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Various ferroic orderings of triclinic tetrachloro-metallate dihydrate crystals

Z Tylczyński^{1,3}, M Członkowska¹ and M Łaniecki^{1,2}

¹ Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

² Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

E-mail: zbigtyl@amu.edu.pl

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Abstract

In the triclinic crystals $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ the ferroelastic domain structure has been observed for temperatures from 100 K to the dehydration point. On heating at a few degrees before the dehydration point the structure has been found to reorganize. On heating in $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ (but not in $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$) a dielectric anomaly typical of a weak ferroelectric phase transition has been noted. The low-frequency dielectric dispersion in the low-temperature phase is attributed to the oscillations of the domain walls. The activation energy of this motion is 73 and 67 kJ mol^{-1} in $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, respectively. In the phase transition region the complex permittivity has been found to show oscillations as a function of temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The unhydrated crystals of alkaline halogens with divalent metal halogens, of the general formula A_2BY_4 , have orthorhombic or tetragonal symmetry; an example belonging to this group is Rb_2CaCl_4 . The compounds forming crystals of dihydrate tetrahalogen-metallates ($\text{A}_2\text{BY}_4 \cdot 2\text{H}_2\text{O}$) may contain the following ions: $\text{A}^+ = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$; $\text{B}^{2+} = \text{Cu}, \text{Mn}, \text{Ca}, \text{Ni}$. The crystals from this group can be divided into two classes according to their symmetry and structure. The first class includes crystals with the copper ion ($\text{A}_2\text{CuY}_4 \cdot 2\text{H}_2\text{O}$, where $\text{Y} = \text{Cl}, \text{Br}$) crystallizes at room temperature in the tetragonal symmetry with the space group $P4_2/mnm$ $Z = 4$ [1]. The crystals with the ions Mn^{2+} , Ca^{2+} and Ni^{2+} , including the following four crystals— $\text{Rb}_2\text{NiCl}_4 \cdot 2\text{H}_2\text{O}$ [2], $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ [3], $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ [4] and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ [5]—make the second class with triclinic symmetry and the space group $P\bar{1}$, $Z = 1$. It should be noted that thanks to the presence of the paramagnetic Me^{2+} ions, the crystals from both classes show a ferromagnetic or antiferromagnetic ordering in the cryogenic temperature range [6–11]. Moreover, the crystals with triclinic symmetry have domain structure at room temperature [5]. This study has been undertaken to compare

the thermal, dielectric and optical (domain structure) properties of the following triclinic symmetry crystals: $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$.

2. Experiments and results

All crystals were obtained by evaporation from a saturated water solution of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and RbCl or CsCl at the stoichiometric ratio performed at 300 K and recrystallized three times. The crystals grew in the form of plates with the largest plane in the [101] direction and the $(1\bar{1}0)$ plane being the cleavage one. The crystals of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ were pale pink while that of $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ was colourless.

2.1. TG and DSC analysis

Thermal decomposition of three crystals of dihydrate tetrachloro-metallates was studied by the thermogravimetric (TG) method and differential scanning calorimetry (DSC) using a Setsys TG-DSC 15 (SETARAM) apparatus in the temperature range from 300 to 900 K. The heating rate was 10 K min^{-1} and samples had a mass of 10–15 mg.

According to the results of TG and DSC measurements, all the dihydrate crystals studied undergo decomposition in the

³ Author to whom any correspondence should be addressed.

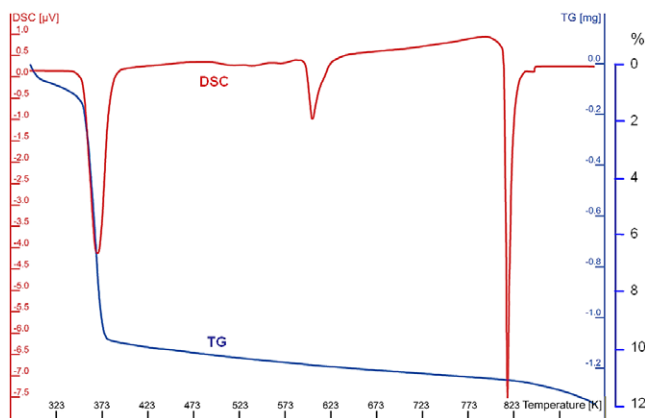
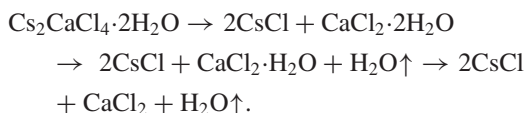


Figure 1. TG and DSC plots for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal at high temperatures.

