

## Electrical properties of pure and doped ammonium alum

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### Abstract

Pure ammonium alum, and Cr-doped and Fe-doped single crystals were prepared. The resistivity and pyrocurrent were measured as a function of temperature. The resistivity varies exponentially with temperature. The activation energy for all samples was calculated. At any temperature, the resistance increased with increase in Cr concentration and decreased with increase in Fe concentration.

### INTRODUCTION

The alums are a large class of double salts having the general formula  $M^+M^{3+}(RO_4)_2 \cdot 12H_2O$ . All alums belong to the cubic system with space group  $Th_6(Pa_3)$ . In this formula,  $M^+$  and  $M^{3+}$  are monovalent and trivalent cations respectively, and the  $RO_4$  group is  $SO_4$ ,  $As_2O_4$ , ..., etc. Because of slight differences in atomic arrangement, there are three types of alum:  $\alpha$ ,  $\beta$  and  $\gamma$  [1]. The crystallography and classification of aluminium alums was originally established by Lipson [2] and Lipson and Beavers [3].

It has been estimated that  $NH_4Al(SO_4)_2 \cdot 12H_2O$ ,  $NH_4Cr(SO_4)_2 \cdot 12H_2O$  and  $NH_4Fe(SO_4)_2 \cdot 12H_2O$  are  $\alpha$  alums [4,5]. The  $NH_4$  and  $Al^{3+}$  alums have six water molecules as nearest neighbours forming a nearly regular octahedron; the water groups around the monovalent and trivalent ions exhibit mutual bonding with each other. The replacement of  $Al^{3+}$  by  $Cr^{3+}$  or  $Fe^{3+}$  causes a slight change in the heat of dissociation [5] with no deformation of the local symmetry [6].

Hepburn and Phillips [5] revealed the remote field effect due to the strong polarizing power of the relatively small  $M^{3+}$  ions and support the view that each  $M^{3+}$  ion exerts its particular stabilizing influence on the alum structure. The smaller the  $M^{3+}$  ion, the greater its polarizing power. This power is responsible for increasing the heat of dissociation of the smallest  $M^{3+}$  alums. It is suggested that an unstable intermediate, probably

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an amorphous lower hydrate or anhydrous salt, forms during dehydration and transforms into a stable crystalline modification. Another explanation suggests that a phase change occurs during dehydration and others have shown that dehydration occurs only at the boundary of the two phases [5].

The aim of the present work is to study the effect of doping on the conduction mechanisms and pyroelectric phenomenon of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

## EXPERIMENTAL

Single crystals of  $\text{NH}_4\text{Al}$  alum salt (General Chemical and Pharmaceutical Co.Ltd, Sudbury, Middlesex, UK) were grown at room temperature by

