The domain structure of the $Rb_2Cd_2(SO_4)_3$ and $Tl_2Cd_2(SO_4)_3$ langbeinite crystals

2. The domain structure in the ferroelectric-ferroelastic phases of the $Rb_2Cd_2(SO_4)_3$ crystals

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Abstract.

The temperature behavior of the domain structure in the ferroelectric-ferroelastic phases of the $Rb_2Cd_2(SO_4)_3$ langbeinite crystals were investigated by the optical microscopy method. The new phase with the point group of symmetry 3 was found in the temperature region 130K<T<113K. By the observation of the domain structure in the temperature region 113K<T<101K the coexistence of the monoclinic and trigonal phase was revealed. The broad maximum of the dielectric permitivity measured at frequency 1MHz around $T=T_{c4}$=113K was found. This maximum significate that phase transition at T_{c4} is the diffuse phase transition.

Key words: $Rb_2Cd_2(SO_4)_3$, langbeinite crystals, domain structure, dielectric permitivity, phase transition.

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1.Introduction

As it was mentioned in the first part of the present paper $Rb_2Cd_2(SO_4)_3$ (RCS) crystals undergo phase transitions with the change of the symmetry $P2_13 \rightarrow P2_1 \rightarrow P1 \rightarrow P_12_12_12_1$ at T_{c1}=130K, T_{c2}=101K and T_{c3}=68K, respectively [1]. The peculiarity of the monoclinic phase of the RCS crystals is the unusual behavior of the spontaneous polarization - the change of sign of the P_s in the single domain sample inside ferroelectric phase at T_i=113K [2]. As it is followed from our previous paper [3] optical birefringence, which was measured on the multidomain crystals also change the sign at that temperature. On the other hand, structural investigations [4] did not find any anomalies in the lattice parameters at T_i. But the intensity of the supperlattice reflection possess the maximum at that temperature [4]. It is interesting to note that according to the phenomenological analysis [5] langbeinite crystals could possess the improper ferroelectric phase transition to the trigonal phase with the space group of symmetry R3. Such phase transition was never found out experimentally. From the phase diagram of the langbeinite crystals that was obtained on the base of the phenomenological analysis [6], it follows that the trigonal phase could appear between cubic ($P2_13$) and monoclinic phase ($P2_1$) or sequence of phase transitions could be the next $P2_13 \rightarrow P2_1 \rightarrow R3$. In such case one can ask: if the temperature T_i is the temperature of phase transition or if it is the temperature of compensation of the supperlattice polarization? It is necessary to note that the domain structure in the phases R3 and $P2_1$ should be different. So, the present paper is devoted to the investigations of ferroelectric-ferroelastic phases in the RCS crystals by the observation of the domain structure.

2.Experimental procedure and results

The investigation of the domain structure of the RCS crystals in the ferroelectric phases was made with the help of the optical polarization microscope with the temperature cooling cell which permit temperature controlling down to liquid nitrogen temperature with the precision not worse than 0.1K. The photographing was made by using photocamera. The RCS crystals were grown at 367K from liquid solution of Rb_2SO_4 and $CdSO_4$ salts mixed in the molar ratio 1:2. Good optical quality crystals with the average size of 10x10x5mm^3 were obtained after two week growing process. Crystal plates of the <111> orientation with thickness of 0.97mm were cut by diamond wire from bulk samples and were polished by a diamond paste. The dielectric permitivity was measured by the capacity bridge on the frequency of 1MHz and 100 kHz.

The domain structure in the RCS crystals appeared at cooling process at $T=T_{c1}$. As it is visible from fig.1 at $T_i<T<T_{c1}$ four different domains exist in the sample - S1, S2, S3, S4. The domain walls between central dark domains S4 and bright domains S1, S2 and S3: S1-S4, S2-S4 and S3-S4 are parallel to the (110), (011) and (101) planes, respectively.

