

# Effect of interlayer exchange interaction and rare earth dilution on the electrical properties of two-dimensional system

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The dielectric permittivity ( $\epsilon'$ ) of the organic complexes of the general formula  $(\text{CH}_2)_n(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$ ,  $n = 5, 6, 7$  and  $0.1 \leq x \leq 0.9$  was studied at different temperatures as a function of the applied frequency. The obtained results contain more than one phase transition depending on the  $\text{La}^{3+}$  ion concentration as well as the applied frequency. The appeared transitions were of thermochromic type (change in crystal symmetry) because it gives a reversible color change with temperature. Varying the layer spacing by varying the number of carbon atom ( $n$ ) will change drastically the permittivity of the sample, due to varying the superexchange interaction through the intervening of the organic group. The AC conductivity for the investigated samples was measured in the same range of temperature and frequency as that of permittivity measurements. The calculated values of the activation energy indicate the semiconducting behavior of these complexes. More than one conduction mechanisms were obtained as indicated from the existence of more than one straight line. Hopping mechanism was the most predominant one that interprets the conductivity in the low temperature region. In the moderate region of temperature the holes play a role. In the high temperature region we expect some ionic conduction which was clear from the high values of activation energy. © 2003 Kluwer Academic Publishers

## 1. Introduction

Recently, the study of the structural phase transitions in the quasi-two-dimensional systems has been a subject of great interest, since this study lead to a great understanding of the physics of magnetism [1], conductivity [2] and other phenomena [3]. These phase transitions appear at temperatures near the ambient have been studied by a variety of experimental techniques, including magnetic susceptibility [1], electrical conductivity [2], nuclear magnetic resonance [4], fluorescent probe parameters [5], X-ray diffraction, differential scanning calorimetric (DSC) [6] and laser Raman spectroscopy [7].

Compounds of the alkylene diammonium family of the general formula;  $(\text{CH}_2)_n(\text{NH}_3)_2\text{MCl}_4$ , where  $n = 2, 3, \dots$  and  $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \dots$  are considered to be a quasi-two-dimensional Heisenberg antiferromagnets and can be grouped as a member of perovskite layered type crystals [8]. They formed of metal-halogen layers, separated from each other by organic groups. The spin ordering in each layer is antiferromagnetic, while the layers are coupled ferromagnetically with each other. This ferromagnetic coupling and consequently the

super exchange interaction was decreased by increasing the layer spacing either by introducing halogen of larger radius or by increasing the number of carbon atoms in the series i.e., increasing  $n$ . Also the super exchange interaction will be affected by changing the type of the metal ion in the layer.

The metal ions in the layer interact directly with each other taking into consideration the nearest neighbor or the next nearest neighbor and so on, giving rise to what is we called short range or long range order interaction, respectively. In addition, metal ions are not exactly in the halogen plane, but arranged regularly one up and one down, thus the metal-halogen-metal bridging angle is not linear and the forward and backward tipping of the octahedra are produced and give what is called puckering effect of the layer [9]. On varying this puckering by an external means such as the frequencies applied to the samples, or the use of different metal ions of different size, the interaction within the layer will be changed in comparison with that between layers thus, the total interaction, either electric or magnetic, is the sum of two types of interactions, one of them is the interlayer and the other is the intralayer interaction.

The effect of layer spacing on the electrical conductivity of  $(\text{CH}_2)_n(\text{NH}_3)_2\text{FeCl}_4$  [2];  $n = 8, 9$  and  $10$  is to decrease the number of charge carriers as well as the interaction between the layers. This will increase the energy barriers and consequently increases the conductivity within the layer.

The effect of dilution (gradual substitution of  $\text{Cd}^{2+}$  by  $\text{Fe}^{2+}$ ) on the electrical properties of  $(\text{CH}_2)_n(\text{NH}_3)_2\text{Fe}_x\text{Cd}_{1-x}\text{Cl}_4$  [10];  $n = 8$  and  $x = 10, 20, 30, 40, 50, 60$  and  $72$  mol% were measured in the temperature range including their phase transition, where it is found that, the dielectric constant increases with increasing iron content.

