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A Multiple Thermal Analysis of Ammonium Heptamolybdate Tetrahydrate

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Crystalline powder of ammonium heptamolybdate tetrahydrate (AHM) was studied by use of thermally stimulated charge (TSC), differential thermal analysis (DTA), permittivity and dielectric loss measurements in the range from 113 K to 300 K.

TSC performed on d.c. poled samples resulted in a homocharge release with a discontinuity in the vicinity of 200 K. TSC carried out in heating-cooling cycles did not confirm a recent assumption of ferroelectric activity in AHM powder. TSC of the unpoled samples showed a peak at (280 ± 10) K indicating a phase transition. A similar result was obtained by DTA showing an endothermic peak at (260 ± 4) K. $\epsilon(T)$ and $\tan \delta(T)$ increased substantially above 200 K because of d.c. conductance, which is probably the reason for the homocharge storage in poled samples.

INTRODUCTION

In a recent paper¹ we reported that the pressed powder of ammonium heptamolybdate tetrahydrate, $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}$ (AHM), after being electrically poled, exhibited a measurable pyrocharge in the region from 113 K to 216 K. The poling was successful with a positive as well as with a negative d.c. field. This preliminary investigation was suggestive of possible ferroelectric properties in AHM. The measurement of the integral released charge against temperature showed a significant discontinuity in the vicinity of 200 K. An assumption was thus made that this discontinuity represented a ferroelectric — ferroelectric phase transition. If the assumption of ferroelectricity in the investigated low temperature region from 113 K to 216 K is correct then one may expect another ferroelectric — paraelectric transition somewhere between 261 K and room temperature. Namely, the crystal structure determined at room temperature² is centrosymmetric and nonpolar one (space group $P2_1/c$; point group $2/m$).

In the present investigation we searched for additional evidence to corroborate the existence of the ferroelectric properties as well as to confirm the phase transition phenomena by use of various methods of thermal analysis.

EXPERIMENTAL

The investigated crystalline powder was of reagent grade. The impurities (trace elements) content of the samples was not checked. However, dislocations in the grains, as well as the possible loss of crystalline water and NH_3 can influence the results even more than the impurities in a reagent grade chemical.

The grain size distribution was from 200 to 1200 μm . For all the electric measurements the original powder (i.e. without grain-size separation) was pressed without any binder into platelets of the size $1.5 \times 1.5 \times 0.2 \text{ cm}^3$. The applied pressure of $3 \times 10^8 \text{ Nm}^{-2}$ was perpendicular to the $1.5 \times 1.5 \text{ cm}^2$ surface. Air-drying silver paint was used for electrodes on both dominant platelet faces. The density of the pressed samples was 92% of the single crystal density. In order to measure the charge generated in polycrystalline AHM during heating or cooling procedure the samples were placed in a corresponding cell.^{3,4} The heating and cooling was performed at a rate of 2 K min^{-1} . Before measuring the charge, in some cases, the samples were electrically poled by a d.c. field. The released charge was integrated and measured by use of a Keithley 616 digital electrometer. The charge and temperature were recorded continuously by a dual trace chart recorder.

The measurement of current released from a dielectric during heating is known as TSDC (thermally stimulated depolarization current)⁵ or, more generally, as TSC (thermally stimulated current).^{6,7} In cases when the released charge was identified, or at least a fraction of it, to be pyroelectric in nature, the method was named more specifically as PTA (pyroelectric thermal analysis).^{3,4}

Differential thermal analysis was performed by heating at a rate of 1 K min^{-1} . The temperature and the temperature difference were measured by a Ni/NiCr thermocouple. The voltage of the differential thermocouple was amplified by use of a Hewlett Packard 419 A DC null voltmeter. The AHM powder was placed in a ceramic sample holder of a 0.25 cm^3 volume. An empty holder of the same size was used as a reference. The holders were designed to be removable from the thermocouple wire.⁸

Dielectric permittivity and dielectric loss against temperature were measured point by point using the bridge method with a field of $5 \times 10^2 \text{ Vm}^{-1}$ and a frequency of 1 kHz.

All measurements were carried out in a closed cell in the presence of air without use of any desiccator (but see in the Results about the DTA measurements).

