Phase transitions stimulated by thermal cycling

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Phase transitions stimulated by thermal cycling have been observed. Their number depends on the number of thermal cycles, *n*, increasing with increasing *n*. A new incommensurate crystal has been observed: $Li_2B_4O_7$. Phase transitions stimulated by thermal cycling are shown to be related to incommensurability effects.

1. Lithium tetraborate ($Li_2B_4O_7$, $I4_1cd$, $Z = 8$, $a = 9.477$ Å, $c = 10.286$ Å) is a pyroelectric with a polar axis along the [001] direction, which exhibits no ferroelectric properties.[1–3] The piezoelectric constants g_{33} and g_n of $Li_2B_4O_7$ reach record-high values, 270×10^{-3} V·m/N and 100×10^{-3} V·m/N, respectively, at room temperature.[2] Flashes of thermoscintillations (emission) have been observed[3] as the temperature was varied in the region 77–250 K in lithium tetraborate not excited by hard photons. Ultrasonic and dilatometric studies indicate the possible existence of a large number of phase transitions in this temperature region.[4] An analysis of the structure and physical properties of $Li_2B_4O_7$ has made it possible for us (in accordance with the incommensurability criteria[2)]; Refs. 5–7) to suggest the existence of an incommensurate phase in lithium tetraborate.

In this letter we are reporting some precise x-ray diffraction studies of the structure and superstructural characteristics of $Li_2B_4O_7$ over the temperature range 80–400 K.

2. The lithium tetraborate single crystals were grown by the Chokralsky method in air from a stoichiometric melt in the [100] and [001] directions. For the measurements we used single crystals which were small plates with dimensions of $4\times3\times1$ mm (with a Mohs hardness ~6). The quality of the samples and their closeness to perfection were monitored by means of Laue diffraction patterns.

The x-ray diffraction was carried out on a Rigaku-Denki x-ray diffractometer by the method of Ref. 8. All the measurements were taken during heating at a rate of 0.2 K/min at temperature steps $\Delta T = 0.5$–1 K.

3. On the temperature dependence of the lattice constant c we find two large discontinuities at $T_1 = 118.5$ K and $T_2 = 147$ K ($\Delta c_1 = 0.00140$ Å and $\Delta c_2 = 0.00400$ Å; Fig. 1a). At the same tempertures we find discontinuities on the $a(T)$ curve, but here they are far smaller. At $T = 95$ K, $c(T)$ and $a(T)$ have slope changes, which correspond to a minimum on the temperature dependence of the intensity of the (00.12) Bragg reflection (Fig. 1).

During subsequent measurement cycles in the temperature interval 80–260 K we observed an extremely unusual behavior of $Li_2B_4O_7$ (Fig. 2): The lattice constant c undergoes some fairly large jumps in this temperature interval. The number and size of

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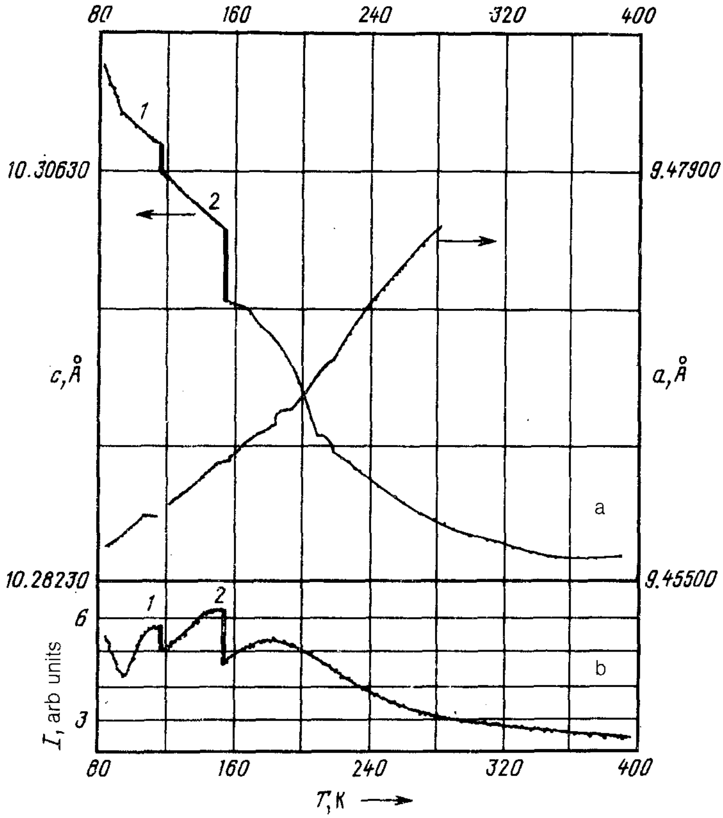