process of dehydration, losing two molecules of crystallization water at temperatures between 350 and 375 K. Polarization microscope observations have shown that the process of dehydration starts on the surface of the crystal at a temperature a few degrees lower than that obtained by TG. Figure 1 presents the TG and DSC curves for the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal. The anomalies appearing in DSC correspond to the dehydration process ($T_{\text{dehyd}} = 347$ K), phase transition $\beta \rightarrow \alpha$ accompanied by a change from tetragonal to orthorhombic symmetry of Cs_2MnCl_4 ($T_0 = 587$ K) and the melting point ($T_m = 802$ K). The results are consistent with literature data: $T_0 = 570$ K [12] and $T_{\text{dehyd}} = 351$ K, $T_0 = 596$ K, $T_m = 811$ K [13]. The dehydration of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ is similar ($T_{\text{dehyd}} = 365$ K) but with no phase transitions of Rb_2MnCl_4 up to the melting point $T_m = 736$ K (figure 2); $T_m = 735$ K [14]. For the crystal $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ dehydration and decomposition are more complex, as illustrated by the TG and DSC curves shown in figure 3:



The temperature of decomposition into CsCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and the temperatures of the loss of the first and the second water molecules are 380, 423 and 506 K, and are close to literature data [14]. However, our results have not confirmed the occurrence of the phase transitions at 323, 360 and 407 K [15]. The relative mass loss related to the loss of crystallization water calculated for the three crystals $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ are 8.9, 7.2 and 7.4%, respectively.

2.2. Ferroelastic domain structure

In all crystals in the plane $(\bar{1}\bar{1}0)$, the domain structure was observed under a polarization microscope at temperatures from 100 K up to the dehydration point. The ferroelastic nature of this structure was evidenced by the ease of movement of the domain walls on application of an external mechanical stress. The domain structures in the crystals were similar

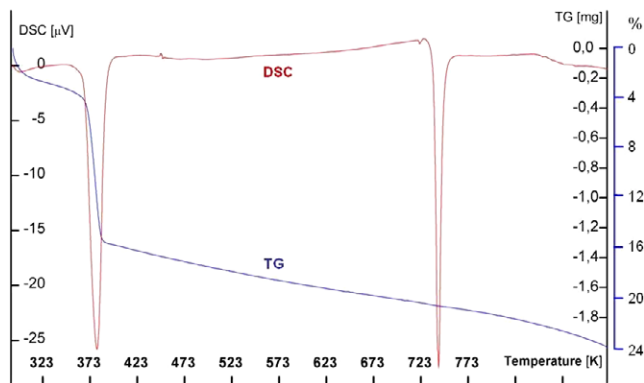


Figure 2. TG and DSC plots for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal at high temperatures.

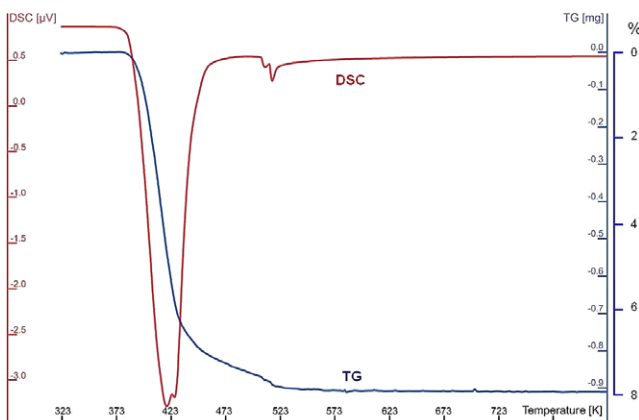


Figure 3. TG and DSC plots for $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ crystal at high temperatures.

but not homogeneous. The observations revealed very fine domains of width smaller than $1 \mu\text{m}$ along with large areas without domain walls. The $(\bar{1}\bar{1}0)$ plane in which the domain walls were observed corresponds to the pseudo-cubic plane of the CsCl sublattice [5]. This plane is an excellent cleavage plane. The domain walls seen in this plane are arranged along the $[101]$ direction and in the direction inclined at the angle of 93° to this direction. The $[101]$ direction is close to that joining the hydroxide apices of the $\text{MeCl}_4(\text{H}_2\text{O})_2$ octahedra via monovalent caesium or rubidium ions. This inclination of the second direction corresponds to the β angle in the triclinic elementary cell. Domain structure was also observed in the (101) plane. Figure 4 presents the domain structures of the crystals studied at a magnification of 200.

The ferroelastic domain structures were unchanged on cooling down to 100 K, while on heating they were observed to rearrange at about 340 K, very close to the dehydration process. Because the temperatures of the domain reorganization and the dehydration are very close it was impossible to draw conclusions as to the character of the reorganization. In different dihydrate tetrachloro-metallate crystals the course of the reorganization of the domain structure was similar: some walls disappeared, some domains were observed to brighten up and some neighbouring ones to darken, and in $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ new domains appeared (figures 5 and 6).

