Vol. A53 (1978) ACTA PHYSICA POLONICA No 6

MARTENSITE TYPE PHASE TRANSITION IN THIN BARIUM TITANATE MONOCRYSTALS

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(Received September 12, 1977)

An account is given of studies to investigate phase transitions in $BaTiO_3$ monocrystals with and without a plane phase boundary. The domain structure formed is examined. Two new types of fronts are found.

The martensite type phase transition is distinguished by the existence of a plane of minimum stress between the phases beyond which the strictly defined domain structure is formed. The domain walls accumulate a part of the nonbalanced mechanical energy at the phase front. This energy is accumulated as the energy of electrostriction stresses.

Transitions of this type, i. e. with a sharp phase boundary, were observed in barium titanate monocrystals by Parker and Burfoot [1, 2]. Di Domenico and Wemple [3] applied the theory of Wechsler, Liberman and Read [4] of a phase transition of the type: austenite-martensite in steel, to phase transitions in monocrystals of KTN and $BaTiO_3+Ce$. Parker and Burfoot proposed a theory of phase front motion by controlled growth of the new phase [5–8]. Investigations of the nature of the phase boundary by Borodin and co-workers have also been reported in literature [9–11]. Martensite type phase transitions have also been observed in crystals of lead titanate [12, 13]. Due to the possibility of screening the spontaneous polarisation by the free charges and also the high value of spontaneous distortion in lead titanate, a simpler domain structure and good agreement with theory is found. While most of papers were based on the investigations of phase transition and the nature of the phase boundary, the domain structure arising behind the front was observed only in transmitting light and not systematically.

In the lead titanate crystals, phase transition with a plane phase boundary makes it possible to get some strongly defined domain structures. We were interested in investigating the domain structure which appears after the plane front, and comparing the newly created domain structures with the previously existing structures in lead titanate. The comparing of barium titanate to lead titanate led us to investigate two new types of phase fronts previously not observed in barium titanate.

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Tests were conducted on thin crystals of $BaTiO_3$ grown by a modified Remeika method. Cuboidal plates of dimensions 3×4 mm^2 were cut from the butterfly wings. The edges of the crystals were parallel to the crystallographic axes. The thickness of the tested crystals was of the order of $20 \div 80$ μm, since in barium titanate crystals of this thickness plane fronts are most frequently observed.

Conductivity of crystals at the Curie point was smaller than 10^{-8} (ohm cm)$^{-1}$. Observations were carried out with a polarisation microscope. On a small table of microscope was installed a gradient furnace with the vertical optical channel. Temperature gradient in the furnace was $2°K \cdot mm^{-1}$. The interior of the furnace was cooled at a cooling rate of $10 \div 30$ deg min^{-1}. The influence of the temperature gradient and cooling rate on the explored phenomena was not observed (only frontal velocity is dependent on the temperature gradient and cooling rate). An etching method was used to bring out the domain structure on the surface. Observations of the structure were conducted in a metallographic microscope, using the reflection method.

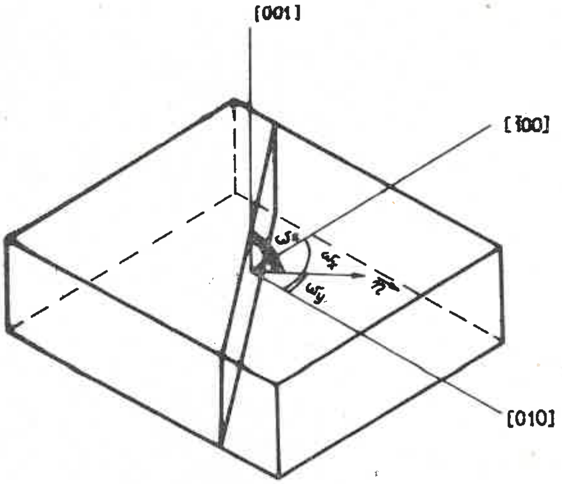

Fig. 1. Schematic diagram of a "sharp" phase front

— In about 60% of the tested crystals no martensite type phase fronts were observed at any orientation of the temperature gradient. Also variations in the magnitude of the gradient and cooling rate did not cause the occurrence of a sharp phase boundary. The transitions usually exhibit a complicated appearance and are different in different crystals, as seen on the example in Fig. 1. Domain structure formed in phase transition obviously is nonstable and changes in the cooling process. In the following heating and cooling processes it is complicated and nonrepetitive.