RESULTS

A curve showing the integral released charge versus temperature in an arbitrary low temperature region from 144 K to 217 K is given in Figure 1. The sample of the pressed AHM powder used for this measurement had been previously poled in a d.c. field of $3.4 \times 10^5 \text{ Vm}^{-1}$ at 216 K for 30 minutes. After poling the sample was shortened, cooled down to 133 K and left in shortened state for another 30 minutes before heating. The curve obtained shows a characteristic discontinuity in the vicinity of 200 K (in this particular case it is 202 K) in a similar way as the one described in a previous paper.¹ The same experiments repeated with various AHM samples showed a certain variety in results. Very often, instead of a sudden increase at one temperature, a stagnation in charge release occurred between 195 K to 213 K (Figure 2). In order to check the possible influence of the poling temperature some experiments were performed applying a different poling temperature, such as 168 K. One typical result chosen among many measurements is shown in Figure 3. The curve is quite different in comparison with the first two in Figures 1 and 2. However, a significant discontinuity appears again at 200 K as an inflection.

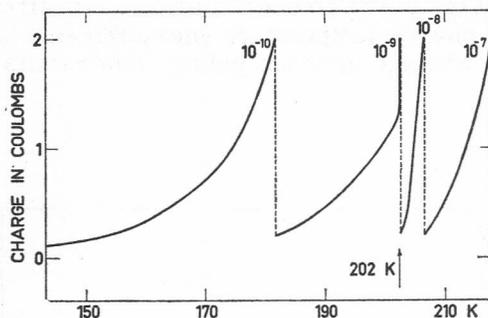


Figure 1. Thermally stimulated charge of polycrystalline ammonium heptamolybdate tetrahydrate (AHM), previously poled with $3.4 \times 10^5 \text{ Vm}^{-1}$ at 216 K.

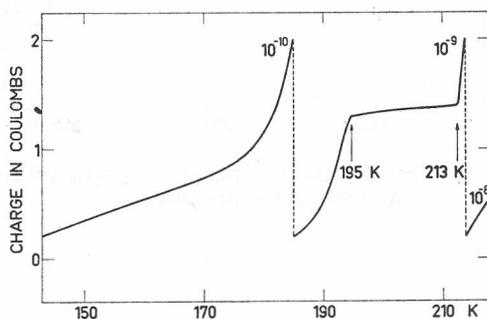


Figure 2. Variation in results of thermally stimulated charge of polycrystalline AHM, poled with $3.4 \times 10^5 \text{ Vm}^{-1}$ at 216 K.

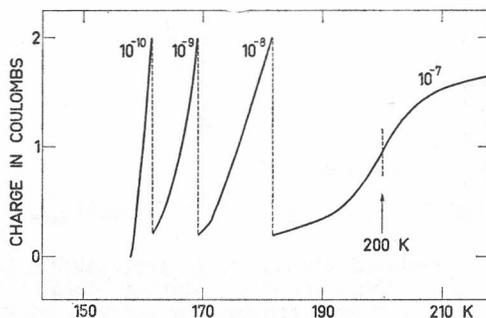


Figure 3. Thermally stimulated charge of polycrystalline AHM, poled with $3.4 \times 10^5 \text{ Vm}^{-1}$ at 168 K.

The described method of the thermal analysis of poled samples was not suitable at higher temperatures, because the amount of the released charge increased too rapidly with temperature making difficulties in ob-

servation of the charge curve course. Therefore, an attempt was made to perform the same charge-temperature measurements at higher temperatures on samples without previous poling. The results are presented in Figure 4.

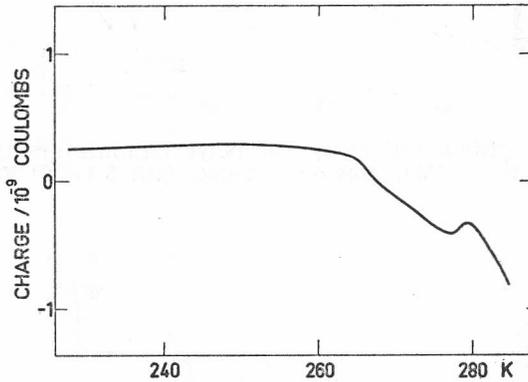


Figure 4. Thermally stimulated charge of polycrystalline AHM, without previous poling.