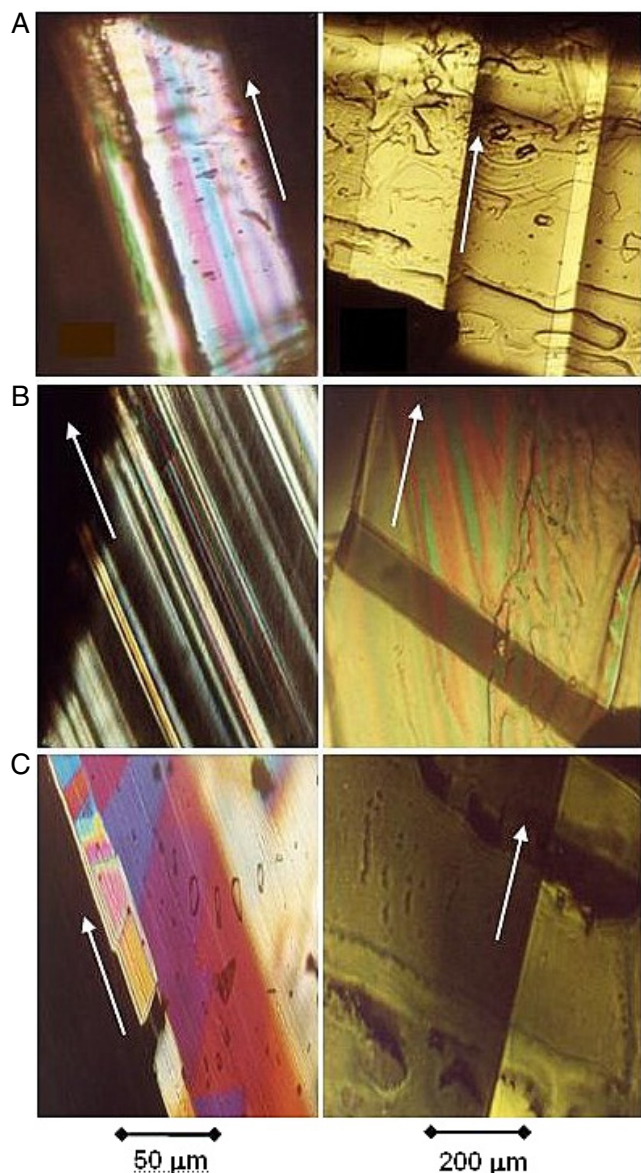


Figure 4. Domain structures in $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ (A), $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ (B) and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ (C) crystals. White arrows indicate the $[101]$ direction. Left and right sides present small and large domain structures of different samples.

As the ferroelastic domain structure occurs up to the dehydration temperature—the point of crystal degradation—the symmetry of the prototype paraelastic phase cannot be studied by diffraction methods and can only be hypothesized. Taking into consideration the orientations of the domain walls and comparing the crystallographic structures of crystals of triclinic symmetry with those of crystals of tetragonal symmetry it can be concluded that the symmetry of the prototypic phase would be cubic if a different elementary cell was chosen, the more so that the chlorine ions make a somewhat distorted cubic sublattice [5]. If so, the hypothetical phase transition would be of first order and without preservation of the relation between the group and the highest subgroup of symmetry.

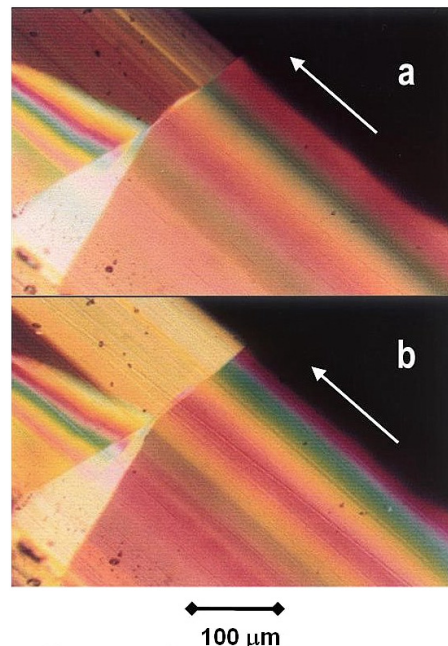


Figure 5. Reorganization of the domain structure in $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal: (a) below 335 K, (b) above 335 K. White arrows indicate the $[101]$ direction.

