Phase Transition in β-Alanine Amino Acid Crystals

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Abstract

Single β-alanine crystals are grown by a triple cross-crystallization from the saturated aqueous solution of chemically pure β-Ala powder and then dried in the vacuum thermostat at 340K. β-Ala single crystals belong to the point group of symmetry *mmm* at the room temperature. It is found that the temperature dependences of thermal expansion and the optical manifest anomalous behaviour at T=204K, thus testifying the existence of phase transition at this temperature. The temperature hysteresis of the Curie temperature T_c means that the phase transition in β-Ala crystals is of the first order. The spontaneous deformations and birefringence increments calculated by us depend linearly on temperature. It is shown that the phase transition in β-Ala crystals could be ferroelectric or higher-order ferroic.

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Key words: birefringence, thermal expansion, biological crystals

Introduction

The present paper is devoted to studies of phase transitions in biological crystals. We have reported in our previous works [1] the results concerning the growth and the optical microscopy studies of lysozyme protein crystals. However, these crystals have been too small in size and temperature instable, thus hindering us from clarification of the phase transition availability. In the present work we have chosen structurally simpler biological crystalline compound, the amino acid β-ala crystals [2-6]. Molecule of β-Ala is extended along the C-C-N skeleton, with COO^- and NH_3^+ terminal groups, and it consists of 13 atoms. The β-Ala crystallizes in the space group *Pbca* (D_{2h}^{15}), with 8 molecules in the unit cell. At the room temperature these crystals belong to the point group of symmetry *mmm* [11]. As far as we know there are none reports about the structural phase transitions in the β-alanine crystals

Results and discussion

The single crystals under test were grown using triple cross-crystallization from the saturated aqueous solution of chemically pure β-Ala powder. Afterwards, they were dried in a vacuum thermostat at 340 K. For our experiments, we used single crystal plates of β-Ala, which were perpendicular to the cleavage plane (010) and had the average dimensions of $2\times2\times1 mm^3$. The optical birefringence was studied with the Senarmont method (λ=632.8nm), whereas the thermal expansion with the aid of the automated dilatometer.

The temperature dependences of the relative thermal expansion *ΔL/L* and the thermal

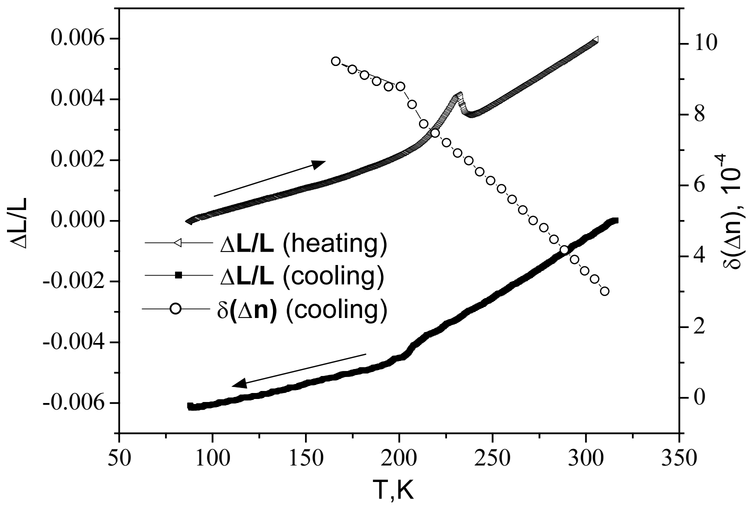


Fig. 1. Temperature dependences of thermal expansion $\Delta L/L$ and optical birefringence for β-Ala crystals.