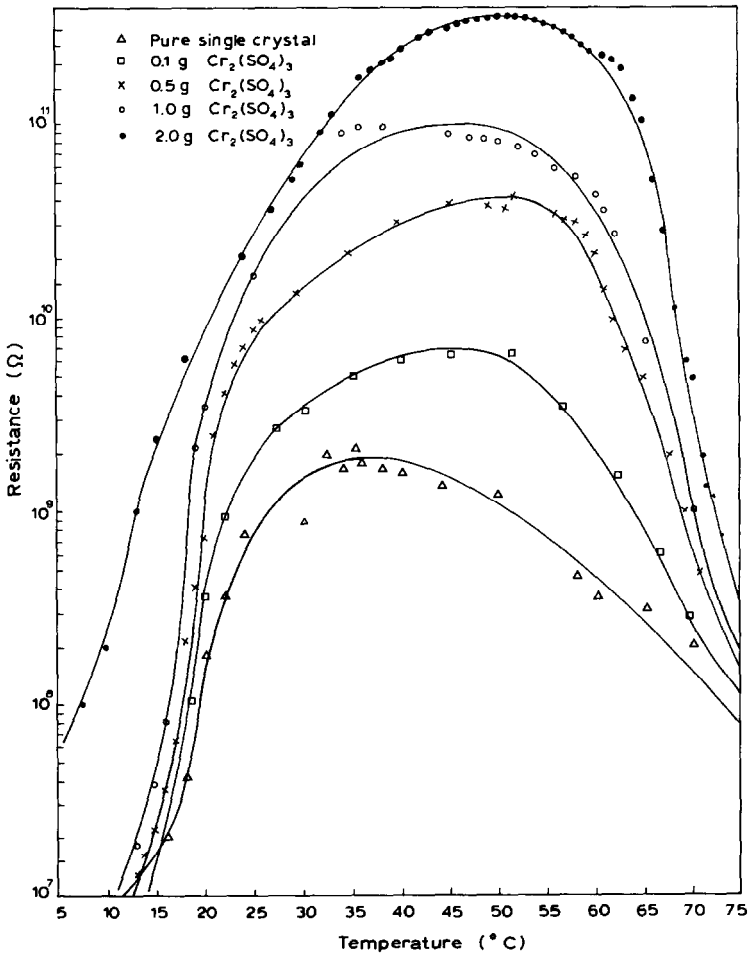


Fig. 1. The variation of the d.c. resistance with temperature ( $\log R$  vs.  $T$ ) for the pure single crystal.

slow evaporation of the saturated aqueous solution. The crystals grow in the form of a regular octahedron and the unit cell is cubic. Using an X-ray diffractometer, the lattice constants calculated showed a good agreement with those recorded in the A.S.T.M. cards.

The single crystals obtained were rectangular. The two faces parallel to the [100] plane were coated with silver paste to form a crystal condenser. Two thin copper wires 0.25 mm in diameter were fixed on the coated surface using a conducting cement. Discs 1 cm in diameter and 0.25 cm thick with two electrodes were prepared by compression of a crushed single crystal at a pressure of  $25 \text{ kg cm}^{-2}$ .

The doped crystals were prepared by adding 0.1%, 0.5%, 1% and 2% by weight  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{NH}_4\text{Al}$  alum and the crystals were grown at room temperature.

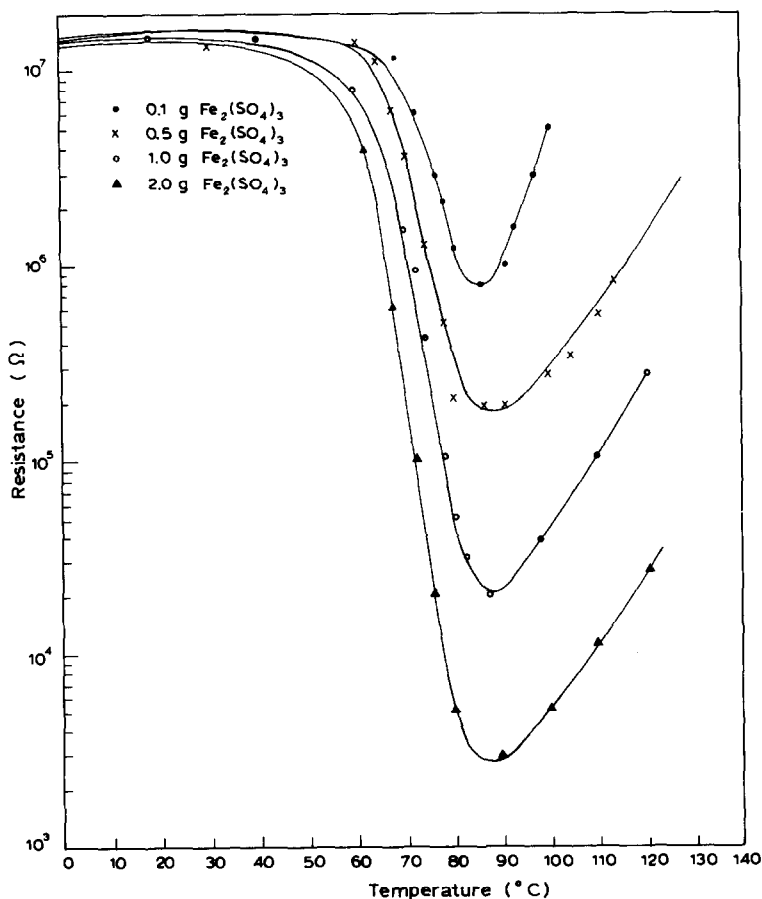


Fig. 2. The variation of the d.c. resistance with temperature (log  $R$  vs.  $T$ ) for the Fe-doped single crystal.

The resistance was measured by applying an electric field across the opposite coated faces. The samples were placed in a metallic cell which provides proper shielding and the current was measured by noting the voltage across a standard resistance using a Keithley nanovoltmeter. Measurements were taken in the temperature range 0–380 °C. Calcium chloride grains were spread on the bottom of the cell to avoid condensation of water vapour on the crystal surfaces.