— In about 20% of the tested crystals a "sharp" front was observed (Fig. 2 and Photo 3). This front usually occurred independently of the temperature gradient and cooling rate, although at high rates the disturbance of the phase front motion was found. This "sharp" type front occurred for the orientation of the temperature gradient [110]. We

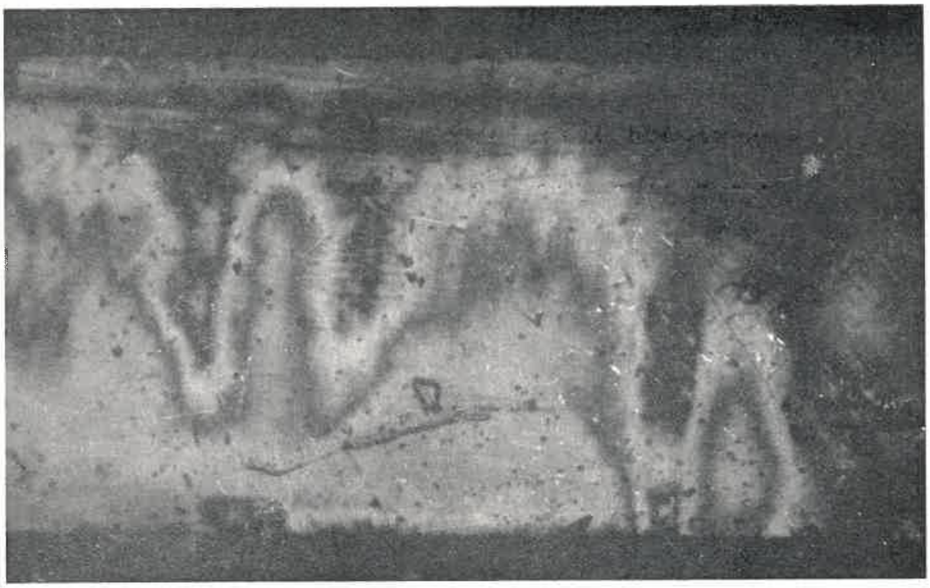

Fig. 3. Photograph of a transition without a flat phase boundary (100×)

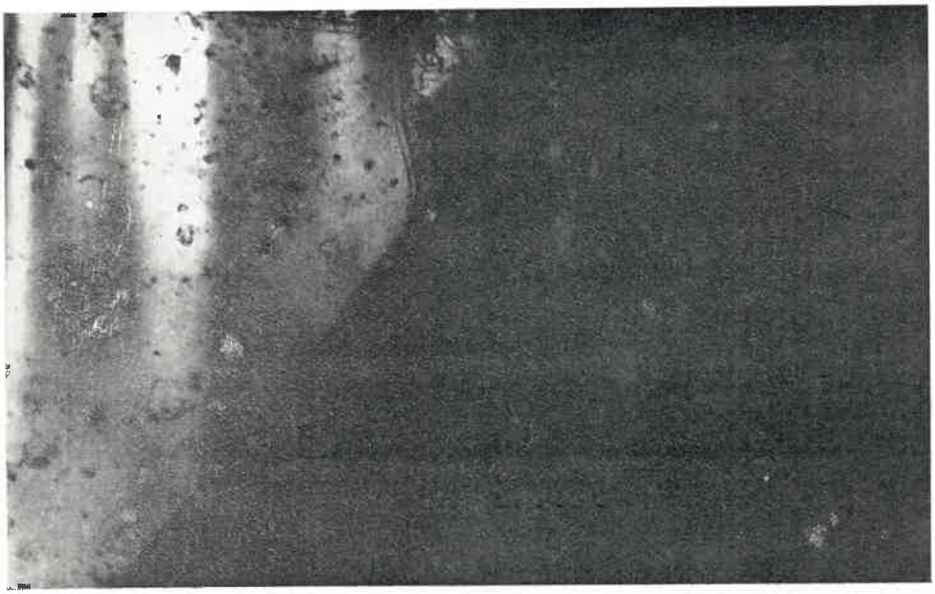

Fig. 4. Photograph of a "sharp" phase front (100×)

