A NEW CRYSTAL WITH COUPLED FERROELASTIC-FERROELECTRIC PROPERTIES

J. RAVEZ, B. ELOUADI, J. P. CHAMINADE, A. LEVASSEUR and P. HAGENMULLER

*Laboratoire de Chimie du Solide du C.N.R.S., Université de BORDEAUX I,
351 cours de la Libération, 33405 TALENCE, France*

A single crystal $\text{Pb}_{2.07}\text{K}_{0.56}\text{Nb}_{0.91}\text{Ta}_{4.15}\text{O}_{15}$ has been grown by the flux method. It crystallizes with the tetragonal tungsten bronze structure. Two transitions have been determined by dielectric, pyroelectric and birefringence

measurements: ferroelastic-ferroelectric phase $\xrightarrow{371 \text{ K}}$ ferroelastic-paraelectric phase $\xrightarrow{658 \text{ K}}$ paraelastic-paraelectric phase. Spontaneous polarization and spontaneous strain are respectively equal to $29 \mu\text{C} \cdot \text{cm}^{-2}$ and 8×10^{-4} at room temperature. Polar axis is along the [010] direction. Electrical switching of the ferroelastic domains at room temperature shows clearly the existence of a ferroelastic-ferroelectric coupling.

1. INTRODUCTION

Most crystals of tetragonal tungsten bronze structure containing alkali and alkaline earth ions show decoupled ferroelastic-ferroelectric properties.¹⁻⁷ Barium sodium niobate $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ represents a typical example of this behaviour as it undergoes two transitions at 543 and 858 K corresponding respectively to the vanishing of the ferroelastic and ferroelectric phases.

We have shown recently that Pb^{2+} ions introduced into such a structure should be able to induce a partial coupling of the ferroelastic-ferroelectric properties, since they are known to orientate the polar axis along the [010] direction and to introduce a slight orthorhombic distortion into the initially tetragonal unit cell. One ferroelastic state could then be transformed into another by a 90° rotation of the polarization vector in the (001) plane under electric field.⁸

However in spite of the application of very high fields by Francombe and Lewis to PbNb_2O_6 and by Nakano and Yamada to $\text{Pb}_2\text{KNb}_5\text{O}_{15}$, no rotation of the polarization vector has been observed at room temperature.^{9,10} This may be due to their large strong spontaneous strains $e_s (= (b - a)/(b + a))$, at 298 K) $= 8.7 \times 10^{-3}$ and 6.1×10^{-3} for PbNb_2O_6 and $\text{Pb}_2\text{KNb}_5\text{O}_{15}$, respectively which make it difficult to switch between two ferroelastic states. The large value of their spontaneous strains which relate to the relatively high Curie temperatures ($T_c = 843 \text{ K}$ and 683 K for PbNb_2O_6 and $\text{Pb}_2\text{KNb}_5\text{O}_{15}$, respectively) might

resulted in requiring higher switching field than the breakdown field of each material.

We have thought that this coupling could be facilitated by lowering the Curie temperature. For this purpose we set out to replace niobium by tantalum which greatly diminishes T_c .^{11,12} We have already pointed out the advantages presented by the phases of the $\text{Pb}_2\text{KNb}_5\text{O}_{15}$ – $\text{Pb}_2\text{KTa}_5\text{O}_{15}$ system whose T_c could be decreased from 683 to 225 K.⁸ Therefore we set out to prove the existence of the ferroelastic-ferroelectric coupling in single crystals of lead potassium niobate tantalate. We selected the initial ratios $\text{Ta/Nb} = 4$ and $\text{Pb/K} = 2$, corresponding to its Curie temperature of 353 K and a relatively low spontaneous strain of 4×10^{-4} .

2. GROWTH AND CHARACTERIZATION OF THE SINGLE CRYSTALS

The melting point of $\text{Pb}_2\text{KNbTa}_4\text{O}_{15}$ was determined by D.T.A. ($T_m = 1850 \pm 20 \text{ K}$). A TGA study of the same material showed a very high weight loss of about 20% during 10 hours. It was therefore necessary to use the flux technique for growing such crystals to reduce the loss of volatile oxides by lowering the crystallization temperature. After some preliminary experiments and following the works of GALASSO and WHIPPS on barium strontium niobate, a mixture of lead and potassium borates was chosen as flux.^{13,14}

A systematic study was made of the following variables:

- the solute composition
- the K/B, Pb/B and Pb/K ratios in the flux
- the ratio solute weight/flux weight
- the crystallization technique: isothermal evaporation of the flux or slow cooling.

Crystals of largest dimensions and best quality were grown by slow cooling from an initial melt of 13.37 g of PbO, 6.22 g of K_2CO_3 , 1.33 g of Nb_2O_5 , 8.84 g of Ta_2O_5 and 11.14 g of B_2O_3 (CERAC products with a purity better than 99.9%) corresponding to a ratio of solute weight/flux weight ≈ 0.6 .