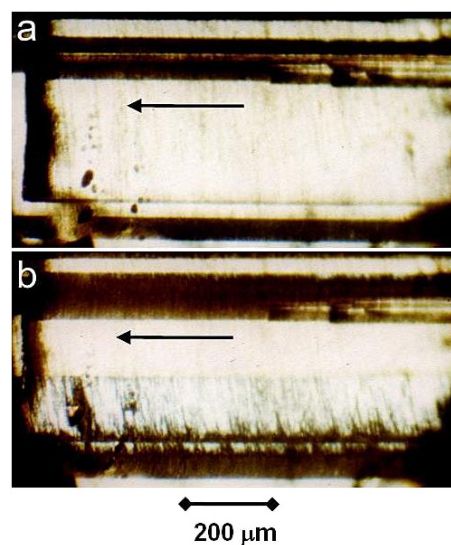


Figure 6. Reorganization of the domain structure in $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal: (a) below 333 K, (b) above 333 K. Black arrows indicate the $[101]$ direction.

2.3. Dielectric properties

Relative complex dielectric permittivity was measured by a HP42484A (Hewlett-Packard) impedance analyser in the frequency range 100 Hz–1 MHz and for temperatures between 100 K and dehydration temperatures for samples cut out in the $(1\bar{1}0)$ plane from all crystals. The surfaces of the samples were covered with gold vacuum evaporated electrodes. The rate of temperature change was 0.5 K min^{-1} , and the measuring field was 0.2 V mm^{-1} . The dry nitrogen atmosphere was used for all dielectric measurements.

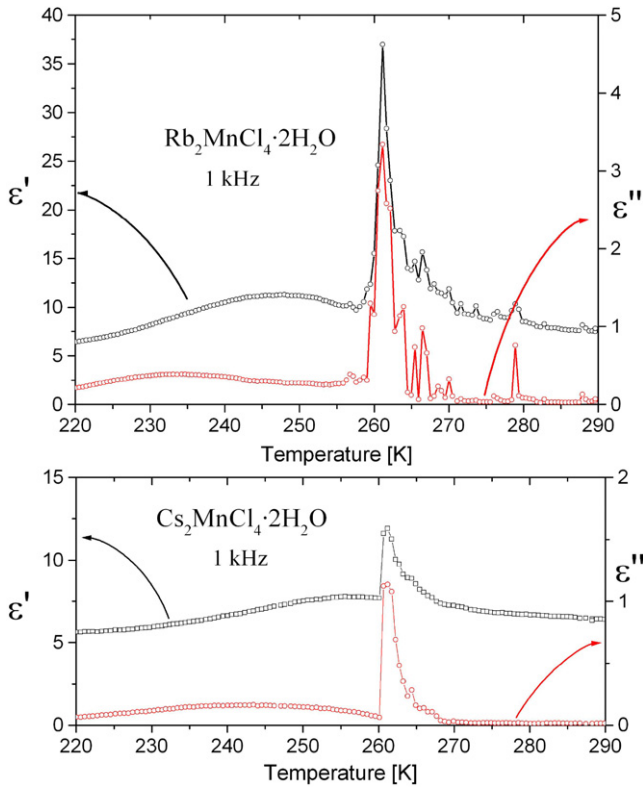


Figure 7. Dielectric permittivity for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals on heating at 1 kHz.

In all crystals studied on heating from RT up to the temperature of dehydration, no dielectric anomalies were observed to suggest phase transitions. About 10 K below the temperature of dehydration a strong increase in the imaginary component of the complex permittivity appeared, related to an increase in the electric conductivity.

2.3.1. Ferroelectric phase transition. Below RT, the temperature dependences of permittivity of the crystals $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ reveal anomalies typical of a weak ferroelectric phase transition. No anomalies were observed for the $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ crystal in the temperature range studied. For the former two crystals the phase transition temperature on heating is 261 K. Figure 7 presents the temperature dependences of the real and imaginary components of permittivity for the two crystals on heating at 1 kHz. The phase transition of first order as confirmed by the large temperature hysteresis, $\Delta T_C = 21$ K for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\Delta T_C = 17$ K for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, and there were jumpwise changes in ϵ' and ϵ'' just below T_C . In the frequency range applied, the maximum value of the real component of permittivity minus background and the maximum value of the imaginary component strongly depend on frequency ($\Delta\epsilon'$ decreases 30 times from 100 Hz to 1 MHz). The changes, illustrated in figure 8, indicate the relaxational character of the order parameter. The anomalies in permittivity observed on cooling were much smaller. The ferroelectric character of the phase transition was confirmed by our earlier measurements of spontaneous

