PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. 49 (1980) SUPPL. B, pp. 134–136.

Domain Structure Realignment Peculiarities of Improper Ferroelectric-Ferroelastic $NaH_3(SeO_3)_2$ in the Regions of $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ Phase Transitions

V. M. RUDYAK and T. I. IVANOVA

Kalinin State University, Kalinin 170013, USSR

The Barkhausen effect (BE) technique and direct optical observations were used to study the domain structure (DS) realignment in $NaH_3(SeO_3)_2$ single crystals in the regions of $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ phase transitions. Taking the advantage of this experimental approach some new details of DS realignment were revealed. It was found, for example, that in the vicinity of a phase transition electric fields perpendicular to ferroelastic domain walls (DW) may cause a ferroelastic DS realignment. With the aid of additional dielectric hysteresis loop observations it was also found that there exists a narrow temperature range near to $\alpha \rightleftarrows \beta$ phase transition where $NaH_3(SeO_3)_2$ is a ferroelastic and not a ferroelectric.

$NaH_3(SeO_3)_2$ is known to undergo phase transitions on changing the temperature: at $-79°C$ from its monoclinic paraphase α to the electrically biaxial tryclinic ferroelectric phase β, where the crystal also exhibits ferroelastic properties, and at $-172°C$ from its β-phase to the monoclinic ferroelectric phase γ.[1] The combination of ferroelectric and ferroelastic properties determines the DS peculiarities of this crystal and its behaviour on changing the temperature and external electric fields.[2–4]

The Barkhausen effect (BE) proved to be a sensitive indicator of domain structure (DS) kinetics with no regard to direct observation possibilities.[5,6] On this account in the present work we applied the BE technique and optical observations simultaneously to study the DS realignments in $NaH_3(SeO_3)_2$ affected by electric fields or by temperature (in zero field) in the region of $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ phase transitions.

The experimental set-up[7] enabled to perform BE measurements and DS observations at the same time. To observe the DS the laser light was directed along the Z-axis of Z-cut specimens. Two pairs of gold electrodes served to apply the electric field either along X or Y directions. The electric state of the sample could be changed in a step-like manner.

It was found that the BE outline in $NaH_3(SeO_3)_2$ crystals subjected to external electric fields remains essentially the same within the whole β-phase temperature range. At the time the topography of Barkhausen jumps (BJ) which correspond to the visually not observed ferroelectric substructure reorientation differ substantially from that corresponding to the visually observable changes in ferroelastic DS. These sizes and durations of ferroelastic BJ are approximately one order of magnitude larger than that of ferroelectric ones.

With rising of the temperature the number of BJ due to substructure realignment drops, while the total number of BJ of both types increases. This indicates an increase in ferroelastic DS mobility and weakening of its stability in regard to the external field, although visually the changes are not observable.

It has been shown earlier[2–4] that constant electric fields oriented perpendicular to the ferroelastic domain wall (DW) influence only on the ferroelectric substructure, while a field parallel to ferroelastic DW realigns the ferroelastic DS. Further it has been confirmed[7,8] that in a field parallel to ferroelastic DW the crystal behaves like a pure ferroelectric with distribution of the number of BJ on field similar to uniaxial ferroelectrics.[6] In fields parallel to ferroelastic DW curves of BJ distribution on field display bends, related to the changes in the electric state of the sample. At this point the DS realignment is visually observed and BJ are predominantly of the ferroelastic type.

In this work it was for the first time observed that ferroelastic DS may be realigned in fields

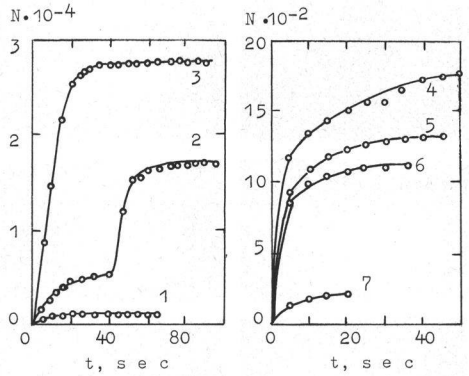

Fig. 1. Rise of the BJ number with time when the sample's electric state is changed along the hysteresis loop branch. The steps in electric field changing are (in V/cm) 0–80 (curve 1) 80–160 (2) 160–240 (3) 240–320 (4) 320–400 (5) 400–480 (6) and 1520–1600 (7).