FIG. 1. a—Temperature dependence of the lattice constants a and c of lithium tetraborate during the first thermal cycle ($n = 1$); b—temperature dependence of the intensity (I) of the (00.12) Bragg reflection during the first thermal cycle ($n = 1$).

the jumps depend on the number of thermal cycles. The jumps in c are accompanied by simultaneous and sharp changes in the intensity (I) of the Bragg reflections, accompanied by a negligible decrease in the half-width of the reflections. The nature of the anomalies allows us to conclude that $Li_2B_4O_7$ undergoes first-order phase transitions in the temperature interval 80–260 K. On the curves of $c(T)$ the distribution of the jumps changes with the number of thermal cycles, n: With increasing n, the number of jumps increases. The temperatures at which the jumps occur are not the same for the different measurement cycles. An abrupt expansion of the crystals is observed only in the temperature interval 80–260 K; there is no evidence of it at all at higher temperatures. The dilatometric measurments yielded a similar result.

We carried out x-ray diffraction experiments to observe incommensurate satellites in the lithium tetraborate. Superstructural reflections $(0,0,l \pm \delta)$, with an intensity about three orders of magnitude lower than that of the Bragg reflections (Fig. 3), were observed along the [00l] direction. Cross sections taken near reciprocal-space points showed that the modulation wave vector is strictly parallel to the c axis, i.e., that we

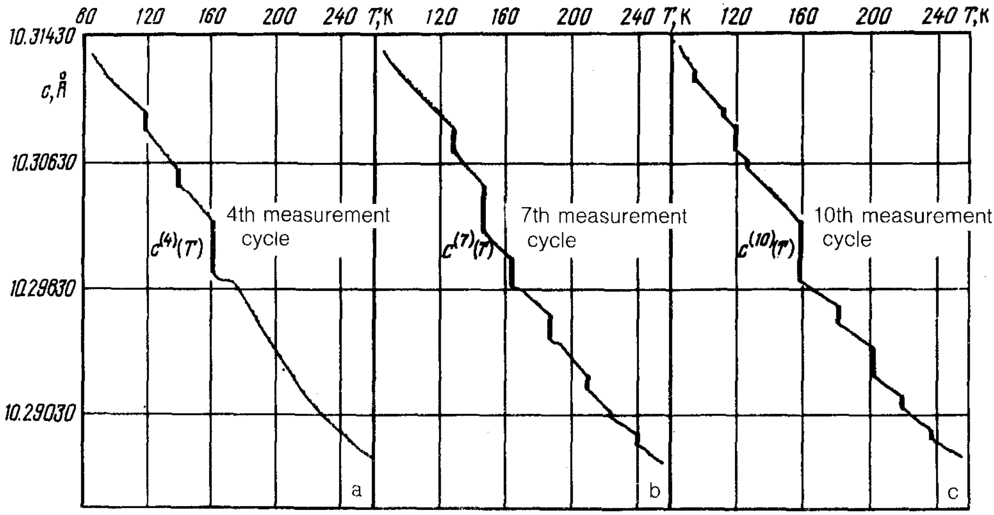

FIG. 2. a, b, c—Temperature dependence of lattice constant c of lithium tetraborate in the temperature interval 80–260 K during the fourth ($n = 4$), seventh ($n = 7$), and tenth ($n = 10$) thermal cycles, respectively.