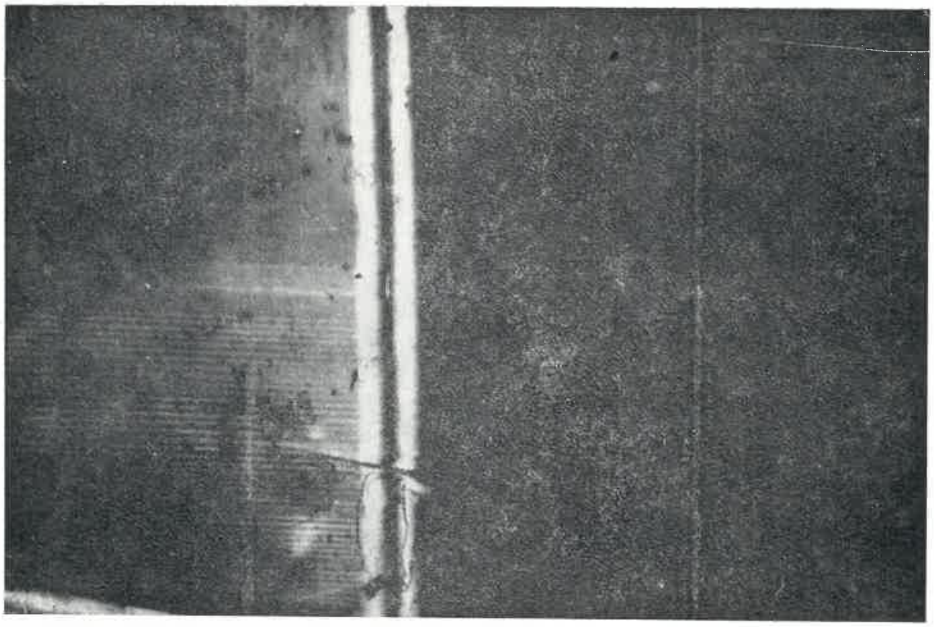

Fig. 5. Photograph of a "wide" phase front (100×)

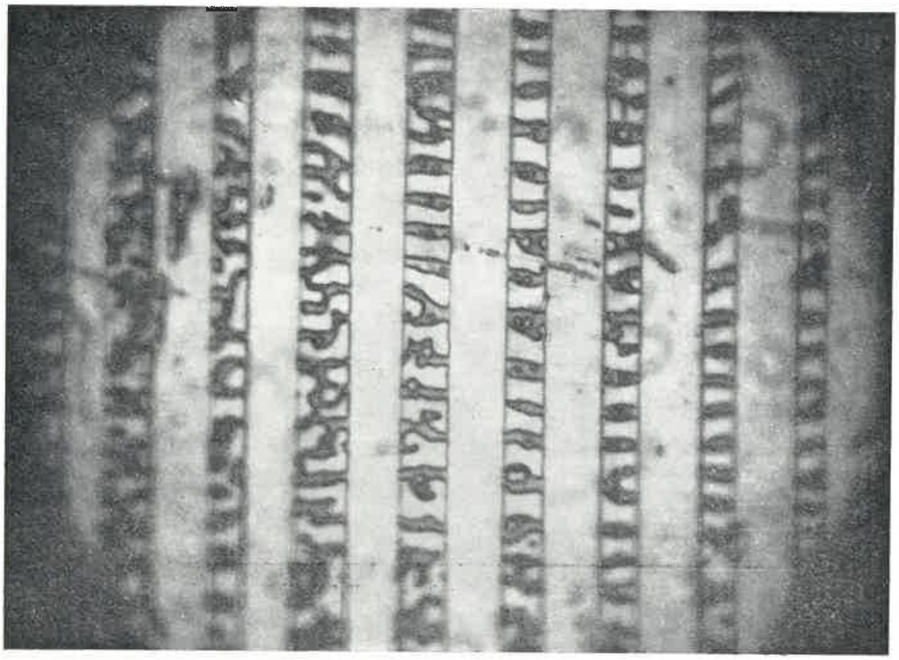

Fig. 6. Domain structure after transition of a "sharp" front (1000×)