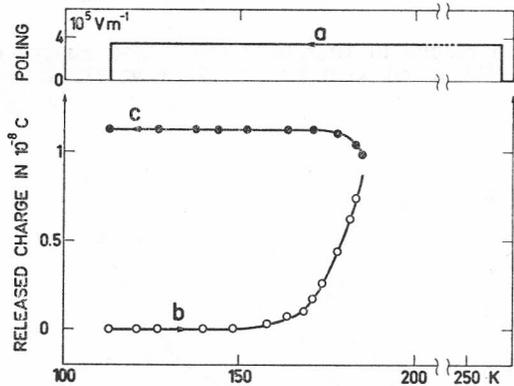


Figure 5. Thermally stimulated charge of polycrystalline AHM, in the region from 113 K to 185 K. (a) Poling carried out during cooling; (b) charge released by heating; (c) charge released by consecutive cooling.

The released charge curve shows a peak at approximately 280 K. Analogous experiments were carried out with three AHM samples. Distinct peaks appear in all cases at (280 ± 10) K.

The charge that goes out from a previously poled polycrystalline AHM during heating was interpreted as an induced pyrocharge.¹ In order to

confirm the pyroelectric nature of the generated charge the additional measurements were made by consecutive heating and cooling. The results of such an experiment, performed below 200 K, are presented in Figure 5. The poling by a d.c. field of $3.4 \times 10^5 \text{ Vm}^{-1}$ took place during the cooling from 260 K to 113 K (curve a). After relaxation in a shortened state for 30 minutes at 113 K the measurement of released charge was performed during the heating (curve b). The experiment was stopped at 185 K in order to avoid the possible phase transition in the vicinity of 200 K. Immediately after heating the experiment was continued by cooling (curve c) in the range from 185 K to 113 K. A similar experiment carried out above 200 K is presented in Figure 6. The poling was performed from 260 K to

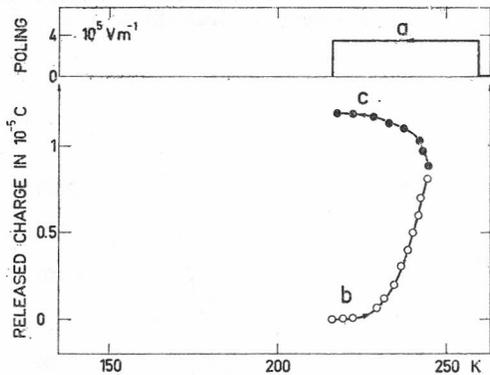


Figure 6. Thermally stimulated charge of polycrystalline AHM, in the region from 216 K to 246 K. (a) Poling during cooling; (b) charge released by heating; (c) charge released by consecutive cooling.

216 K (curve a). The charge generated by heating was recorded in the interval from 216 K to 246 K (curve b) with subsequent charge recording during the cooling from 246 K to 216 K (curve c). The heating-cooling cycle was again performed far from the possible phase transitions at 200 K and 280 K.

The differential thermal analysis was carried out from 113 K to 300 K. Parts of the obtained curves are shown in Figure 7.

Curve (a) was obtained from the fresh AHM powder directly taken from the sealed bottle which was opened just before the measurement. In the low temperature region around 200 K the curve is flat. However, an endothermic peak appears reproducibly at (261 ± 4) K, indicating a phase transition temperature.

Curve (b) was obtained from the AHM powder previously exposed to saturated water vapour at room temperature for 12 hours. Some water was also present in the closed DTA cell during the measurement procedure. The resulting curve shows an additional peak at a somewhat higher temperature. This may be, most likely, due to the water adsorbed by AHM.