The pyroelectric current was detected by connecting a picoammeter (TM9A) in series with the test sample which is polarized by an electric field of  $100 \text{ V cm}^{-1}$  for 30 min at room temperature. The samples were heated by an automatically regulated electrical furnace with a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$ .

## RESULTS

The variation of the d.c. resistance as a function of temperature ( $\log R$  versus  $T$ ) for the pure single crystals, doped crystals and pure crushed

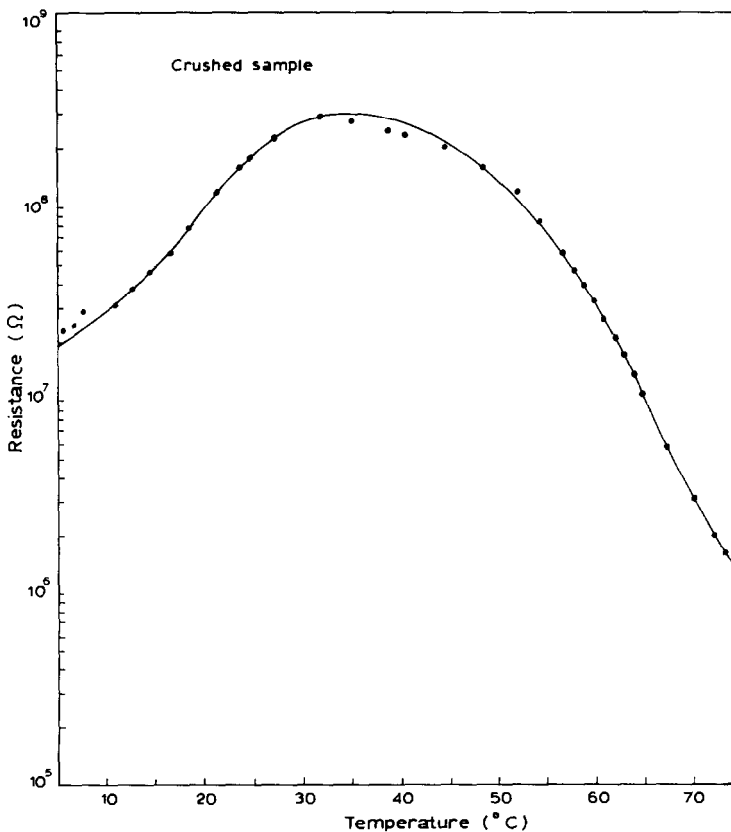


Fig. 3. The variation of the d.c. resistance with temperature ( $\log R$  vs.  $T$ ) for the crushed single crystal (tablet).

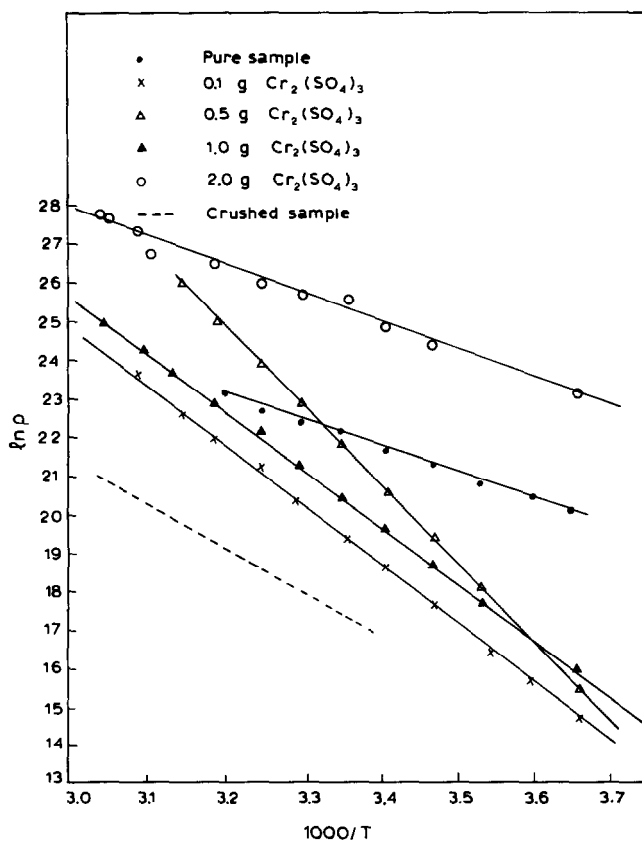


Fig. 4. The relation between  $\ln \rho$  and  $1/T$  for the pure and Cr-doped single crystal.