The present work was designed to investigate the effect of interlayer spacing and magnetic dilution (gradual substitution of  $\text{Mn}^{2+}$  by  $\text{La}^{3+}$ ) on the electrical properties of  $(\text{CH}_2)_n(\text{NH}_3)_2\text{La}_x\text{Mn}_{1-x}\text{Cl}_4$  complexes;  $n = 5, 6, 7$  and  $0.0 \leq x \leq 0.9$  and to correlate the obtained results with the percolation theory proposed by Monte Carlo group [12]. Such studies also give us information on the dominant types of charge carriers and the mechanism of its migration.

## 2. Experimental

The investigated samples have been prepared using analytical grade chemicals (BDH) according to the procedure mentioned by Remy and Laves [12]. Preparation was carried out by dissolving stoichiometric amounts of diammonium halide  $(\text{CH}_2)_n(\text{NH}_3)_2\text{Cl}_4$  ( $n = 5, 6$  and  $7$ ),  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  in triply distilled water. The mixture was heated on water bath at about  $80^\circ\text{C}$  for about 2 h, after which a sudden cooling was achieved to precipitate the sample. The obtained plate like crystals were filtered, washed with a mixture of ether and ethanol (in ratio 2:1) to remove traces of unreacted diammine and then dried in a vacuum desiccator.

Powder pellets of 1.3 cm in diameter and nearly 1.5 mm thickness was prepared under a pressure of  $5 \text{ tone cm}^{-2}$ . The two surfaces of each sample were polished and coated with silver paint (BDH) and checked for Ohmic contact. The relative permittivity as well as the ac electrical conductivity were measured using Hioki 3530 (Japan) with well-shielded cables at frequencies of 100, 200, 400, 600, 800 and 1000 kHz.

The temperature of the sample was measured using a T-type thermocouple just in contact with the sample to avoid any temperature gradient. The accuracy in measuring temperature is better than  $\pm 1^\circ\text{C}$  and in ac measurements is  $\pm 1\%$ .

## 3. Results and discussion

Fig. 1a–d is a typical curve represents the dielectric constant  $\epsilon$  against absolute temperature as a function of the applied frequency (100–1000 kHz) for the complexes  $(\text{CH}_2)_6(\text{NH}_3)_2\text{La}_x\text{Mn}_{1-x}\text{Cl}_4$ ;  $0 \leq x \leq 0.9$ . The general trend of the data for all investigated samples is the increase in  $\epsilon$  with increasing temperature passing by the different transitions. In Fig. 1a where  $x = 0.1$ , three transitions at about 335, 395 and 433 K are obtained.

The first transition is attributed to the structural phase transition, which is accompanied by a reversible color change with temperature, which needs small thermal energy to be achieved. This structural phase transition was appeared in all investigated samples but shifts in position depending on the  $\text{La}^{3+}$  ion concentration. The peak position shifts to lower temperature with increasing the applied frequency. By increasing the lanthanum content from 0.1 to 0.3, the structural phase transition was shifted to higher temperature and appeared sharply, while the step transitions at 395 and 433 were shifted to 430 and 460 K respectively. The intensity of the step transition as well as the background representing the dielectric constant above 500 K was decreased. A peculiar behavior was observed at  $x = 0.5$  where the intensities of the dielectric constant peaks were increased and the last transition (step one) becomes hump and shifted toward higher temperature (595 K). In addition, the structural phase transition, which was appeared sharp at lanthanum content, less than 0.5 becomes broader. This peculiarity may be attributed to the effect of the critical concentration ( $x = 0.5$ ) according to the percolation theory [11]. By increasing the La content than 0.5 Fig. 1d the thermochromic transition decreases in value while the step transition becomes peak. This may be due to the direct effect of the  $\text{La}^{3+}$  ions on the structure of the system, where the main skeleton is due to La and the perturbation is due to Mn content. Generally, the increase in the dielectric constant ( $\epsilon$ ) with increasing temperature was ascribed to both the thermal energy and the applied electrical field, where the small thermal energy liberate the localized (frozen) dipoles and the applied electric field aligned them in its direction. This process increases the polarizability as well as  $\epsilon$ . This behavior was very clear before each transition. After each transition, the dielectric constant decreases due to the predominance of the thermal energy on the applied electric field with the result of decreasing  $\epsilon$ . The second transition for all samples is expected to be order-disorder transition, which need higher energy than the first one. The third transition is considered as a chain melting one, which vary in position from one sample to another.