The domain walls between central, dark part of the fig.1 (domain S4) and bright regions (domains S1, S2, S3) look like diffuse boundaries and are inclined to the surface of the crystal plate. These domain walls are parallel to the principle crystallographic planes (001), (100) and (010).

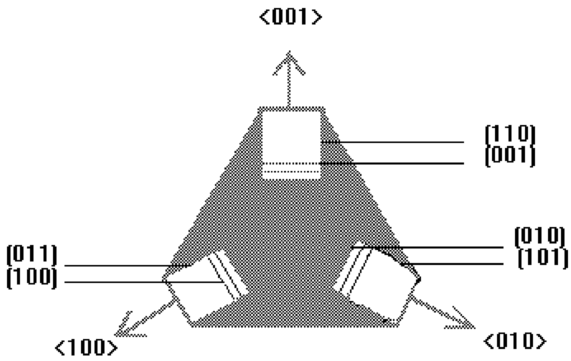
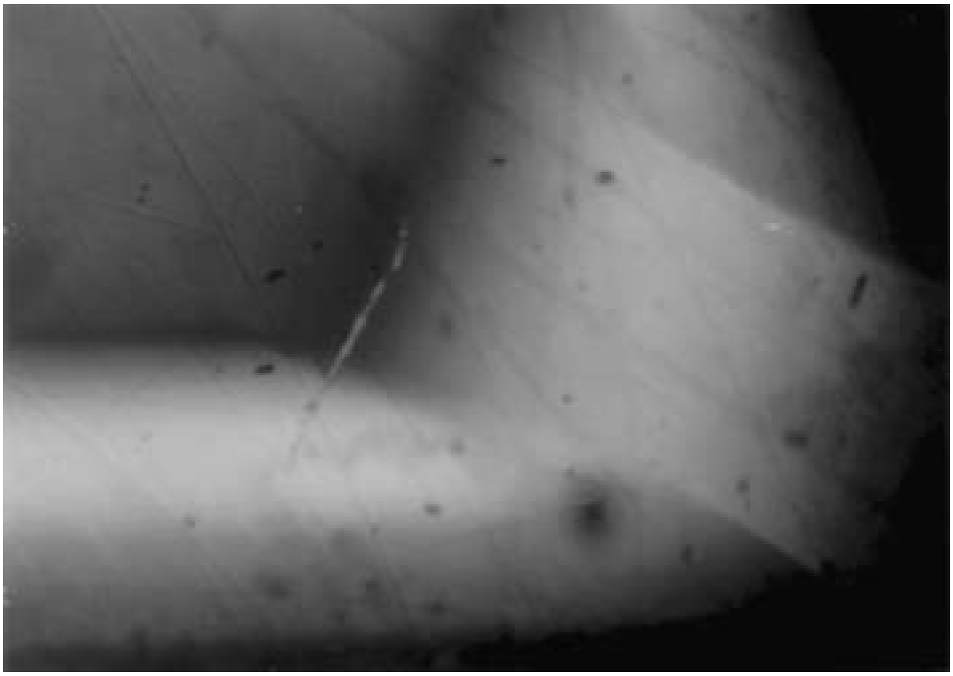


Fig.1. The domain structure in the RCS crystals at $T_i<T<T_{c1}$ (schematical view). Four different domains exist in the sample - S1, S2, S3, S4.

So, one can conclude that in the RCS crystals in the temperature interval $T_i<T<T_{c1}$ simultaneously exist four different orientation states which are separated by three pairs of the mutually perpendicular domain walls. The extinction positions in S1, S2 and S3 orientation states differ in 30^o. It is interesting to note that domain S4 extinct in any position between crosses polarizes. It means that the direction <111> in S4 domain in the temperature interval $T_i<T<T_{c1}$ coincide with the optically isotropy direction. At the temperature interval $T_{c2}<T<T_i$ the central and non-central dark parts of the sample become optically anisotropical (fig.2). It means that bellow T_i new three domains S5, S6, S7 appeared in the RCS crystals. The domain walls between central - hexagonal domain S4 and new S5, S6, S7 domain are inclined to the (111) surface and are parallel to the principle crystallografical planes. At T_i the movement of the phase boundary was not visible. Bellow T_{c2} domain structure become more complicated (fig.3). The S5, S6 and S7 are splitted in to the layers like domains with domain walls parallel, perhaps, to the {100} planes. At heating process we observed the changing of domain structure in the back order.