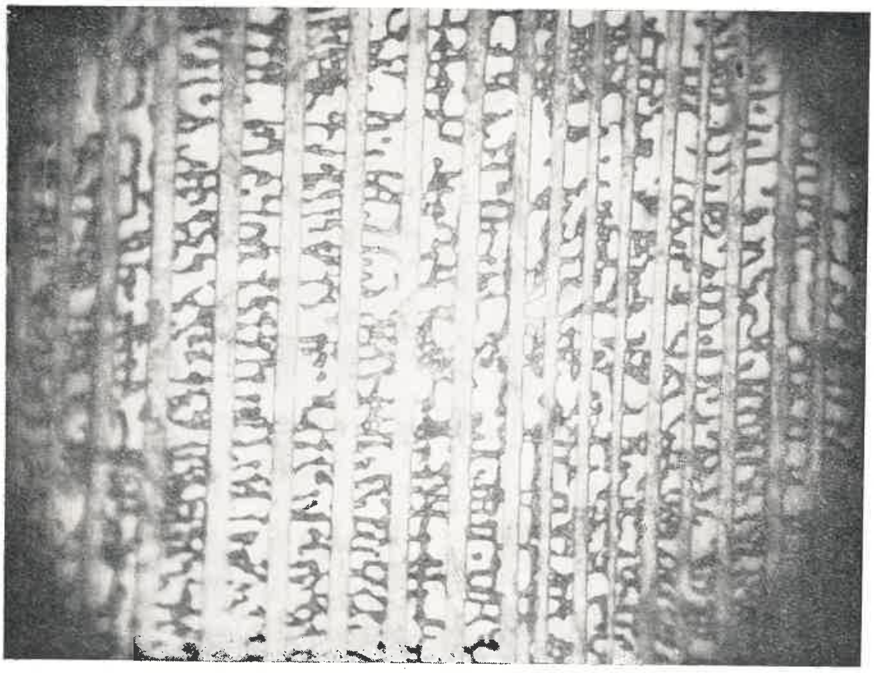

Fig. 7. Domain structure after transition of a "wide" front (1000×)

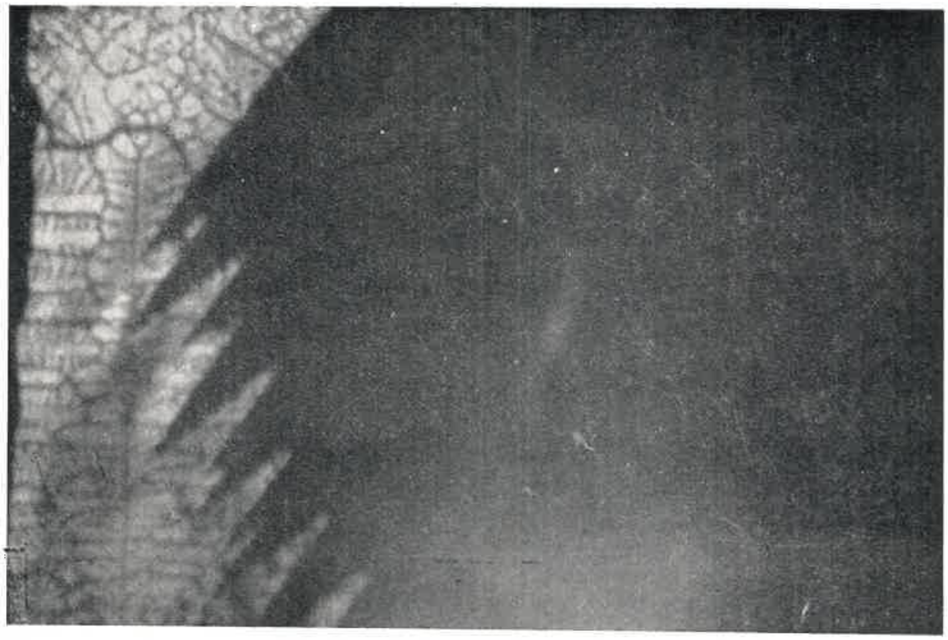

Fig. 8. Photograph of a "sawform" phase front after which a sandwich structure arised (100×)

