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Dielectric Constant and Pyroelectricity for the Compounds $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$(x = 0 and 1)

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The dielectric constant as well as the pyroelectric current for the compounds $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$ (x = 0 and 1) are measured in the temperature range including the phase transition points. The effect of replacing Cl^- ions by Br^--ions on the Puckering and the canting angle of the system is discussed together with the effect of phonon-magon interaction on the dielectric constant.

INTRODUCTION

The pervoskite-type layer structures of the general formula $(CH_2)_9(NH_3)_2MCl_{4-x}Br_x$[1–5] ($M = Fe^{2+}$, Mn^{2+} .... and x = 0, 1 and 2) paid our attention due to their interesting structural transition, magnetic and electric properties. The structure of these compounds consists of layers of corner sharing Cl_6-octahedra. This arrangement resembles one layer of a perovskite with the metal ions occupying the B-sites in the horizontal layers. The A-sites above and below the cavities of the octahedral layers are occupied by the alkylenediammonium chains. The NH_3 groups are attached to the layers by weak N-H ... Cl bonds. This results in a monoclinic unit cell at low temperature. Another interesting feature of these layered compounds is the appearance of more than one phase transition below and above room temperature. Most of these transitions are structural phase transitions because they are accompanied by a reversible colour change with temperature. Generally these observed phase transition can be seperated into two classes. One of these transitions which will be considered here is the order-disordered transitions of the alkylenediammonium chains. The MCl_4^{2-}-ions which form the layer will affect the phase transitions indirectly by both linear or non-linear coupling.

In the present work the investigated compounds are simple dielectrics with spontaneous polarization and lie belong to the group of the materials which show pyroelectricity. This encouraged us to study the phase transition by both dielectric constant and pyroelectic current measurements to

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seek any evidence of coupling between the dielectric constant and magnetic properties.

EXPERIMENTAL

All chemical used were Analar grade. The compounds under investigation were prepared from the starting materials in stoichiometric amount of amine salts in acidified distilled water. The ferrous chloride is added to the solution in the presence of a stream of oxygen free nitrogen gas, to prevent any oxidation process. As previously reported[6], the mixture is heated under nitrogen atmosphere for about one hour and then slowly cooled. Recrystallizations were carried out in ethanol. After that the powdered samples are compressed to pellets with diameter of 16 mm and thickness of 1mm under a pressure of 15 tons/cm^2. The upper and lower surfaces of each sample were coated with liquid gold (BDH, England) and checked for contact effect.

The dielectric constant measurements were carried out at different frequencies (10, 20 and 30 kHz) under vacuum using the bridge described elsewhere[1]. The data were collected on heating process after cooling samples to liquid nitrogen in a vacuum cryostat. The pyroelectic current is measured by using sensitive multimeter LEVEL, type TM9H, where this type detect a current of 10^{-12} ampere.

Chemical analysis of the samples are performed before collecting the data and listed in Table 1.

TABLE 1

CHEMICAL ANALYSIS OF THE COMPOUNDS
$(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$ (x = 0 and 1)

Compound	C%		H%		N%		Cl%		Br%	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$(CH_2)_9(NH_3)_2FeCl_4$	30.27	30.18	6.38	6.71	7.89	7.82	39 61	39.68	—	—
$(CH_2)_9(NH_3)_2FeCl_3Br$	26.90	26.85	5.95	5.97	7.00	6.96	26.51	28.88	19.93	19.67

RESULTS AND DISCUSSION

The experimental results presented in Fig. 1 show the dependence of dielectric constant (ϵ) on temperature for the compound $(CH_2)_9(NH_3)_2FeCl_4$ at different frequencies (10, 20 and 30 kHz). From the figure it can be seen two phase transition at each one of the measured frequency. The first phase transition exists between 255 to 290K and the second one exists between 315 to 340K. The peak position of each one of the two phases is shifted to lower temperatures by increasing frequencies.