alums is shown in Figs. 1–3. For pure single crystals, the resistance increases with increasing temperature from 0 to 35 °C (the dehydration temperature), and then decreases (Fig. 1). The same behaviour is repeated for the  $\text{Cr}^{3+}$ -doped crystals with a shift of the dehydration temperature to 52 °C (Fig. 1); the resistance increases as Cr content increases. From Fig. 2, it is clear that doping with  $\text{Fe}^{3+}$  has the unexpected result that  $R$  does not change, within a small range, and then a steep decrease in resistance takes place with increasing temperature, falling to a minimum value at a critical temperature of  $88 \pm 2$  °C; then  $R$  starts to increase with increasing temperature. The electrical resistance for pure crushed samples shows the same behaviour as that of pure  $\text{NH}_4\text{Al}$  alum crystals (Fig. 3).

The variation of the resistivity with temperature, plotted as  $\ln \rho$  against  $1/T$ , for pure, doped and crushed samples is shown in Figs. 4 and 5. It can be seen that the variation of  $\ln \rho$  with  $1/T$  is linear up to the dehydration temperature for all tested samples.

The activation energy dependence on the concentration of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  is shown in Fig. 6.

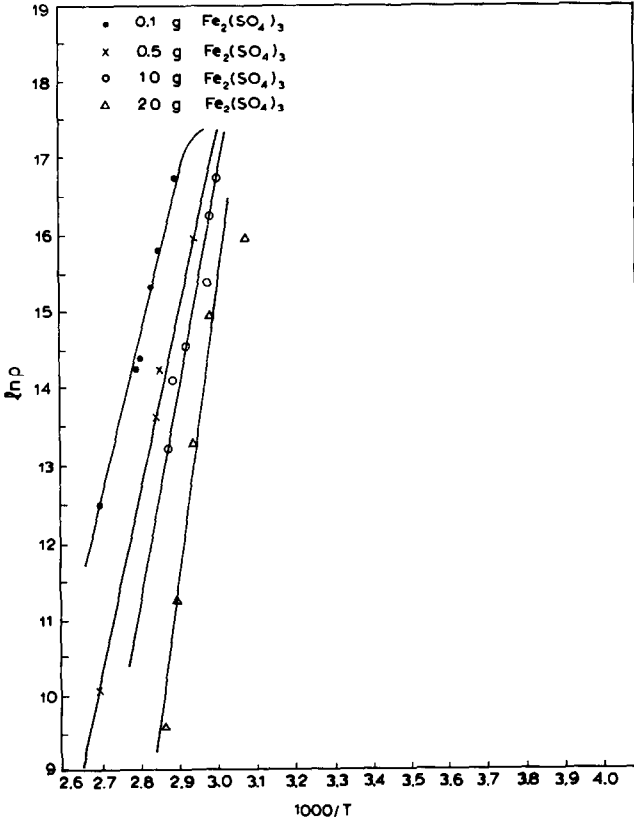


Fig. 5. The relation between  $\ln \rho$  and  $1/T$  for the crushed and Fe-doped single crystal.

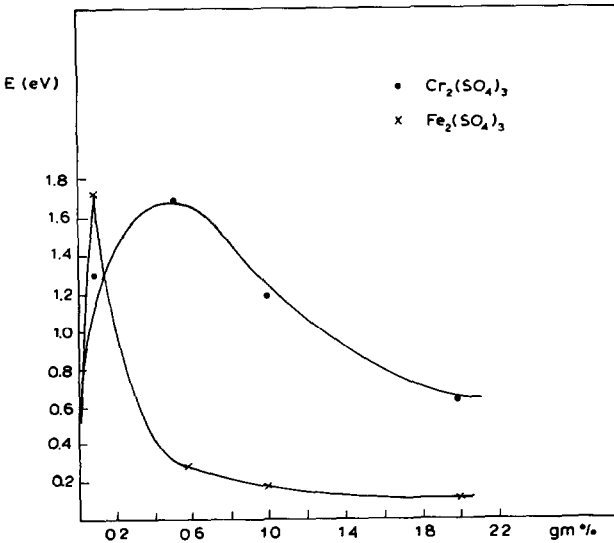


Fig. 6. The dependence of the activation energy on Cr and Fe content.