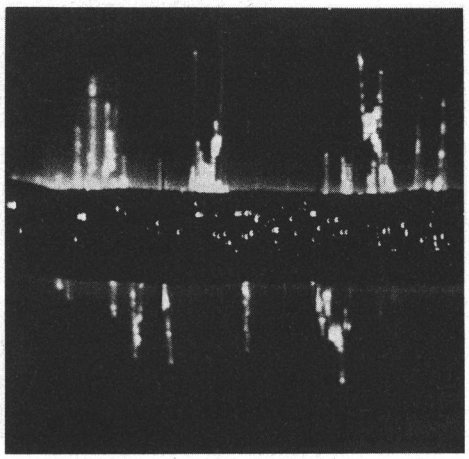

Fig. 2. BJ corresponding to an $\alpha \rightarrow \beta$ phase transition.

perpendicular to ferroelastic DW. This realignment proceeds only in fields near to coercive ones and is most pronounced at temperatures near to phase transition. Figure 1 shows the rise of BJ number with time when the electric state of the sample is changed along the hysteresis loop branch in a field perpendicular to ferroelastic DW. Each curve of Fig. 1 corresponds to one step of electric field alteration. Of interest is curve 2, which corresponds to a field near to the coercive one. Since this curve exhibits two regions of saturation it may be inferred that two different mechanisms are responsible for maintaining stable DS configurations. Visually a partial ferroelastic DS realignment is observed at the moment of increasing of the number of BJ; at the same time the number of ferroelastic BJ increases vastly. Following reasons may be responsible for this realignment: a) in the vicinity of coercive fields (especially near to phase transition) the DS is more mobile and less stable than at other stages of the hysteresis loop; b) mechanical vibrations of the sample may be induced by BJ;[9] near to phase transition these vibrations are apparently responsible for DS realignment.

The DS realignment and BE due to changing of the temperature in zero field were also studied in the vicinity of phase transitions. It was found that both $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions are accompanied by a large number of BJ of both polarities. For an initially depolarized sample the numbers of BJ of both polarities are nearly the same. Figure 2 shows BJ, which correspond to an $\alpha \rightarrow \beta$ phase transition. Note that only ferroelectric BJ are present. The rise of the number of $\alpha \rightarrow \beta$ phase transition BJ with time is shown in Fig. 3.

Ferroelectric BJ of both polarities are also observed in zero field in the course of $\beta \rightleftarrows \gamma$ phase transitions, but their number is 4 to 5 times smaller than at $\alpha \rightleftarrows \beta$ phase transitions.

It was found further that at the $\beta \rightarrow \alpha$ transition BJ appear long before the point of transition and proceed with no observable DS changes. After this in a time depending on the rate of heating the DS becomes less distinct and a phase boundary appears. No BJ are observed

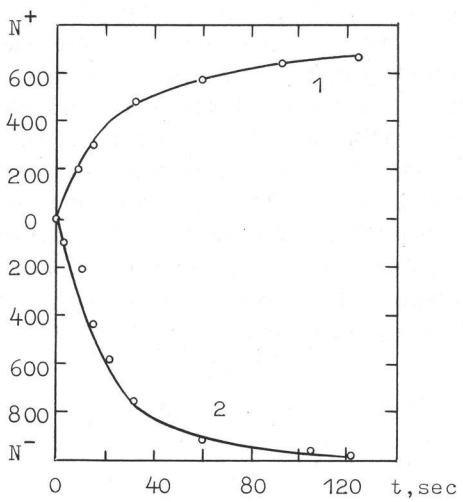

Fig. 3. Rise of the number of phase transition BJ with time. Curve 1—BJ of positive polarity, 2—negative polarity.