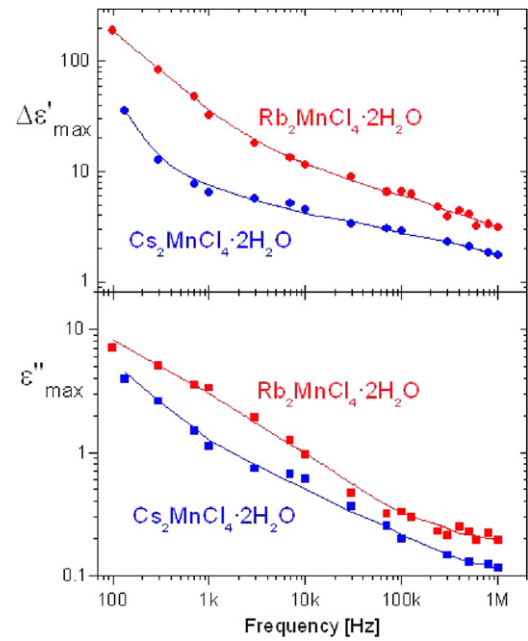


Figure 8. Maximal values of ϵ' and ϵ'' at T_C on heating for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals.

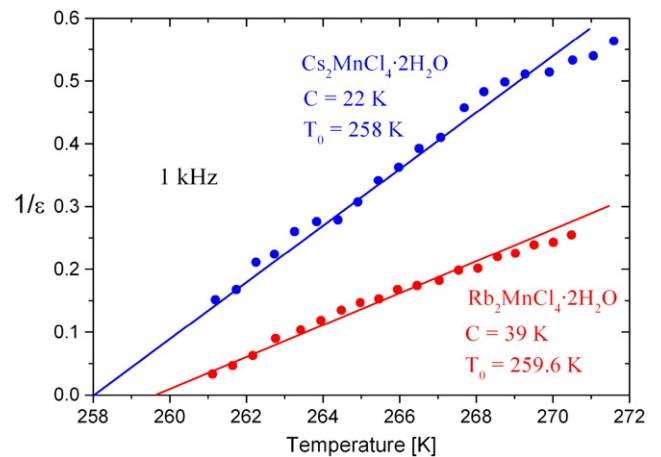


Figure 9. Reciprocal dielectric permittivity in the paraelectric phase of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ for 1 kHz.

polarization, whose value for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ was $1.9 \times 10^{-3} \text{ C m}^{-2}$ at 220 K [16]. So one can suppose that the low-temperature phase of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ should be ferroelectric too. The temperature changes in the inverse permittivity in the paraelectric phase, shown in figure 9, obey the Curie–Weiss law. The Curie–Weiss constant is low ($C = 39$ K) for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and 22 K for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. Consistent with the properties of the low-temperature phase, its symmetry should be triclinic with the point group 1. Confirmation of this supposition would require x-ray or neutron scattering measurements.

Although all the crystals studied have the same symmetry and crystallographic structure, the ferroelectric phase transition takes place only in the crystals containing the Mn^{2+} ions. The reason for this difference can be the structure of the

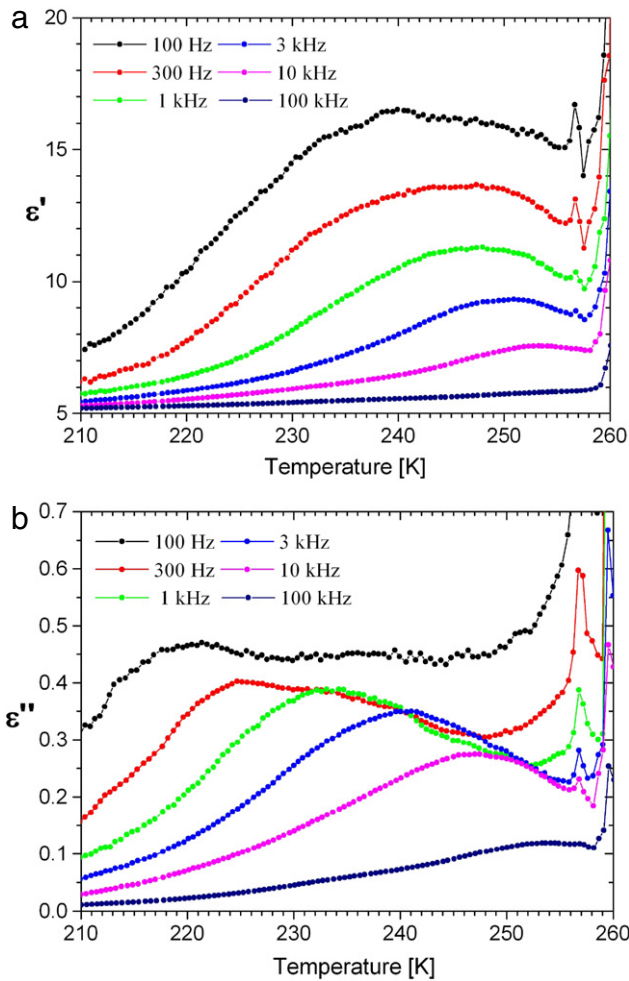


Figure 10. Low-frequency dielectric dispersion for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$: (a) ϵ' , (b) ϵ'' .