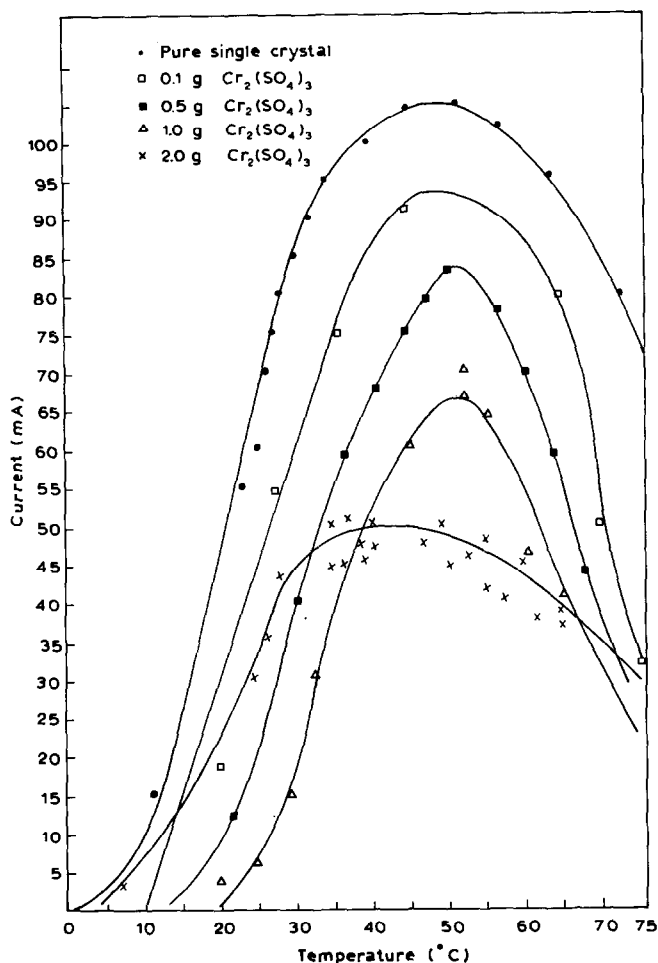


Fig. 7. Effect of doping with Cr on the pyroelectricity of  $\text{NH}_4\text{Al}$  alum.

Figures 7 and 8 show the temperature dependence of the pyroelectricity for pure and doped single crystals normal to the  $[100]$  and  $[\bar{1}00]$  faces. An electric field ( $100 \text{ V cm}^{-1}$ ) was first applied to the samples for 30 minutes at room temperature.

## DISCUSSION

The structure of  $\text{NH}_4\text{Al}$  alum which is  $\alpha$  alum is not affected by doping with  $\text{Cr}^{3+}$  or  $\text{Fe}^{3+}$ . The  $d$  values are not changed; hence doping does not produce a deformation of the local symmetry [5–7]. On the other hand, the electrical properties of such alums are very sensitive to doping.

For pure crystals (Fig. 1), the electrical resistance increases with temperature during the dehydration process to a critical temperature of  $32 \pm 2^\circ \text{C}$ .

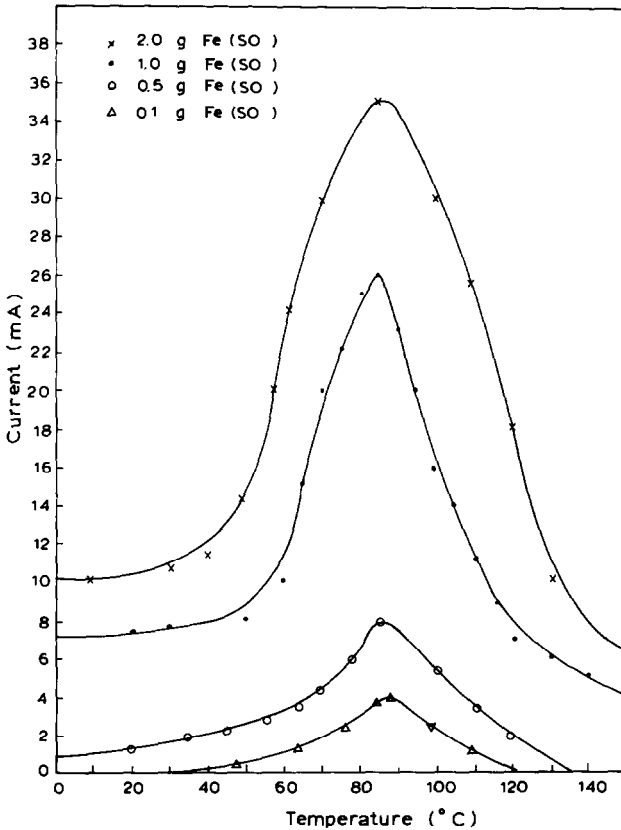


Fig. 8. Effect of doping with Fe on the pyroelectricity of  $\text{NH}_4\text{Al}$  alum.