Comparing the data from Fig. 1a–d one can find that, the dielectric constant decreases with increasing La content up to  $x = 0.3$  and reaches maximum value at  $x = 0.5$  which is considered as a critical concentration after which the La behaves as a separate lattice and not as an impurity atom. On increasing the La content the polarization will be hindered partially and the dielectric constant decreases until reaching about 25 at  $x = 0.9$  as in Fig. 1e. At room temperature the value of the dielectric constant for the complex with  $x = 0.0$  is 20 while, that at  $x = 0.1$  is about 93. This behavior can be explained as follows: the first ionization potential of  $\text{Mn}^{2+}$  (7.435 eV) is greater than that of  $\text{La}^{3+}$  (5.577 eV) though, the energy required to remove an electron from the half filled  $3d^5$  of manganese is greater than that required to remove a single  $5d^1$  electron of lanthanum. The result of this process is the increase in the polarizability for the complex with  $x = 0.1$  than that with  $x = 0.0$  as can be seen also from Fig. 1c. In other words,

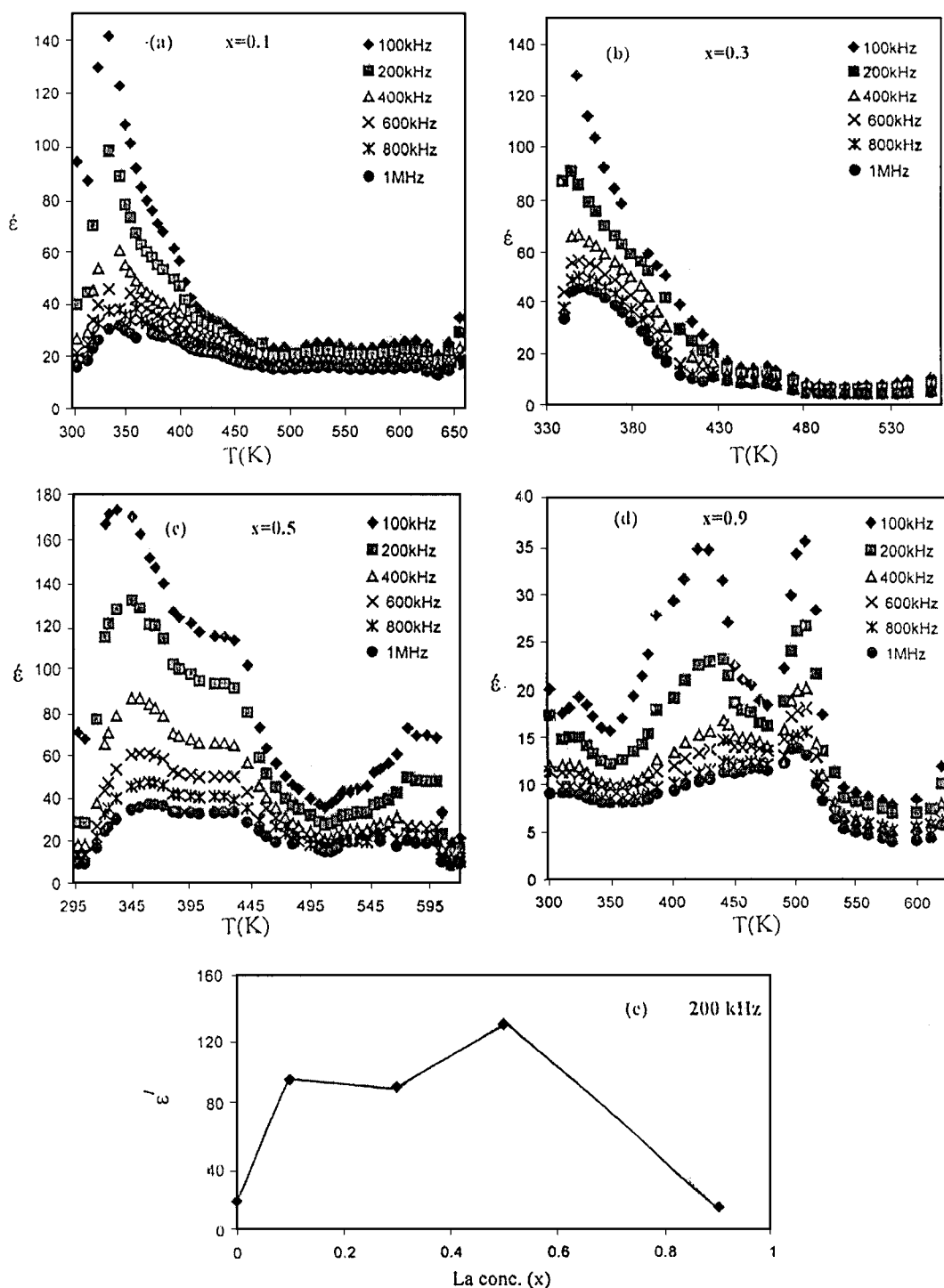


Figure 1 (a–d) Typical curve correlates the dielectric constant ( $\epsilon'$ ) and absolute temperature at different La concentration and different frequencies for  $(\text{CH}_2)_6(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$ . (e) Relation between dielectric constant ( $\epsilon'$ ) and La concentration at 200 kHz for  $(\text{CH}_2)_6(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$ .