$\text{BCl}_4(\text{H}_2\text{O})_2$ octahedra. The ratio of the Me–Cl to Me–O bond lengths in the crystals with the Mn^+ ions is $(\text{Mn–Cl})/(\text{Mn–O}) \approx 1.08$, while in the crystal with the Ca^{2+} ions the analogous ratio is $(\text{Ca–Cl})/(\text{Ca–O}) \approx 1.03$. The $\text{CaCl}_4(\text{H}_2\text{O})_2$ octahedron is inclined at about 10° with respect to the axis joining water molecules with the central ion, while the $\text{MnCl}_4(\text{H}_2\text{O})_2$ octahedron is inclined only at 1.5° .

2.3.2. Dispersion of domain walls. Below the phase transition point low-frequency dielectric dispersion was observed. Figures 10 and 11 present the temperature changes in ϵ' and ϵ'' in the low-temperature phase for the $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals. With increasing frequency the maximum of the imaginary component of permittivity was shifted towards higher temperatures. The frequency dependences of the real and imaginary components of permittivity confirm the relation of the dispersion observed with the relaxational processes. The changes similar to those observed for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ were reported for the classical ferroelectric crystals TGS, KDP and BaTiO_3 , in which they were assigned to the oscillatory movement of the domain walls under the

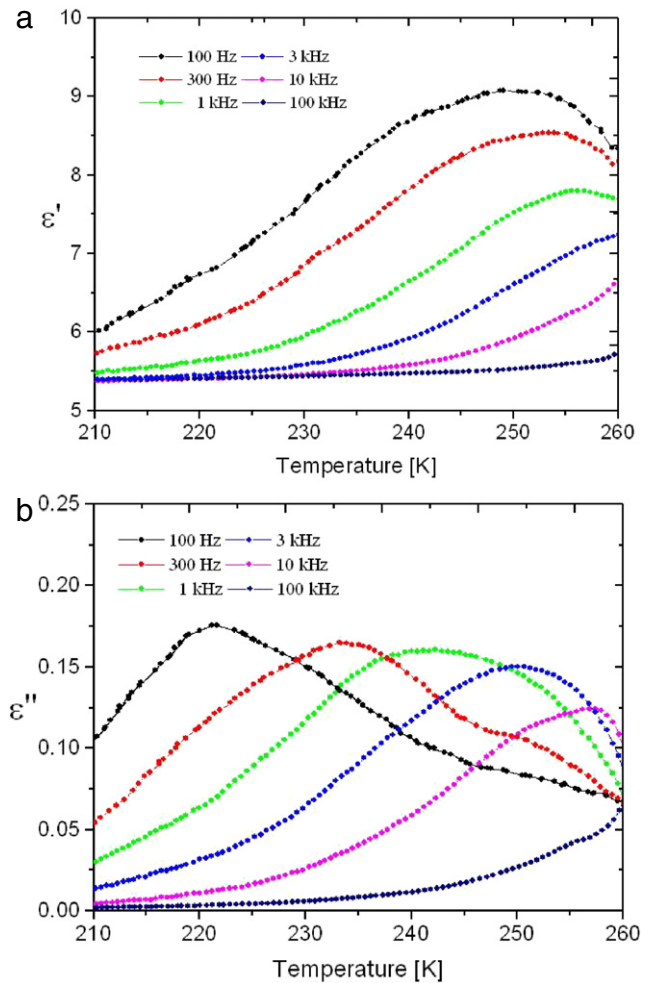


Figure 11. Low-frequency dielectric dispersion for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$: (a) ϵ' , (b) ϵ'' .

applied electric measuring field [17, 18]. Therefore, it can be supposed that in the crystals studied in this work the observed dispersion is caused by a similar motion. Figure 12 presents the relaxation frequency as a function of the inverse temperature for both crystals. The activation energies of this process obtained from the Arrhenius law were 73 and 67 kJ mol^{-1} for crystals with Rb^+ and Cs^+ ions, respectively.