This may be due to the diminution of the protonic polarization caused by the expansion of the crystal lattice as the temperature rises. Such a protonic polarization may have a larger value on forming a hydroxyl radical when the strength of the hydrogen bond is weakened by the lattice loosening. The ionic nature of this hydrogen atom will increase, leading to an increase in the resistivity. Above the dehydration temperature, the resistance decreases as the temperature increases. This could be attributed to the increase in the number of vacant sites due to the removal of water molecules. At any point in the hydrated crystalline zone, the water molecules may be regarded as moving from one site to the next, resulting in more conduction.

The same phenomenon was observed for the crushed sample. The dehydration temperature was unchanged. The increase in the electrical resistance is not highly sensitive, as for the single crystal; this may be due to the higher porosity of the compressed crushed samples. Also the high value of the activation energy could be attributed to the higher density of obstacles due to voids, diffused silver atoms and disordering [8] (Fig. 4).



TABLE 1

Thermal activation energy values for different compositions

Composition	% doping	$\Delta E$
Pure single crystal of $\text{NH}_4\text{Al}$ alum		0.37
Crushed samples of $\text{NH}_4\text{Al}$ alum		0.537
Single crystal of $\text{NH}_4\text{Al}$ alum doped with Cr	0.1	1.344
	0.5	1.715
	1.0	1.292
	2.0	0.649
Single crystal of $\text{NH}_4\text{Al}$ alum doped with Fe	0.1	1.72
	0.5	0.293
	1.0	0.211
	2.0	0.143

On doping with  $\text{Cr}^{3+}$ , the observed shift of the dehydration temperature to  $52 \pm 2^\circ\text{C}$  and the increase in the resistance with Cr content (Fig. 1) may result from the nature of the trivalent cations. The  $\text{Al}^{3+}$  cation is replaced by the larger  $\text{Cr}^{3+}$ , causing more collapse in the lattice.

The interesting feature of the resistance versus temperature plots (Fig. 2) is the decrease in resistance with increase in temperature, and the shift of the dehydration temperature to  $88 \pm 2^\circ\text{C}$ . This anomalous behaviour is somewhat similar to what is usually observed in ferroelectric materials.

Thermal activation energy values were calculated from the slopes of the resistivity-temperature curves of Figs. 4 and 5 using the relation

$$\rho = C \exp(\Delta E/KT) \quad (1)$$

where  $\rho$  is the resistivity,  $C$  is a constant,  $\Delta E$  is the activation,  $K$  is the Boltzmann constant and  $T$  is the absolute temperature. The results of these calculations are given in Table 1. The activation energy as a function of Cr and Fe content is shown in Fig. 6. It is seen that the alum with 0.5% Cr has the maximum  $\Delta E$ . This may result from the collapse of the structure which produces an amorphous zone [9]. More rearrangement occurs for the lattice as the Cr concentration increases, accompanied by an increased metallic character, which is responsible for the decrease in the activation energy.

For doping with 0.1% Fe, the activation energy is higher than that for pure alum, which is due to the increase in the amorphous nature of the structure. The decrease in the activation energy as Fe concentration increases could also be related to the increase in the metallic character of the samples.

The results of Figs. 7 and 8 indicate a pyroelectric effect for the pure and doped crystals of ammonium alum. The variation of polarization was

detected as a current. The pyroelectric current  $i$  can be expressed by [10]

$$i = A \left( \frac{dP_s}{dt} \right) = A \frac{dP_s}{dT} \frac{dT}{dt} \\ = A\gamma \frac{dT}{dt} \quad (2)$$

where  $P_s$  is the spontaneous polarization of the sample per unit area at any temperature  $T$ ,  $A$  is the surface area of the samples and  $\gamma$  is the pyroelectric coefficient.

Doping with Cr decreases the pyroelectric current. This may result from the lower polarizing power of  $\text{Cr}^{3+}$  cations than that of  $\text{Al}^{3+}$  cations, owing to the larger size of the  $\text{Cr}^{3+}$  cations. The increase in the Cr radii results in a decrease in its electrostatic field as measured by  $1/\alpha^2$  ( $\alpha$  is the radii of Cr cations) and this reduces the pyroelectricity phenomenon in the crystal. The increase of the pyrocurrent in the case of  $\text{Fe}^{3+}$  may be due to the change in domain alignment and change in the spontaneous polarization of the individual domains.

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