to polarization caused by the combined effect of the intrinsic dipolar defects and space charge. The increase of conductivity at temperatures below the transition temperature is mainly due to the ionic carriers in the materials under investigation.

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