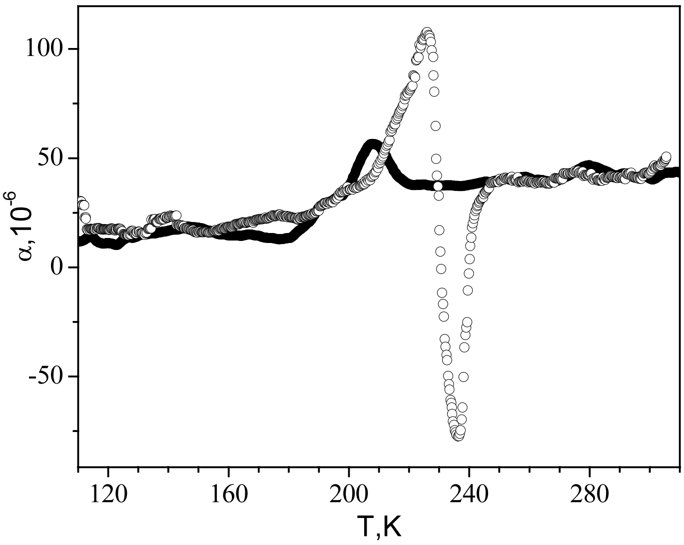
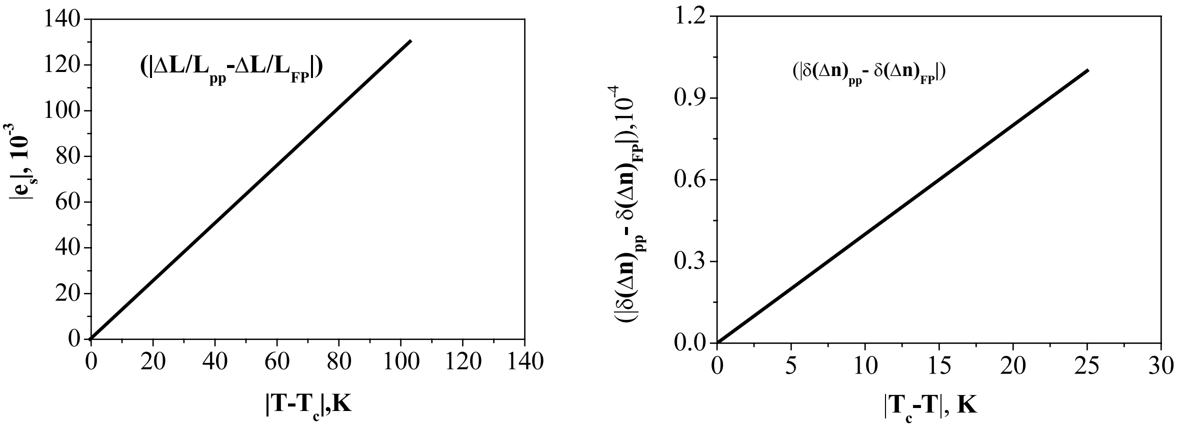


Fig. 2. Temperature dependence of thermal expansion coefficient α for β-Ala crystals (open circuits – heating, crosses - cooling).

expansion coefficient α are shown in Fig. 1,2. From the temperature dependencies of thermal expansion and optical birefringence it is clearly visible that the β-Ala crystals undergo a structural phase transition at T=204K at cooling rune. The small anomalies at T_c observed for the curves $\Delta L/L=F(T)$ are associated with expansion and compression of sample due to the absorption and emission of the phase transition latent heat in the heating and cooling runs, respectively. The temperature hysteresis of T_c is also observed in the thermal expansion. It means that the phase transition is of the first order, though close to the second one. The calculated temperature dependences of the spontaneous deformations and the increment of optical birefringence are linear (Fig.3), since the order parameter depends on temperature as $\eta^2 \propto e_s \propto \delta(\Delta n) \propto (T-T_c)$. According to a simple group theoretical analysis, a few types of phase transitions are possible from the initial point group of symmetry *mmm*: a ferroelectric one with the change of symmetry *mmmFmm2*, a ferroelastic (*mmmF2/m*), as well as higher-order ferroic (*mmmF222*) and ferroelectric-ferroelastic (*mmmF1*). In the case of *mmmF2/m* and *mmmF1*, a domain structure should be visible below T_c. However, we have not observed the appearance of domains at $T<T_c$. It means that the phase transition in β-Ala crystals has either ferroelectric or higher-order ferroic character.



a b

Fig. 3. Temperature dependences of spontaneous deformation (a) and optical birefringence (b) increment for β-Ala crystals.

Conclusions

Single β-alanine crystals were grown by the triple cross-crystallization from the saturated aqueous solution of chemically pure β-Ala powder. Afterwards they were dried in the vacuum thermostat at 340K. We used the single crystals of β-Ala with the average dimensions of $2\times2\times1mm^3$ for our experiments. At the room temperature, β-Ala crystals belong to the point group of symmetry *mmm*. We measured the thermal expansion and the optical birefringence. It was found that all the temperature dependences show the anomalous behaviour at T=204K. This significant fact testifies the existence of phase transition at this temperature. The temperature hysteresis of T_c implies that the phase transition in β-Ala crystals is of the first order. The calculated spontaneous deformations and the birefringence increment depend linearly on temperature. It is shown that the phase transition in β-Ala crystals could be either ferroelectric or higher-order ferroic.

References

1. Vlokh R, Marsel L, Tesluk I, Vlokh OG. Growth and optical microscopy observation of the lysozyme crystals. Ukr. J. Phys. Opt, **2** (2001) 84.
2. Machida K, Kagayama A, Saito Y, Uno T. Spectr. Acta., **34A** (1978) 909.
3. Takeda M, Javazzo RES, Garfincel D, Scheinberg IH, Edsall JT. J. Am. Chem. Soc. **80** (1958) 3813.
4. Shrader D. Raman: Infrared Atlas of Organic Compounds. Weinheim. Germany: Verlag Chemic; 1989.
5. Leifer A, Lippincott ER. J. Am. Chem. Soc. **79** (1957) 5098.
6. Jose P, Pant LM. Acta Crystallogr., **18** (1965) 806.