since the ionic radius of  $\text{Mn}^{2+}$  ion (0.80 pm) is smaller than that of  $\text{La}^{3+}$  ion (1.06 pm) therefore the distortion of the square planers in the metallic layer will be increased, pushing the metal ions towards the plane. Accordingly, the interlayer spacing will be relatively increased. This means that, the polarizability (which is the summation of interlayer and intralayer exchange) is decreased and in turn  $\epsilon'$  up to  $x = 0.3$ .

Fig. 2a–c is a typical curve correlates the ac conductivity and the reciprocal of absolute temperature at different frequencies (100–1000 kHz) for the complexes  $(\text{CH}_2)_7(\text{NH}_3)_2\text{La}_x\text{Mn}_{1-x}\text{Cl}_4$  where  $0 \leq x \leq 0.9$ . From the figure it is clear that, more than one straight

line is obtained indicating the presence of more than one conduction mechanism. Three regions of the conductivity behavior for all the investigated samples are observed. The first region in which the conductivity is nearly constant with temperature, because the thermal energy is not sufficient to activate the mobility of the charge carriers. In the second region, the conductivity increases gradually with increasing temperature and frequency because the thermal energy is quite sufficient to liberate more charge carriers and the electric field accompanied with the applied frequency aligned them in its direction. At the end of this region (i.e., in the beginning of the third region), all the straight lines