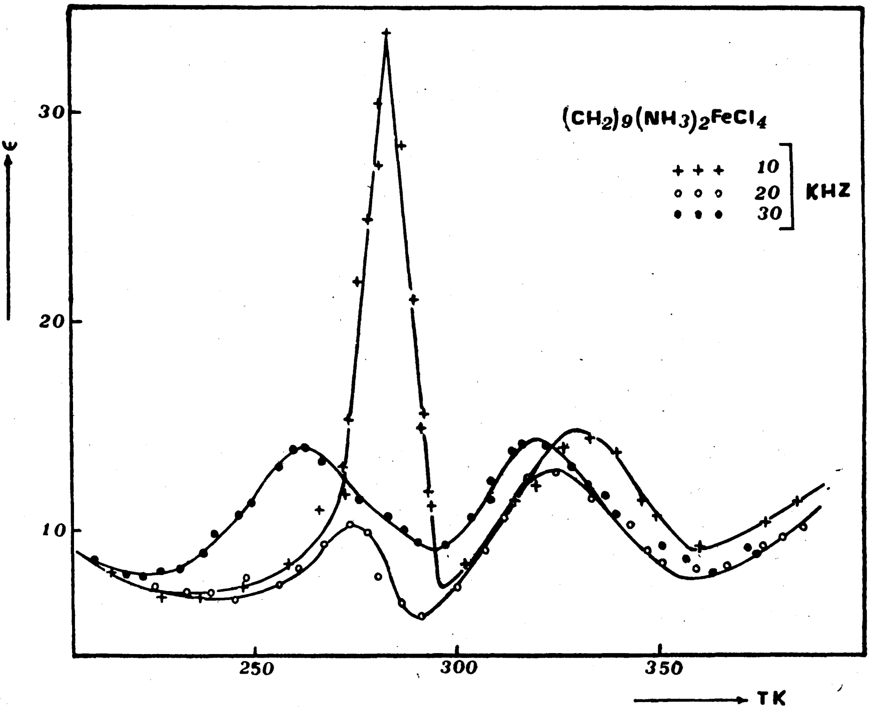

Fig. 1. Relation between the dielectric constant (ε) and temperature (T) at different frequencies $(CH))_9(NH_3)_2\ FeCl_4$.

The dielectric constant (ε) as a function of temperature for the compound $(CH_2)_9(NH_3)_2FeCl_3$ Br at different frequences (10, 20 and 30 kHz) is shown in Fig. 2. From which it can be seen an appreciable decrease in dielectric constant with temperature from 370 K to 300 K. Below 300 K a very small decrease in (ε) is observed.

From Figs. 1 and 2 one can safely state that the general features of the two compounds are completely different except for a very small decrease in dielectric constant down to 200 K. In Fig. 1 there are two peaks. The symmetry of each peak is decreased by increasing frequencies. While Fig. 2 showing only one peak above room temperature in a form of shoulder at 330 K. The lower phase transition is detected in-Cl_4 compound, but it is not detectable for -Cl_3Br compound. The disappearance of the second phase transition may be due to presence of Br^--ions of larger size in the out of plane position.[7]

It is known that[8] in compounds in which the dielectric constant decreases with temperament and below the Neel temperature, the magnetostriction effect plays an important role. This effect will cause a lattice contraction along the direction of magnetic moments. The increase in phonon energy along the direction will cause a decrease in the dielectric constant. This behaviour if often occurs in the two-dimentional antifer-

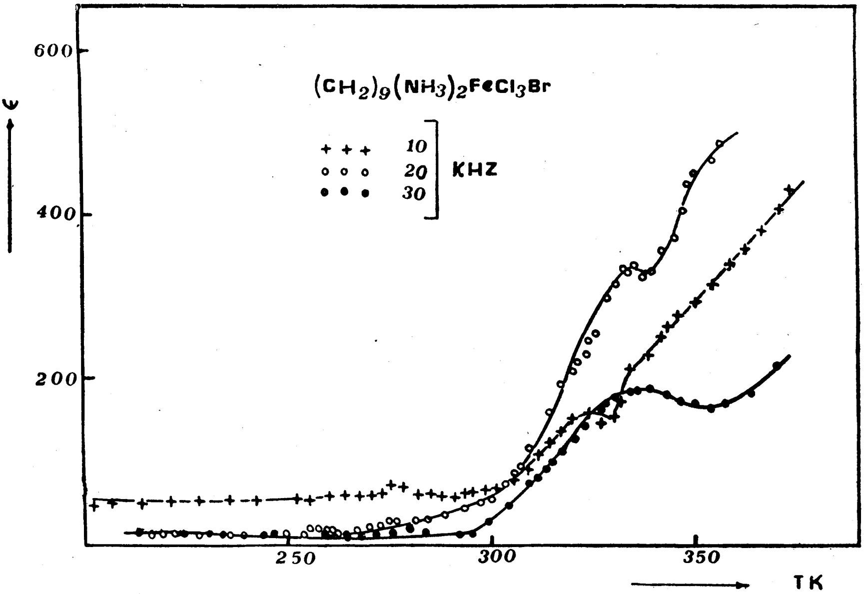

Fig.(2)

Fig. 2. Relation between the dielectric constant (ε) and temperature (T) at different frequencies for $(CH_2)_9(NH_3)_2$ $FeCl_4$.

romagnetic compounds like those under investigation. In addition to the magnetostriction effect, there are some form of polar optic phonon-magnon coupling which can increase the energy of the lowest frequency transverse polar phonon[8]. This will lead to a decrease in the dielectric constant with decreasing temperature below T_N.

In the present work the values of the dielectric constant are calculated from the measured sample capacitances without any correction for the sample thermal contraction on cooling or expansion on heating. Usually this correction term is small and neglected. The values of the electric dipole moments for the two compounds $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$ (x=0 and 1) are calculated at the background and the phase transition points using the equation[9]

$$\chi = \frac{k}{N\mu^2}(T - \frac{N\mu^2\beta}{k})$$

and the data are listed in Table 2, where χ is the electric susceptibility, N is the number of electric dipoles per unit volume, $\beta = 4\pi/(2\epsilon + 1)$ and k is the Boltzman constant. The change in the dipole moment observed in Table 2 indicate that the polarization and the symmetry of the crystals are changing with the temperature.