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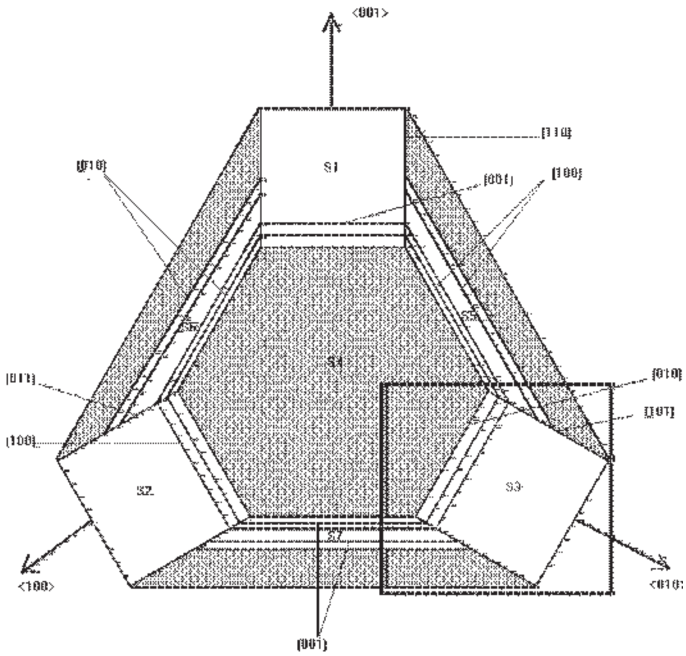
a)



b)

Fig.2. The domain structure in the RCS crystals at $T_{c2}<T<T_i$:
a) microphotograph, b) schematical view

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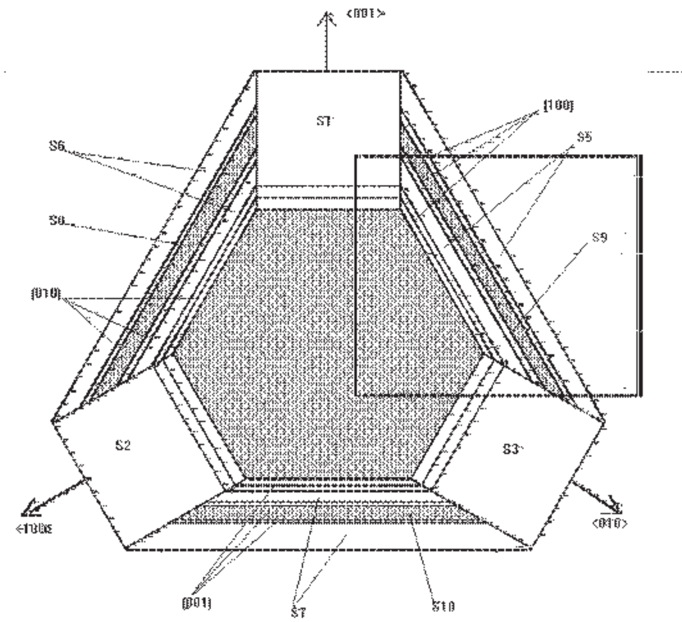
a)



b)

Fig.3. The domain structure in the RCS crystals at $T<T_{c2}$: a) microphotograph, b) schematical view

3.Discussion

The principle question on which we should find the answer after the above mentioned investigations is: if the T_i temperature is the temperature of phase transition or if it is the temperature of spontaneous polarization compensation due to the existing of the superlattice structure in the RCS crystals in monoclinic phase? As it is followed from data presented in [2] and [3] the spontaneous polarization and optical birefringence possess monotonic temperature dependence in the vicinity of T_i. It means that around T_i the domain structure should not be visible due to the absence of birefringence. But as it follows from the results of our observations – the domain structure exists at T_i and in the temperature range $T_i<T<T_{c1}$ four different orientation states exist. These domains possess different spontaneous deformations and one of them (S4) is optically single-axial. The optical axis of the S4 domain coincides with the <111> direction. It is necessary to note that at ferroelectric-ferroelastic phase transition with the change of symmetry 23→3 four orientation states could appear which differ by spontaneous deformation tensor and the domain walls between them should be parallel to {100} and {110} planes.