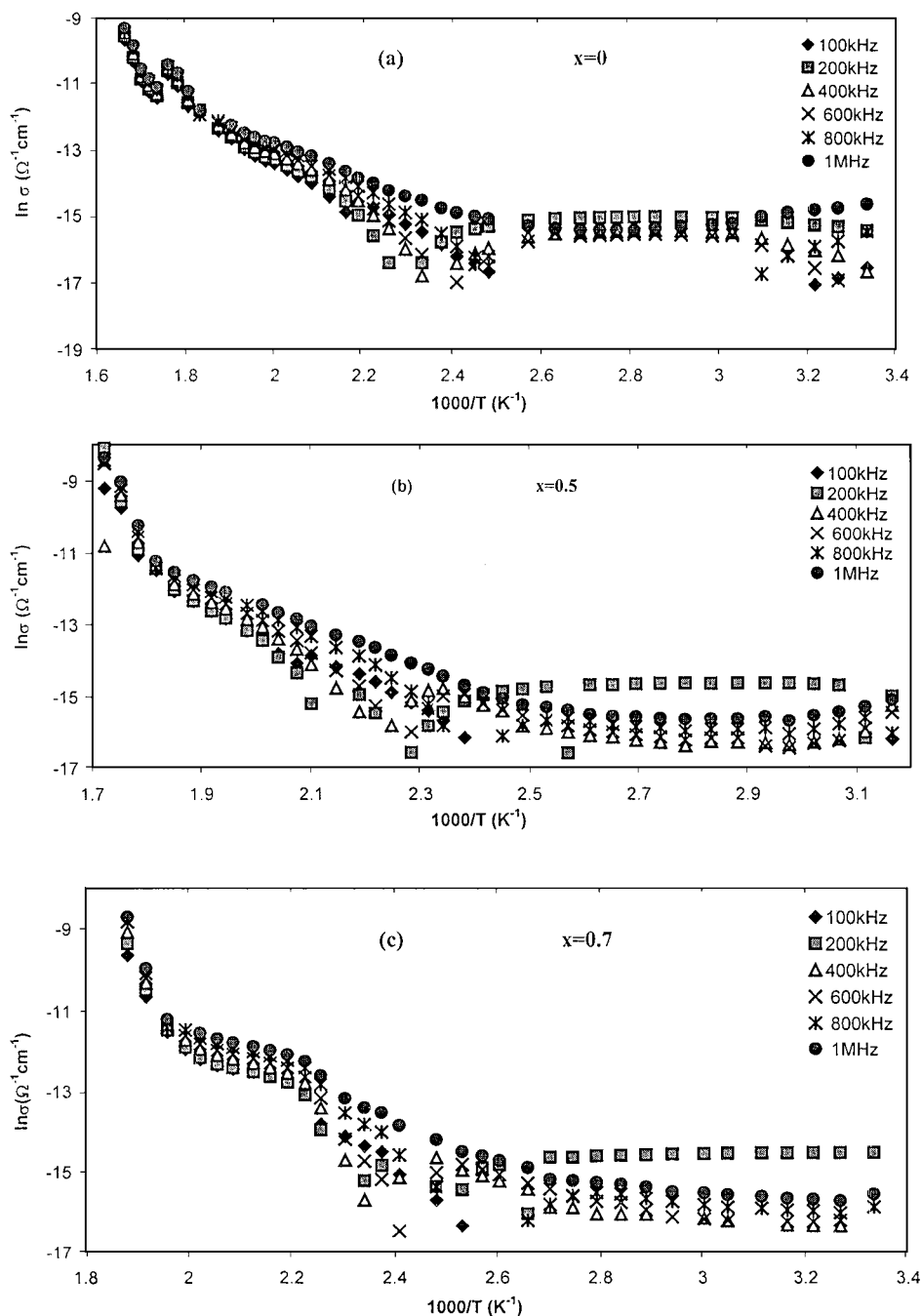


Figure 2 (a–c) Relation between  $\ln \sigma$  and reciprocal of absolute temperature at different frequencies for  $(\text{CH}_2)_7(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$ .

overlapped at a point before passing by the transition region in which the increase in conductivity is due to thermally activated mobility and not to the thermally creation of charge carriers. The values of the calculated activation energy Table I, indicate the semiconducting behavior of these complexes. The ammonium groups are hydrogen bonded with the halogen ions at the corners of the square planes and covalently bonded with the organic groups between the layers. This will play a significant role in the conduction process. The electronegativity of  $\text{Mn}^{2+}$  (1.55 Pauling's) is greater than that of  $\text{La}^{3+}$  (1.10 Pauling's) affect directly on both activation energy and conduction processes at room and any other temperature as in Fig. 2. This was enhanced by the values of activation energy  $E_I$  as in Table I where  $E_I$  decrease with increasing the lanthanum content ( $x$ ). The increase in  $E_{II}$  with increasing the lanthanum con-

centration in this high temperature region may be due to either the disordering of the dipoles, the participation of ions in the conductivity in this region or both in cooperation with each other. In general the conductivity of the investigated complexes can be discussed