2.3.3. Permittivity oscillations in the vicinity of the phase transition. In the vicinity of the phase transition exclusively on heating, unusual changes were noted in the real and imaginary components of permittivity of the crystals $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. They appeared as oscillations as a function of temperature (figures 13 and 14), and the amplitude of the oscillations strongly decreased with increasing frequency and for 10 kHz the oscillations in ϵ'' were undetectable. For the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal the amplitude of the oscillations was a few ten times smaller than for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. The distances between the neighbouring maxima were about 2.2 K for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and about 1.2 K for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. Changes of such a character have not been hitherto reported. They may be related to the

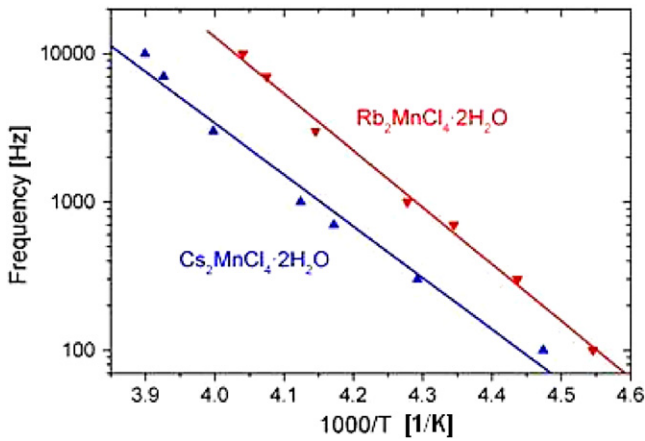


Figure 12. The relaxation frequency as a function of the inverse temperature.

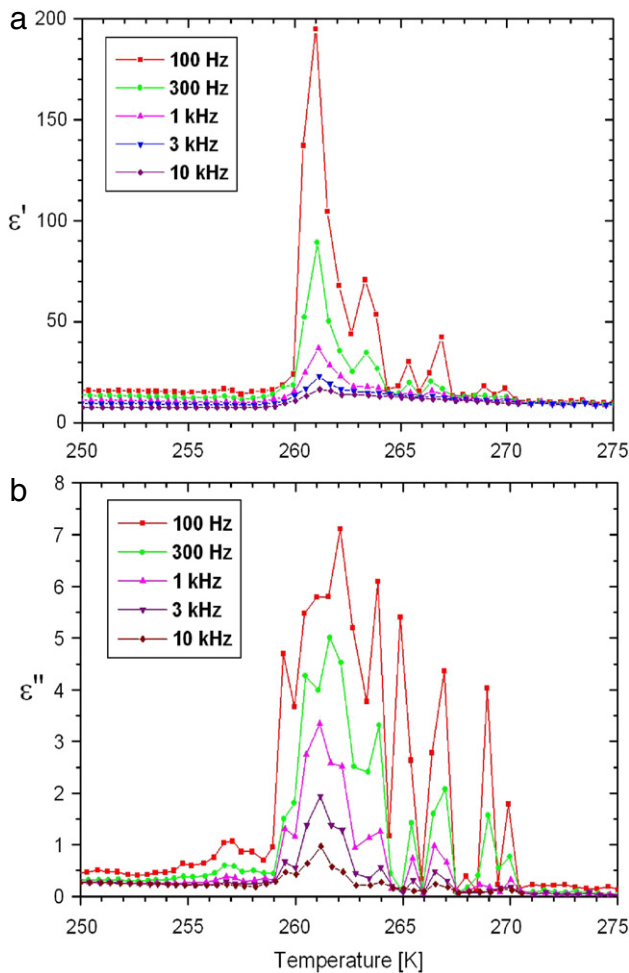


Figure 13. Oscillation of ϵ' (a) and ϵ'' (b) for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ (heating).

ferroelastic domain structure and mechanical deformations in the domain walls. The spontaneous polarization changing as a function of temperature may interact with the deformations at the structural defects leading to local changes in the permittivity, whose magnitude changes starting from a certain

