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

1. The domain structure in the ferroelastic phase of the $Tl_2Cd_2(SO_4)_3$ crystals

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Abstract

The "non-permissible" domain structure in the ferroelastic phase of TCS crystals was found out. The orientation of the domain walls between three pairs of domains S2-S3', S1-S2' and S1-S3' were found to be (110), (101) and (011), respectively. The regions of the paraelastic phase was not observed between the domains. The orientation of the domain walls in the ferroelastic phase of the TCS crystals confirm the conception about the existing of the parent phase with the point group of symmetry $\bar{4}3m$ in the langbeinites.

Key words: ferroelastics, domains, langbeinites, $Tl_2Cd_2(SO_4)_3$.

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Introduction

Crystals which belong to the langbeinite mineral family usually undergo phase transitions with the change of symmetry $P2_13 \rightarrow P2_12_12_1$ or $P2_13 \rightarrow P2_1 \rightarrow P1 \rightarrow P2_12_12_1$ [1]. The phase with symmetry $P2_12_12_1$ is proper ferroelastic as well as the phases with symmetry $P2_1$ and P1 are improper feroelectrics [2]. Only two langbeinite compounds -$Rb_2Cd_2(SO_4)_3$ (RCS) and $Tl_2Cd_2(SO_4)_3$ (TCS) undergo full sequence of the phase transitions [3,4]. TCS crystals possess phase transitions from the cubic to the monoclinic phase at T_{c1}=130K, from the monoclinic to the triclinic phase at T_{c2}=127K and from the triclinic to the orthorhombic phase at T_{c3}=98K as well as RCS crystals possess phase transitions at T_{c1}=130K, T_{c2}=101K and T_{c3}=68K, respectively [3,4]. In our previous paper [5] we reported that the $K_2Cd_2(SO_4)_3$ (KCS) langbeinites which undergoes phase transitions with the change of symmetry $P2_13 \rightarrow P2_12_12_1$ possesses ferroelastic domain walls in the low temperature phase. These domain walls are "non-permissible" according to the Sapriel theory [6] in connection with the noncompatibility of spontaneous strains of the neibouring domains. The existing of these walls was described on the base of assuming that langbeinites has the parent phase with the point group of symmetry $\bar{4}3m$. It is interesting to note that the domain boundaries in the KCS crystals are thick (the average thickness is 16 - 40μm) and the region of domain boundary is the region of cubic paraelastic phase. The orientation of walls was experimentally determined as {110} and theoretically explained on the base of assuming of the parent phase. From this explanation follows that the orientation of these domain walls can not sufficiently deviate from the {110} planes in the case of different value of spontaneous deformation tensor. The TCS crystals should possess other value of spontaneous deformation tensor than KCS. So, the first problem of present investigations was the determination of the orientation of domain walls in the ferroelastic phase of the TCS crystals. The next question was: does the paraelastic region which play the role of the domain boundary in the case of KCS crystals will play the same role in the TCS crystals in which ferroelastic phase is not in the temperature contact with cubic paraelastic phase?

Experimental procedure and results

The investigation of the domain structure of the TCS crystals in the ferroelastic phase was made by the optical polarization microscope with the temperature accessories. The cooling cell permit temperature controlling down to liquid nitrogen temperature with precision not worse than 0.1K. The photographing was made by using of photocamera. The TCS crystals were grown at 367K from liquid solution of Tl_2SO_4 and $CdSO_4$ salts mixed in the molar ratio 1:2. Good optical quality crystals with the average size $10x10x5mm^3$ was obtained after two weeks of growing process. The crystal plates of the <111> orientation with thickness 0.91mm were cut down by a diamond wire from bulk samples and were polished by diamond paste. The reason of choosing the <111> direction of the observation of domains is connected with the orientation of the optical indicatrix in the neibouring domains. In the case of the ferroelastic phase transition in the langbeinite crystals, due to the piezooptical effect induced by the spontaneous deformations, extinction position in the neighbour domains is the same if the direction of the observation coincide with the principle crystallographic axis. When the direction of the observation is parallel to the <111> direction, the extinction position in different domains differs into 30^o and the domain structure could be visible.

The ferroelastic domain structure apeared at T_{c3}=98K at cooling and was saved down to the liquid nitrogen temperature without any changes (fig.1,a). We have observed three pairs of domains S2-S3', S1-S2' and S1-S3' with domain walls orientation between them (110), (101) and (011), respectively (fig.1,b). The mechanical strains on the domain walls as well as regions of paraelastic phase were not visible. The overlapping of different domains in the direction of light propagation was observed. These domains had disappeared at T_{c3} at heating. In the ferroelectric-ferroelastic phases with the point group of symmetry 2 and 1 we have observed 90^o domains which disappeared in the cubic phase.

Discussion.