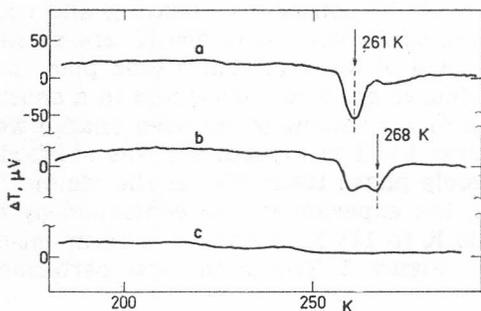


Figure 7. Differential thermal analysis curve for AHM. ΔT -temperature difference in μV of the Ni/NiCr thermocouple. (a) fresh reagent grade sample; (b) sample exposed 12 hours to the saturated water vapour; (c) sample left 12 hours in air of 50% relative humidity.

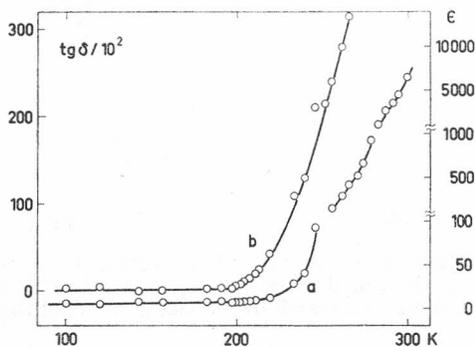


Figure 8. Dielectric thermal analysis of AHM. (a) Relative dielectric permittivity, ϵ ; (b) dielectric loss, $\text{tg } \delta$.

In cases when the AHM powder was not »fresh« but was left for a certain time in air the peaks were much smaller or completely absent. For instance, curve (c) shows a result obtained from the powder previously dried 12 hours in air of 50% relative humidity.

The last thermal analysis used for phase transition detection was the measurement of permittivity and $\text{tg } \delta$ versus temperature, results of which are presented in Figure 8. The measurements were performed only during the heating.

DISCUSSION

If one takes into consideration the results of the TSC measurements in the low temperature region published recently¹ as well as the results in the present paper for AHM it follows that the curves are not quite reproducible. However, the only reproducible phenomenon is a characteristic discontinuity close to 200 K. The temperature at which this discontinuity appears is independent of the poling temperature. This eliminates a possibility that the discontinuity in question is due to poling performed at a specific temperature. Namely, in some cases, the poling temperature may greatly influence the released current and produce characteristic jumps in the recorded curves.⁹ The $\epsilon(T)$ and $\text{tg } \delta(T)$ measurements had no such counterpart effects whatsoever in the range close to 200 K. Usually, the permittivity measurements are not sensitive enough to detect phase transitions. The clamped grains in a pressed pellet may completely lose any dielectric anomaly at the transition point.¹⁰ In addition, this low temperature TSC transition at 200 °K has no counterpart in the DTA investigation (Figures 7a, b, c) using different water vapour pretreatments of AHM. Hence, it appears that at this rather low temperature the TSC transition cannot be due to any change in the composition of the sample with regard to its water content.

The recent assumption of a phase transition near 200 K is thus still acceptable but should be confirmed using single crystal samples.

The pyroelectric origin of the generated charge and thus the ferroelectric nature of AHM is not confirmed by the experiments with consecutive heating and cooling cycles. If the charge were pyroelectric its release had to continue also during cooling with the sign of current reversed.¹¹ The results in Figure 5 show that the charge in the beginning of the cooling increases to a small extent but that, afterwards, within some ten degrees, it becomes constant. It means that the corresponding current does not change its sign but falls to zero. Similar effects occur in Figure 6 for the other, higher temperature region. Here, the charge release during the cooling is somewhat prolonged due to a higher temperature, but it also levels off. Hence, it is obvious that the charge release is just a thermally stimulated discharge without any pyroelectric component.

Generally, a poling by electric fields smaller than approximately $1 \times 10^6 \text{ Vm}^{-1}$ may cause a bulk polarisation or attract the heterocharged carriers toward the electrodes.¹² A heating after poling stimulates the relaxation phenomena and causes a heterodischarge. If the poling is performed in a stronger field a dielectric sample receives charge of the same sign by injection. Afterwards during the thermal stimulation such a sample releases a homocharge. Very often the released charge is a sum of charges with different origin. In the AHM case the poling in a relatively weak field produces a significant amount of the homocharge. In spite of the possibility that the poling applied on the polycrystalline AHM might also cause some heterocharge phenomena, the total poling effect is homocharge. It could happen only due to the charge carriers, which are able to accept the homocharge from the electrodes during poling, and then release it during thermal stimulation.