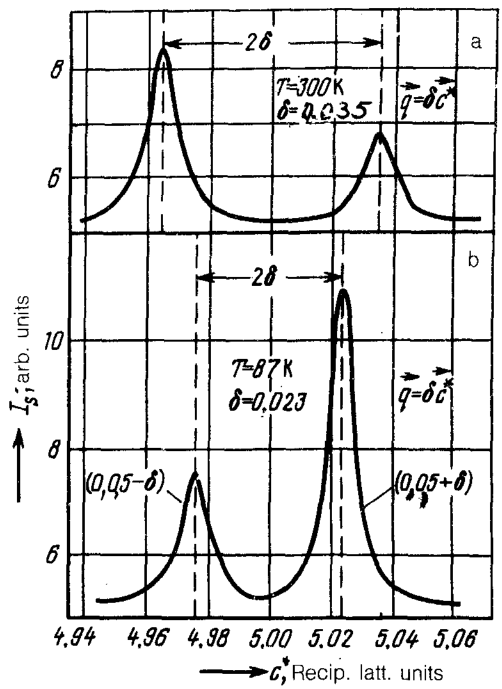

FIG. 3. a—Profiles of the satellites ($005 \pm \delta$) at $T = 300$ K; b—profiles of the satellites ($005 \pm \delta$) at $T = 87$ K (the satellite profiles were recorded for different thermal cycles).

have $\mathbf{q} = \delta \mathbf{c}^*$ ($\delta = 0.035$ at $T = 300$ K). The modulation period turned out to be very large and strongly dependent on the temperature ($L = 290$ Å at $T = 300$ K and $L = 440$ Å at $T = 87$ K).

We found that the thermal cycling also has a pronounced effect on the behavior of the satellites. During the first few measurement cycles, the ratio of the intensity of the inner satellite (at the left in Fig. 3) to that of the outer satellite (on the right), both in liquid nitrogen and at $T = 300$ K, is ~ 2 ($I_{\text{inner}}/I_{\text{outer}} = 2$). During subsequent thermal cycles ($n > 5$), the intensity becomes redistributed between the satellites, and at $T = 80$ K we find that $I_{\text{inner}}/I_{\text{outer}}$ is ~ 0.5, although at $T = 300$ K this ratio remains at its previous value of 2 (Fig. 3). These "conversions" involving the satellites may be evidence of some serious transformations in the superstructure in the temperature interval 80–260 K which are caused by the thermal cycling. It is in this temperature interval that an unusual cascade of phase transitions has been observed (Fig. 2). Incommensurate crystals exhibit "memory" effects,[5] which are possibly being manifested in an extermely peculiar way in this case—through a thermal cycling.

Restoring the lithium tetraborate crystal to its original state "as grown" requires allowing it to "rest" for about three weeks at room temperature in an unsqueezed state. After this rest, the measurements reveal a dependence of the physical properties of $Li_2B_4O_7$ on the thermal cycling which is of the same nature as that described at the beginning of this paper.

4. a) We have observed a new incommensurate crystal, $Li_2B_4O_7$, with a modulation wave vector $\mathbf{q} = \delta \mathbf{c}^*$ ($\delta = 0.035$ at $T = 300$ K) and with a wide temperture region in which the incommensurate phase exists ($80 \text{ K} > T_c < T_i > 400$ K, where T_i is the temperature of the phase transition from the normal phase to the incommensurate phase, and T_c is the temperature of the phase transition from the incommensurate phase to the commensurate phase). The period of the superstructure is 290 Å at room temperature.

b) We have observed that thermal cycling causes a redistribution of the intensity between the inner and outer satellites.

c) We have observed phase transitions stimulated by thermal cycling. It has been shown that the number of phase transitions stimulated by the thermal cycling depends on the number of thermal cycles and that the relaxation time for the crystals is ~ 3 weeks.

d) We have detected a second-order phase transition at $T = 95$ K and an anomalous temperature dependence of the intensity of Bragg reflections in the temperature region in which the phase transitions stimulated by the thermal cycling occur (Fig. 1b).

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[2)]1. Invariance—the absence of a thermal expansion along one or several crystallographic directions in the temperature region in which the incommensurate phase exists. 2. The presence of a global hysteresis. 3. A large number of phase transitions. 4. A layered structure of the crystal.

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