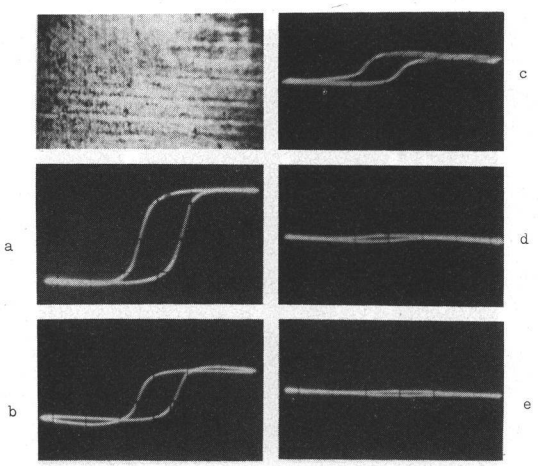

Fig. 4. Dielectric hysteresis loops succession during the $\beta \rightarrow \alpha$ phase transition. The domain structure (at the left) remains unchanged.

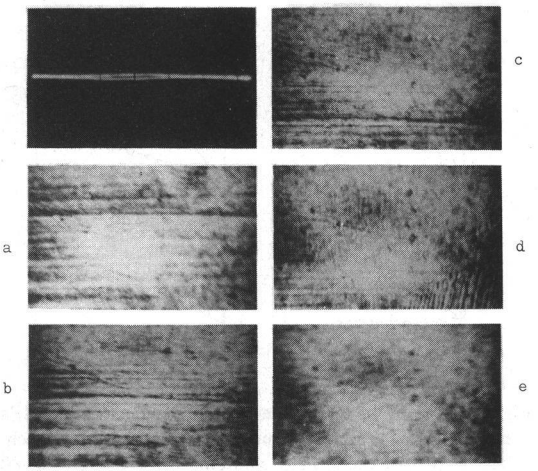

Fig. 5. Phase boundary movement during the $\beta \rightarrow \alpha$ phase transition after the hysteresis loop (at the left) being vanished.

when this boundary moves. In the course of $\alpha \rightarrow \beta$ phase transition at first the phase boundary appears, then the ferroelastic DS becomes clearly resolved and in a time of 10–30 seconds (depending on the heating rate) the BE manifests itself. These findings indicate that spontaneous polarization and spontaneous deformation are disappearing at the $\beta \rightarrow \alpha$ phase transition (or appearing at the $\alpha \rightarrow \beta$ one) not at the same time.

In addition to this simultaneous DS and dielectric hysteresis loop observations showed that at the $\beta \rightarrow \alpha$ transition at first the hysteresis loops vanish while the DS remains unchanged (Fig. 4), and only then the DS becomes less discernable and a phase boundary movement is observed (Fig. 5). All this outline repeats in the opposite succession at the $\alpha \rightarrow \beta$ transition.

An application of a constant electric field after passing through of the phase transition BJ but in a condition when the DS is still observed or when the phase boundary moves causes no BJ. This is a convincing confirmation of disappearance of ferroelectric properties at the time of ferroelasticity still preserved. So it may be concluded that there exists a narrow temperature range near the $\alpha \rightleftarrows \beta$ transitions where $NaH_3(SeO_3)_2$ is a ferroelastic and not a ferroelectric.

The authors are indebted to N. M. Schagina for supplying single crystals, L. A. Shuvalov for valuable discussions and R. M. Grechishkin for helpful assistance.

References

1) L. A. Shuvalov and N. R. Ivanov: Phys. Status Solidi **22** (1967) 279.
2) A. A. Askochenskii, L. A. Shuvalov and V. A. Kirikov: Izv. Akad Nauk SSSR Ser. Fiz. **35** (1971) 1877.
3) L. A. Shuvalov, V. A. Kirikov, P. S. Grosdover, I. S. Zheludev and V. I. Petrov: Phys. Status Solidi **28** (1975) 677.
4) V. A. Kirikov *Dissertation* (*IK AN SSSR, Moscow*, 1975).
5) V. M. Rudyak: *Abstracts of the 2nd Intern. Meeting on Ferroelectricity, Kyoto*, (1969) p. 70.
6) V. M. Rudyak: Usp. Fiz. Nauk **101** (1970) 429.
7) T. I. Ivanova, V. M. Rudyak and N. M. Schagina: Izv. Akad Nauk SSSR Ser. Fiz. **43** (1979) 1730.
8) V. M. Rudyak and T. I. Ivanova: Ferroelectrics **26** (1980) 805.
9) V. V. Ivanov, A. A. Bogomolov and V. M. Rudyak: Izv. Akad Nauk SSSR Ser. Fiz. **39** (1975) 987.