TABLE I Values of activation energy at different frequencies for the complex  $(\text{CH}_2)_7(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$

| $f$ (kHz) | $x = 0$    |               | $x = 0.5$  |               | $x = 0.7$  |               |
|-----------|------------|---------------|------------|---------------|------------|---------------|
|           | $E_I$ (eV) | $E_{II}$ (eV) | $E_I$ (eV) | $E_{II}$ (eV) | $E_I$ (eV) | $E_{II}$ (eV) |
| 100       | 1.170      | 2.062         | 0.876      | 2.45          | 0.448      | 2.58          |
| 200       | 1.102      | 2.062         | 0.726      | 2.45          | 0.431      | 2.58          |
| 400       | 0.938      | 2.062         | 0.710      | 2.45          | 0.396      | 2.58          |
| 600       | 0.621      | 2.062         | 0.606      | 2.45          | 0.363      | 2.58          |
| 800       | 0.589      | 2.062         | 0.550      | 2.45          | 0.351      | 2.58          |
| 1000      | 0.557      | 2.062         | 0.492      | 2.45          | 0.301      | 2.58          |

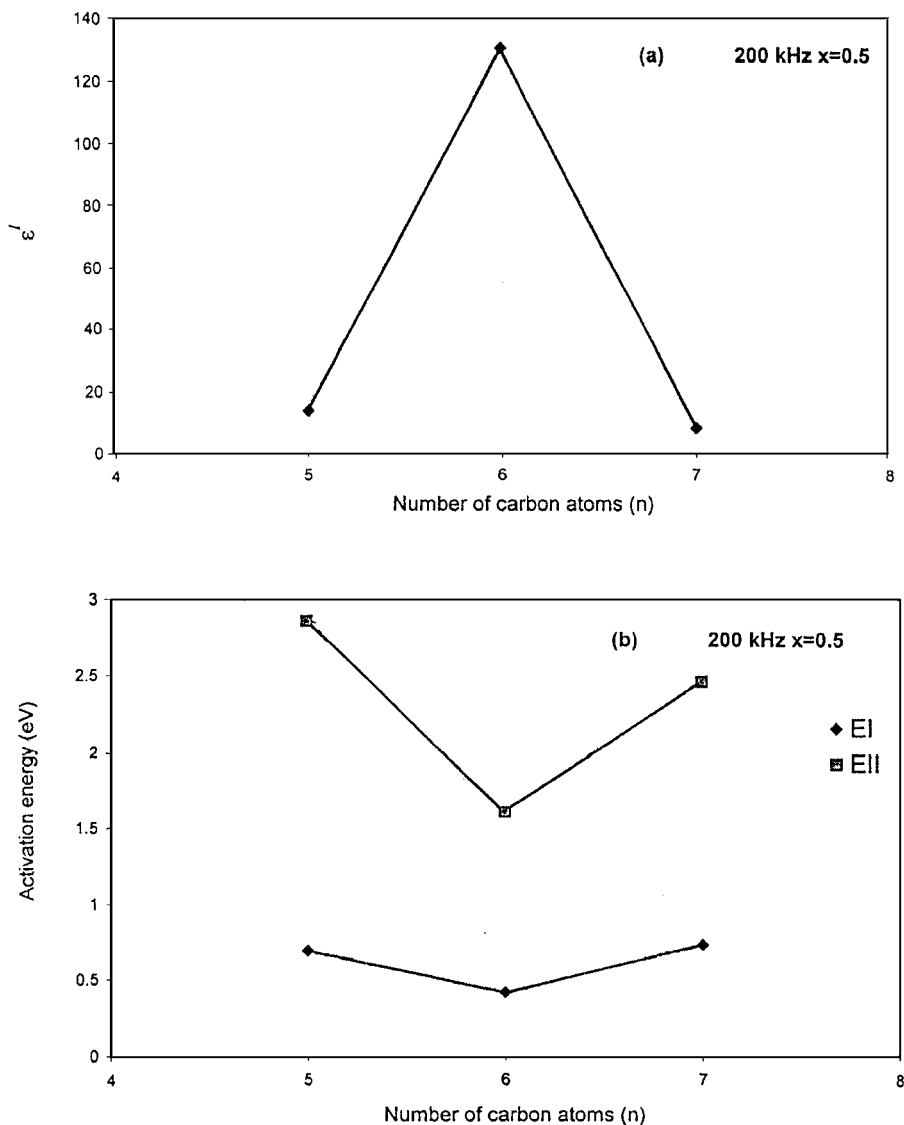


Figure 3 (a) Relation between dielectric constant ( $\epsilon'$ ) and the number of carbon atoms ( $n$ ) in the alkylene diammonium group at 200 kHz and  $x = 0.5$ . (b) Relation between the activation energy and the number of carbon atoms ( $n$ ) in the alkylene diammonium group at 200 kHz and  $x = 0.5$ .

as it forms from two parts: one below the phase transition which is frequency dependent and donated by  $\sigma_w$  and the other above it which is frequency independent and donated by  $\sigma_{dc}$ . In conclusion one can say that, the replacement of  $\text{La}^{3+}$  instead of  $\text{Mn}^{2+}$  ions pushes the metal ions towards the plane and increases the polarization in the planes. At high concentration of lanthanum the deformation in the system increases with the result of decreasing  $\epsilon'$ . The microstrain produced from the deformation due to  $\text{La}^{3+}$  ions affect directly on the hopping process, where at high temperature and high La content the trapped charge carriers will be liberated with the result of increasing conductivity in the planes. The conduction in the investigated samples is expected to be partially due to electrons ( $n$ -type semiconductor) and partially due to holes produced from the microstrain ( $p$ -type semiconductor) due to the replacement of  $\text{La}^{3+}$  of large ionic radius instead of  $\text{Mn}^{2+}$  of smaller ionic radius, where the remainder positive charge play a role in the conductivity behavior. The two processes act in cooperation with each other with the result of increasing the activation energy in the high temperature region, Table I.