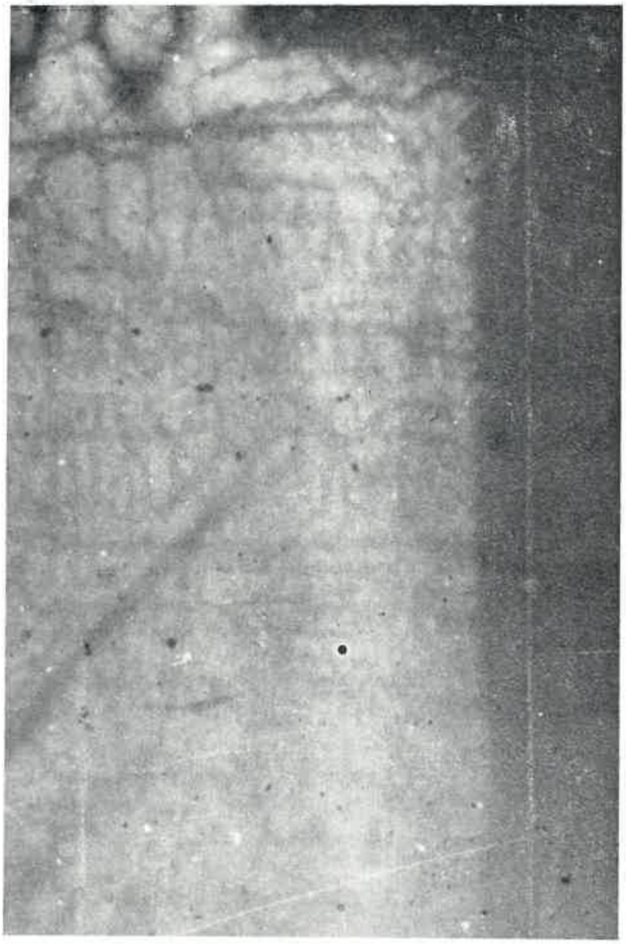

Fig. 9. Photograph of a "sawform" phase front after which $a-a$ domain structure occurred (500×)

think that the frontal plane is a plane of type (560). Photo 4 shows an example of the domain structure arising after the passing of a "sharp" front. In the *c*-domains, it is a clearly visible 180° structure, which ensures the minimisation of the depolarisation field energy, and also *a–c* domain structure, which ensures minimisation of the elastic energy at the phase front. Observations of a domain structure in polarised transmitted light and experimental etching of hot crystal show that *a–c* domain images do not change with temperature, and 180° division of *c*-domains takes place just on the phase front or not far from it. It is of interest to note that both the absolute widths of the *a*- and *c*-domains and the relation between their widths can change from crystal to crystal, and also over the surface of one crystal, but on the average the *a*-domains are 2–3 times wider.

— In about 10% of the crystals a "wide" front was observed (Fig. 5 and Photo 6). The phase front width is comparable with the thickness of the crystals within the limits of acceptable error. A phase front of this type occurred for the orientation of the temperature gradient [100]. It looks like the frontal plane is the plane (056). Photo 7 shows an example of domain structure formed after the passing of a "wide" front. In this case the *c*-domain structure is also visible. In this example, as previously, the absolute width of the domains and also the ratio of their widths can change slightly but on the average the width of the *c*-domains is 2–3 times greater.

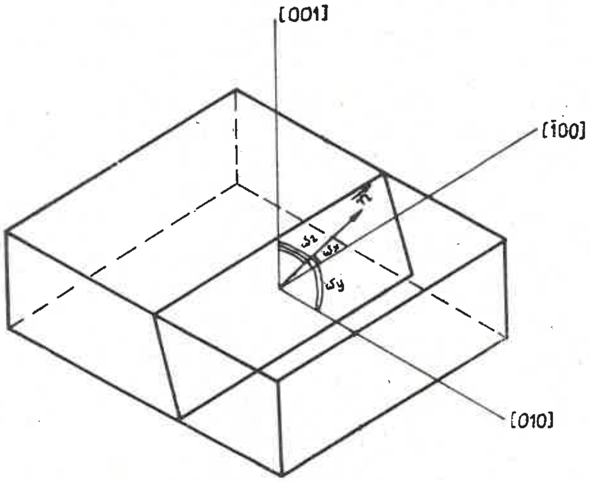

Fig. 2. Schematic diagram of a "wide" phase front

— Crystals were found in which, for one orientation of the temperature gradient, a "sharp" front was observed, and after rotating through 40° a "wide" front appeared. It made possible the observation of domain structure in crystal in part of which a "sharp" (560) front occurred and in part a wide one.