The assumption of a phase transition near 280 K is based on two independent methods, TSC and DTA. The difference in the phase transition temperature can be explained if one takes into account that the way of temperature measurements of the samples in these two methods are quite different. In the TGA and DTA of AHM (ref. 13), commercial samples ground and grain-size separated (112 μm) were used without any indication of relative humidity pretreatment. On the other hand those measurements were performed well above room temperature and as to the crystalline water they were found to be stable below 353 °K under the atmospheric pressure (and below 313 °K under 1.3 Pa (10^{-2} torr)). Therefore, any fine effects with regard to water in AHM could not be observed, as we were able to note them (Figure 7). Hence, the higher temperature TSC transition at 280 °K could be related to a specific, and yet unknown, role of the water in the structure of the original sample, as reflected by the 261 K peaks (Figure 7), which is not due to adsorbed water as is the peak at 268 K in the water saturated sample (Figure 7b).

The permittivity and $\tan \delta$ measurements do not show any particular transition temperature. The intensive rise of both curves (Figure 8) indicates that a significant d.c. conductance takes place in AHM above 200 K. This conductance is the most probable reason for the homocharge storage in the poled and frozen samples.

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REFERENCES

1. M. Topić and A. Moguš-Milanković, *Czech. J. Phys.* **B 33** (1983) 235.
2. H.T. Evans Jr., B.M. Gatehouse, and P. Leverett, *J.C.S. Dalton* (1975) 505.
3. M. Topić, *J. Appl. Cryst.* **12** (1979) 54.
4. M. Topić and A. Moguš, *Ferroelectrics* **34** (1981) 61.
5. J. Vanderschueren and J. Gasiot, *Topics in Applied Physics*, **37**, Springer-Verlag, Berlin 1979, p. 135.
6. S. Mascarenhas, *Radiat. Eff.* **4** (1970) 263.
7. V.K. Novik and N.D. Gavrilova, *Ferroelectrics* **34** (1981) 47.
8. W.M. Wendlandt, *Thermal Methods of Analysis*, Interscience Publ., New York 1964, Fig VI2, b.
9. J. van Turnhout, *Topics in Applied Physics* **33**, Springer-Verlag, Berlin 1980, p. 103.
10. L.E. Cross, A. Fouskova and S.E. Cummins, *Phys. Rev. Lett.* **21** (1968) 812.
11. J. van Turnhout, *Topics in Applied Physics* **33**, Springer-Verlag, Berlin 1980, p. 163.
12. B. Tareev, *Physics of Dielectric Materials*, Mir Publishers, Moscow 1979, p. 216.
13. A. Louisy and J.-M. Dunoyer, *J. chim. phys.* **67** (1970) 1390.

SAŽETAK

Višestruka termička analiza amonij heptamolibdat tetrahidrata

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Ispitivana su svojstva kristalnog praha amonij heptamolibdat tetrahidrata (AHM) korištenjem metode termički stimuliranog naboja (TSC), diferencijalne termičke analize (DTA) kao i mjerenjem dielektričke permitivnosti te dielektričkih gubitaka u intervalu od 113 K do 300 K.

TSC mjerenja na uzorcima, koja su prethodno bila izložena djelovanju isto-smjernog električkog polja, pokazuju izboj istoimenog naboja s diskontinuitetom u blizini 200 K. TSC mjerenja izvedena s uzastopnim grijanjem i hlađenjem uzorka ne potvrđuju pretpostavku o feroelektričnoj aktivnosti AHM. TSC krivulje dobivene bez prethodne obrade uzorka u električnom polju pokazuju maksimum kod 208 ± 10 K indicirajući točku faznog prijelaza. DTA krivulje pokazuju endotermni maksimum kod 260 ± 4 K. $\epsilon(T)$ i $\text{tg } \delta(T)$ intenzivno rastu iznad 200 K zbog električke vodljivosti AHM kristala, koja vjerovatno uzrokuje spremanje istoimenog naboja u uzorcima koji su prethodno bili izloženi djelovanju električkog polja.