In our previous paper [5] we have assumed that in KCS crystals were coexisting of enantiomorphic structures. This was deduced from the consideration that there is a prototype phase for langbeinite family crystals belonging to the point group $\bar{4}3m$. In this case, there are two modifications in the system with the point group 23 related by $\bar{4}$ and m_d symmetry elements which transform the coordinate system (xyz) to (yxz). The free energy to describe the ferroelastic phase transition in ferroelastic langbeinites is given in the term of the two independent strain components which construct the basis function of the two-dimensional irreducible representation of the point group 23 as follows [2] :

$$F = \alpha(u_1^2+u_2^2)+\delta_1 u_1(u_1^2-3u_2^2)+ +\delta_2 u_2(u_2^2-3u_1^2)+\beta(u_1^2+u_2^2)^2, \qquad (1)$$

$$u_1=1/(6)^{1/2}(2e_{zz}-e_{xx}-e_{yy}), \qquad (2)$$

$$u_2=1/(2)^{1/2}(e_{xx}-e_{yy}) \qquad (3)$$

It is convenient to introduce the polar coordinate (ρ,θ) to rewrite the above expression as follows:

$$F = \alpha\rho^2+\delta_1\rho^3\cos3\theta+\delta_2\rho^3\sin3\theta+\beta\rho^4. \qquad (4)$$

The stable configuration of θ - value is given by minimizing eq.(4) as

$$\theta_o=\pm 1/3\arctan\delta_2/\delta_1 \qquad (5)$$

where the double sign corresponds to the enantiomorphic modifications. In particular, when $\delta_1=0$, $\theta_o=\pm 30^o$ and the corresponding basis vector is identified to be u_2. In such case, the spontaneous deformations for the six domains of the ferroelastic phase are simply given by the following strain tensor:

$$\text{F1: } \varepsilon_1=\rho_o/(2)^{1/2}\begin{vmatrix} 1 & & \\ & -1 & \\ & & 0 \end{vmatrix} \qquad \text{F1': } \varepsilon_{1'}=\rho_o/(2)^{1/2}\begin{vmatrix} -1 & & \\ & 1 & \\ & & 0 \end{vmatrix}$$

$$\text{F2: } \varepsilon_2=\rho_o/(2)^{1/2}\begin{vmatrix} 0 & & \\ & 1 & \\ & & -1 \end{vmatrix} \qquad \text{F2': } \varepsilon_{2'}=\rho_o/(2)^{1/2}\begin{vmatrix} 0 & & \\ & -1 & \\ & & 1 \end{vmatrix} \qquad (6)$$

$$\text{F3: } \varepsilon_3=\rho_o/(2)^{1/2}\begin{vmatrix} -1 & & \\ & 0 & \\ & & 1 \end{vmatrix} \qquad \text{F3': } \varepsilon_{3'}=\rho_o/(2)^{1/2}\begin{vmatrix} 1 & & \\ & 0 & \\ & & -1 \end{vmatrix}$$

Here, the unprimed and primed domains are associated with different enantiomorphic modifications. In order to investigate the properties of the domain boundaries, we consider the difference of the spontaneous deformations between the domains originated from different enantiomorphic modifications. For instance, we have

$$\Delta\varepsilon(\text{S3'-S2})=\varepsilon_{3'}-\varepsilon_2= \rho_o/(2)^{1/2}\begin{vmatrix} -1 & & \\ & 1 & \\ & & 0 \end{vmatrix} \qquad (7)$$

$$\Delta\varepsilon(\text{S1-S2'})=\varepsilon_1-\varepsilon_{2'}= \rho_o/(2)^{1/2}\begin{vmatrix} -1 & & \\ & 0 & \\ & & 1 \end{vmatrix} \qquad (8)$$

$$\Delta\varepsilon(\text{F1-F3'})=\varepsilon_1-\varepsilon_{3'}= \rho_o/(2)^{1/2}\begin{vmatrix} 0 & & \\ & -1 & \\ & & 1 \end{vmatrix} \qquad (9)$$

From the Sapriel theory, it is easily seen that well-defined {110} - type domain boundaries should be formed between these domains.

The above described domain configuration corresponds to TCS crystals which are not far from the condition $\delta_1=0$ and the domain walls are planer with {110} orientation. The absence of the mechanical strains on the domain walls and the regions of the paraelastic phase between the domains mean that the region of the elastic adaptation between the ferroelastic domains in TCS crystals is thin in the comparison with KCS crystals and values of the two diagonal components of the spontaneous deformation tensor are similar. More over, perhaps paraelastic phase cannot appear as domain wall in the case if the ferroelastic phase is not in the temperature contact with paraelastic one.

Conclusions

1. The “non-permissible” domain structure in the ferroelastic phase of TCS crystals was found out.
2. The orientation of the domain walls between three pairs of domains S2-S3’, S1-S2’ and S1-S3’ were found to be (110), (101) and (011), respectively.
3. The regions of the paraelastic phase was not found between the domains.

The orientation of the domain walls in the ferroelastic phase of the TCS crystals confirm our conclusion about the existing of the parent phase with the point group of symmetry $\bar{4}3m$ in the langbeinites.

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