In lead titanate crystals one more front is observed [12]. It is the "sawform" front, which occurred for the orientation of the temperature gradient [120]. Searching for a front of this type led to the observation of two new types of fronts. Photo 8 shows a phase front consisting of parts of type (560) and (650). Behind it an ordinary, typical for "sharp" front, *a–c* domain structure was observed.

Photo 9 and Fig. 10 show the "sawform" phase front. A 90-degree *a–a* domain structure probably appeared after this front passed. So when the crystal is cooled to room temperature, this structure changes and becomes very complicated. Typical for phase transition in barium titanate crystals is very small domain structure divided into 180-degree domains, some "freedom" of domain width ratio which may be caused by stresses which develope in the cooling process, and the fact that the plane front occurs very rarely and obviously for only one orientation of the temperature gradient.

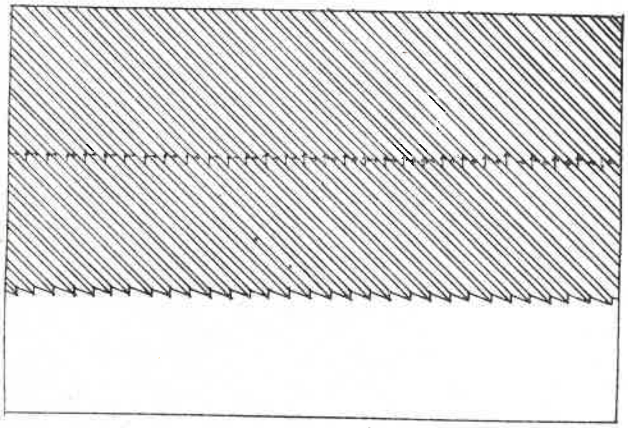

Fig. 10. Schematic diagram of a "sawform" phase front

REFERENCES

[1] T. J. Parker, J. C. Burfoot, *Brit. J. Appl. Phys.* **17**, 207 (1966).

[2] J. C. Burfoot, T. J. Parker, *Brit. J. Appl. Phys.* **17**, 213 (1966).

[3] M. Di Domenico, S. H. Wemple, *Phys. Rev.* **155**, 539 (1967).

[4] M. S. Wechsler, D. S. Lieberman, T. A. Read, *Trans-Amer. Inst. Mining Met. Energs.* **197**, 1503 (1953).

[5] J. C. Burfoot, T. J. Parker, *J. Phys. D* **D2**, 1164 (1969).

[6] T. J. Parker, J. C. Burfoot, *J. Phys. D* **D2**, 1168 (1969).

[7] T. J. Parker, J. C. Burfoot, *J. Phys. Soc. Jap.* **28**, Suppl., 362 (1970).

[8] J. C. Burfoot, T. J. Parker, *J. Phys. Soc. Jap.* **28**, Suppl., 364 (1970).

[9] V. Z. Borodin, M. Y. Gorelov, V. A. Borodina, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **35**, 1868 (1971).

[10] V. A. Borodina, A. A. Sorg, *Mekhanizmy relaksatsyonnykh yavlenii*, Kaunas 1974.

[11] V. Z. Borodin, A. A. Sorg, V. A. Borodina, Y. F. Maltsev, Y. I. Nikiforov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **39**, 766 (1975).

[12] E. G. Fesenko, M. A. Martynenko, V. G. Gavrilachenko, A. F. Semenchev, *Ferroelectrics* **6**, 61 (1973).

[13] E. G. Fesenko, M. A. Martynenko, V. G. Gavrilachenko, A. F. Semenchev, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **39**, 762 (1975).