The paraelastic-paraelectric phase for the monoclinic phase with the point group of symmetry 2 in the langbeinite crystals is a cubic phase with the point group of symmetry 23. In this case according to the Sapriel theory [7] in the monoclinic phase six orientation states and three domain walls with orientation (100), (010) and (001) could appear. However, the domain walls with orientation {110} are forbidden. The existing of domain walls which are parallel to the {110} planes as well as the existing of seven orientation states in the monoclinic phase means-that the phases with the point group of symmetry 3 and 2 coexist at temperature below T_i. The domain walls with {110} orientation which were observed in the monoclinic phase are the remain walls of the trigonal phase. As the confirmation of this fact is the presence of the broad maximum on the temperature dependence of dielectric permitivity around T_i (fig.4).

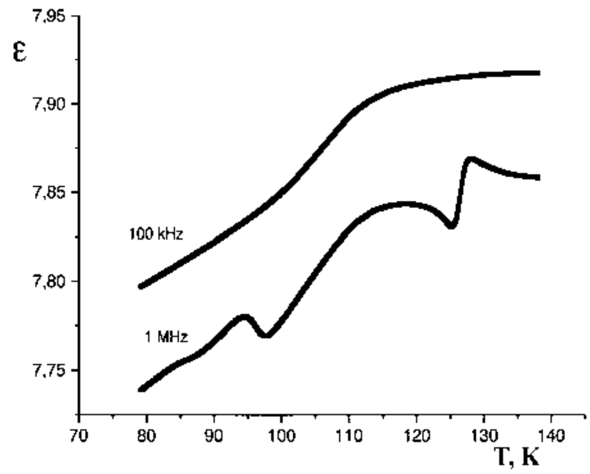


Fig.4. The temperature dependence of the dielectric permitivity of the RCS crystals measured in the <111> direction at 1MHz and at 100kHz.

On the basis of domain structure observation and temperature dependence of dielectric permitivity we can conclude that $T_i=T_{c4}$ is the temperature of diffuse phase transition between trigonal and monoclinic phase. As one can see (fig.3) in the triclinic phase the view of the domain structure is more complicated: inside S5, S6 and S7 domains new domains appeared and the domain walls which are separated there domains are inclined to the (111) - plane. In general, in this phase 12 orientation states could be observed and we found the rising of quantity of the domains at $T<T_{c2}$.

4.Conclusions

1. At the temperature range $T_{c4}<T<T_{c1}$ in the RCS crystals four orientation states which differ by the spontaneous deformation tensor were found. In one of these domains optical axis coincides with the <111> direction. Such domain structure corresponds to the ferroelectric-ferroelastic phase transition with the change of symmetry 23↔3.

2. Around T_{c4} broad maximum and the anomaly dependence of the dielectric permitivity was observed. At the temperatures $T_{c4}<T<T_{c2}$ the existing of no-permissible domain walls for the phase with the point group of symmetry - 2 for which paraelastic-paraelectric phase possesses the point group of symmetry 23 was found. Such behavior of dielectric permitivity and domain structure in the vicinity of T_{c4} means that the phase transition at T_{c4} is a diffuse phase transition and at $T_{c4}<T<T_{c2}$ coexist in the RCS crystals monoclinic and trigonal phases.

3. At T_{c3} the phase transition to the triclinic phase manifests in the complicating of the domain structure, appearing of new domains and domain walls.

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