Fig. 3a represents the dependence of the dielectric constant on the number of carbon atoms in the alkylene diammonium group at 200 kHz and  $x = 0.5$  for  $(\text{CH}_2)_n(\text{NH}_3)_2\text{Mn}_{1-x}\text{La}_x\text{Cl}_4$ ,  $n = 5, 6, 7$ . From the figure it is clear that, the polarization increases with increasing the number of the carbon atoms up to  $n = 6$  after which  $\epsilon'$  decreases. The crystal structure of the complexes with  $n = 5$  and 6 are orthorhombic while those with  $n = 7$  are monoclinic [13–16]. The decrease in  $\epsilon'$  after  $n = 6$  means that, the heptane diammonium complex has a peculiarity in its electrical properties as it was mentioned earlier [13–16]. The increase in the interlayer spacing by increasing the number of the carbon atoms will decrease the exchange interaction between the layers and at the same time increase its value in the layer. This means that, the ratio between the intralayer ( $J$ ) and interlayer ( $J'$ ) exchange interaction constants will be increased.

Fig. 3b enhances our expectation where the activation energy decreases continuously with increasing ( $n$ ) up to 6. This can be explained on the basis of increasing the conduction process in the layer. In other words, by increasing the interlayer spacing, the metal ion will go

apart from the plane, affecting on the canting angle and in turns increase the spin component in the layer. Consequently the nearest neighbor and next nearest neighbor interaction of the layer as well as the electrical conduction will be increased.

#### 4. Conclusion

From the above study, it was concluded that the dielectric constant decreases with increasing La content up to  $x = 0.3$  and reaches its maximum value at  $x = 0.5$  which is a critical concentration. The calculated values of the activation energy ( $E_I$ ) decrease with increasing  $x$  while those of ( $E_{II}$ ) increase. By increasing the number of carbon atoms in the complex, the value of  $\epsilon'$  increases up to  $n = 6$  and then decreases.

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