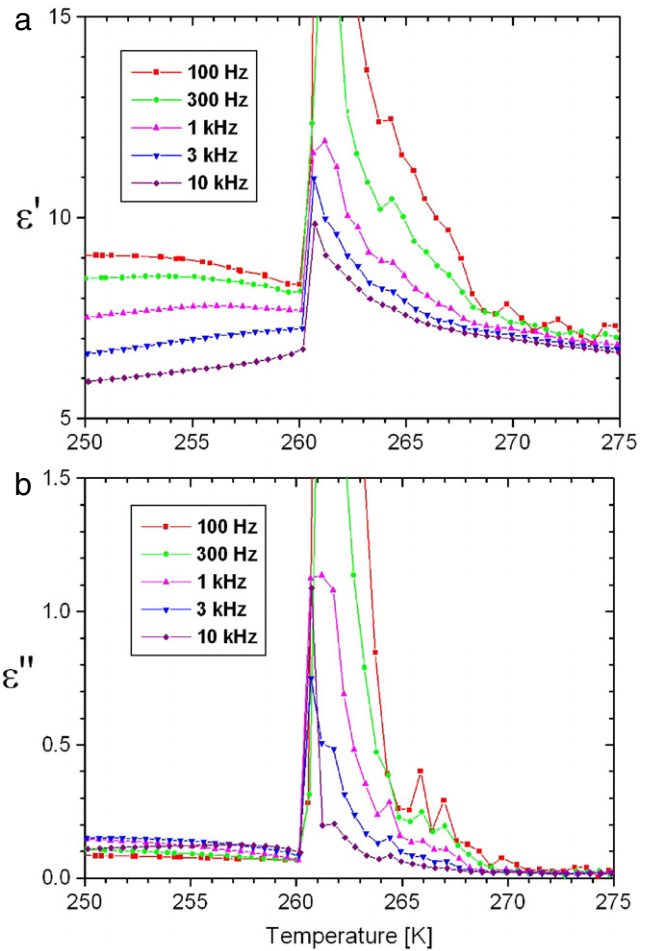


Figure 14. Oscillation of ϵ' (a) and ϵ'' (b) for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ (heating).

critical temperature. The oscillations superimpose on the usual temperature changes in permittivity described by the Curie–Weiss law. Another possible explanation of this phenomenon is coexistence above T_C of the low-temperature ordered phase and the paraelectric one that gives a metastable state. A similar metastable state exists in $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ crystal in the vicinity of this ferroelastic phase transition [19].

3. Summary

Thermal decomposition of three crystals of dihydrate tetrachloro-metallates $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$: $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ has been studied by the thermogravimetric (TG) method and differential scanning calorimetry (DSC). The two crystals containing manganese ions lose their crystallization water at temperatures of 365 and 347 K. The decomposition of the crystal containing calcium ions is much more complicated. At 380 K the crystals separate into CsCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Then calcium chloride subsequently loses two water molecules at 423 and 506 K. For the $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal in the range from LNT to RT a small anomaly on cooling was noted in the DSC curve at 252 K, indicating the occurrence of phase transition [16].

At RT all the crystals have triclinic symmetry with the space group $P\bar{1}$, $Z = 1$ and ferroelastic domain structures in the $(1\bar{1}0)$ plane, visible under a polarization microscope. The structures were similar in all three crystals but not homogeneous; besides very fine domains of width smaller than $1\ \mu\text{m}$, large areas devoid of domain walls were observed. The domain walls in the $(1\bar{1}0)$ plane lie along the direction $[101]$ and along the direction inclined to the former one at 93° . The $[101]$ direction is close to that joining the hydroxide apices of the $\text{MeCl}_4(\text{H}_2\text{O})_2$ octahedra via monovalent ions of caesium or rubidium, while the inclination angle of the other direction corresponds to the β angle of the triclinic elementary cell.

In the temperature range studied, the ferroelastic domain structures remained unchanged, but exclusively on heating the structures were found to reorganize at a few degrees prior to dehydration. The reorganization involved the disappearance of some domain walls, brightening up of some others and darkening of the neighbouring ones, and the appearance of new domains. Taking into regard the orientation of the domain walls and comparing the crystallographic structure of the crystals studied with those of crystals with tetragonal symmetry, it can be concluded that the symmetry of the prototype phase would be cubic if a different elementary cell was chosen.

In the low-frequency range 100 Hz–1 MHz, on heating, a strong anomaly in the dielectric permittivity of the crystals containing manganese ions was observed at $T_C = 261\ \text{K}$. The temperature hysteresis and jumpwise changes in ϵ' and ϵ'' at T_C indicate that the crystals undergo first order phase transitions. As follows from the frequency dependence of the changes, the order parameter has a relaxational character. On the other hand, according to our earlier study of spontaneous polarization [16], the low-temperature phase is ferroelectric. This character of the low-temperature phase is supported by the anomalous changes in permittivity typical of the relaxational motions of domain walls induced by an external electric field. The activation energy of these motions is 73 and 67 kJ mol^{-1} for the crystals with Rb and Cs ions, respectively. An unexpected and interesting result was the observation of oscillatory changes in the real and imaginary components of permittivity as a function of temperature. In the $\text{Cs}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ crystal the oscillations were a few ten times weaker than in $\text{Rb}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ and the amplitude of these oscillations strongly decreased with increasing frequency. The absence of the ferroelectric phase transition in the $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$ crystal could be a result of distortion of the $\text{CaCl}_4(\text{H}_2\text{O})_2$ octahedron with respect to the $\text{MnCl}_4(\text{H}_2\text{O})_2$ one.

The experiment has shown that from among the dihydrate tetrachloro-metallates, the $\text{Rb}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ crystals show an interesting variety of mutually independent types of ordering: ferroelastic, ferroelectric and antiferromagnetic.

	Dehydration temperature
Ferroelastic	345–365 K
Ferroelectric	261 K
Antiferromagnetic	1.8–2.8 K

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