As we mentioned above the dissimilarities in the dielectric constant of $-Cl_4$ and $-Cl_3Br$ compounds may be due to presence of Br^--ions. The Br^--ions of larger size (radius of $Br^- = 1.96$ Å and that of $Cl^- = 1.81$ Å)

TABLE 2

VALUES OF THE ELECTRIC DIPOLE MOMENT (μ) FOR THE COMPOUNDS $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$ WHERE x = 0 AND 1

T (K)	μ(C.Cm.10^{-18}) for compound with x = 0	μ(C.Cm.10^{-18}) for compound with x = 1
200	6.20	5.25
280	8.10	13.38
300	7.10	19.49
320	10.22	40.29
336	9.75	53.56
375	8.90	—
390	10.10	—
440	11.12	—

will occupy the out of plane position[7] which forces the Fe^{2+}-ions towards the horizontal plane. This will cause a change in the puckering of the system as well as the canting angle, leading to a shift in the peak position and values in both magnetic and electrical properties[1,11]. The decrease in the canting angle will cause a decrease in the weak ferromagnetism that exist in the antiferromagnetically ordered state. This will produce an increase in the antiferromagnetism in the layer which change the behaviour of the dielectric constant of the two compounds due to a change in the magnon-phonons interactions. These phonons can modulate the exchange interactions in and between the layers as well as anisotropic exchange. Below the Neel temperature of the samples, the decrease in the spin canting will cause a decrease in the ferromagnetism[8] which give a strong phononmagnon interactions. This magnon-phonon interactions will lead to the anomalies that appeared in the dielectric constant, in the order temperature regime. This will enhance the existence of strong relation between the electrical and magnetic properties of two-dimensionals magnetic system.

The peaks observed in ϵ-values at higher temperatures can be attributed to the change in the electronic configuration which is associated with structural changes in the crystal structure[11,12].

Fig. 3 shows the dependence of the pyroelectric current I_p on the absolute temperature for the compounds $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$ (x = 0 and 1). From the figure, it is clear that the phase transition points appeared in the dielectric constant are nearly the same in pyroelectric current measurements. Changing the temperature of the sample will change the polarization, which is detected in a form of pyroelectric current. The measured values of the pyroelectric current is usually the sum of the

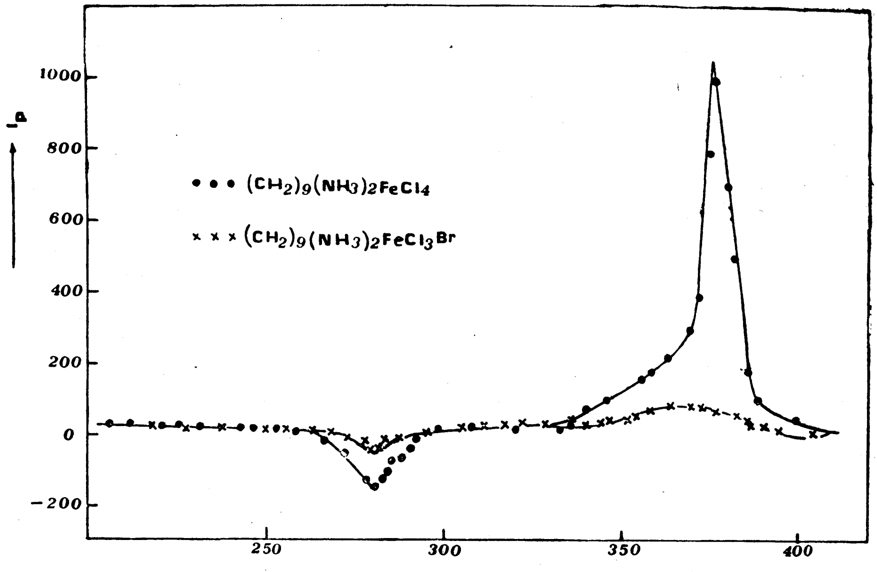

Fig.(3)

Fig. 3. Relation between the pyroelectric current I_p and temperature (T) for the compounds $(CH_2)_9(NH_3)_2FeCl_{4-x}Br_x$. (x = 0 and 1)

primary effect produced from clamping the sample plus the secondary effect produced from freely expanded sample. Recently[2,13] it was found that some of the two dimensional magnets give polarization which increases by increasing the applied electric field and still remains even when removing such field. This phenomena is called the memory effect which is now under investigation for the Fe^{2+}—complexes and will be published latter.

In conclusion one can safely state that the change in dielectric constant with temperature may be due to magnon-phonon interaction. This will approach the strong relation between the electric and magnetic properties of the two dimensional magnetic systems. Also the change in general features of the compounds containing Br^--ions and those containing Cl^--ions may be due to the larger size of Br^- and their exist out of the plane containing Fe^{2+}-ions. The pyroelectric current measured in this work is a direct evidence for the polarization that exist in these compounds even below room temperature.

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