The mixture was ground and subsequently sintered at 1070 K; afterwards the temperature was raised at a rate of 15 K/hour to 1570 K and kept there for 5 hours. The crystallization was achieved by slow cooling of the melt: 2 K/hour between 1570 and 1170 K and 20 K/hour afterwards down to room temperature. Crystals were separated from the flux by heating the mixture in dilute HNO_3 . They are in the form of transparent platelets of about $1 \times 1 \times 3 \text{ mm}^3$ (Figure 1). Their

FIGURE 1 Flux-grown single crystals of lead potassium niobate-tantalate (one scale unit = 1 mm).

composition was determined by atomic absorption in a Perkin-Elmer spectrophotometer 306:

$Pb_{2.07(\pm 0.02)}K_{0.560(\pm 0.005)}Nb_{0.91(\pm 0.03)}Ta_{4.15(\pm 0.12)}O_{15}$.

X-ray analysis has shown that the crystals grow in the [001] direction and crystallize in the orthorhombic system (mm2) with the following lattice parameters:

$a = 17.76 \pm 0.01 \text{ \AA}$; $b = 17.79 \pm 0.01 \text{ \AA}$; $c = 7.804 \pm 0.005 \text{ \AA}$

3. DIELECTRIC AND PYROELECTRIC MEASUREMENTS

Dielectric measurements were made on a single crystal at a frequency of 1 kHz with an automatic capacitance bridge General Radio 1680. Silver paste electrodes were used.

FIGURE 2 Variation of the dielectric constants ϵ'_{22} and ϵ'_{33} with temperature.

The Figure 2 shows the temperature dependence of the real parts of the dielectric constants ϵ'_{22} and ϵ'_{33} measured in the direction [010] and [001]. The value ϵ'_{22} changes abruptly, reaching a maximum of 13500 at $T_{\max} = 371 \pm 5 \text{ K}$. Two weak peaks were observed in the temperature variation of ϵ'_{33} , one at $371 \pm 5 \text{ K}$ and the other at $658 \pm 10 \text{ K}$.

Pyroelectric measurements were made on the other crystal after previous poling at $25 \text{ kV} \cdot \text{cm}^{-1}$. A maximum of the pyroelectric coefficient p was registered at $345 \pm 2 \text{ K}$, but only along the [010] direction (Figure 3). The sign of p was changed by reversal of the previous poling field showing that the crystal is ferroelectric. It

FIGURE 3 Variation of the pyroelectric coefficient with temperature.

FIGURE 4 Variation of the spontaneous polarization with temperature.

was possible to determine the temperature dependence of the spontaneous polarization by integrating $p(T)$ ($P_s = 29 \pm 1 \mu\text{C} \cdot \text{cm}^{-2}$, at 298 K) (Figure 4).

The graphs of the figures 2, 3 and 4 lead to the following conclusions:

- the ferroelectric Curie temperature T_C is 371 K and the spontaneous polarization vector is along the [010] direction,
- the anomaly observed in the curve $\epsilon'_{r33}(T)$ at 658 K corresponds probably to a phase transition in the paraelectric temperature domain.
- the ferroelectric-paraelectric transition could be considered as a diffuse one since ϵ'_{r22} shows a broad peak vs temperature, the difference between T_C and the temperature of the maximum of the pyroelectric coefficient is relatively high ($\Delta T = 26$ K), finally the spontaneous polarization has a long tail in the paraelectric region.

4. BIREFRINGENCE MEASUREMENTS

Birefringence Δn_{ab} was measured by Ehringhaus's method using a polarizing microscope Leitz Ortholux II Pol. The sample temperature was stabilized to within 0.5 K. The experimental device had been tested by preliminary measurements made on $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ crystals: we found that the vanishing temperature of the birefringence is 583 K, which value agrees well with previous results (15).

The sample used is an optically polished (001) plate. It has a thickness of 0.12 mm and a cross section of $0.4 \times 0.4 \text{ mm}^2$. At 298 K two kinds of ferroelastic domains have been observed: their optical indicatrices orient are perpendicularly, in each other so that the

FIGURE 5 Domains switching, at 298 K, for different electric fields (α = dislocation planes, β = domain walls, γ = single domain crystals defects).

domains are oriented at 90° . The figure 5a shows a picture of domains in a part of the crystal, with an explanatory sketch indicating the directions of the optical indicatrices. Very clear growth striations can also be detected on all the pictures.

The temperature variation of Δn_{ab} was measured from 298 to 723 K. The birefringence [$\Delta n_{ab} = (18.1 \pm 0.01) 10^{-3}$, at 298 K] is decreasing sharply as temperature rises. The vanishing of Δn_{ab} at 658 K coincides to the slight peak of ϵ'_{r33} at the same temperature.

The results associated with dielectric and pyroelectric measurements indicate the following sequence of transitions:

orthorhombic biaxial ferroelastic ferroelectric	$\xrightarrow{371 \text{ K}}$	orthorhombic biaxial ferroelastic paraelectric	$\xrightarrow{658 \text{ K}}$	tetragonal uniaxial paraelectric paraelectric
--	-------------------------------	---	-------------------------------	--

Bragg X-ray diagrams obtained at 423 K in [001] direction included intermediate strata corresponding to a doubling of the c parameter of the tetragonal

unit cell. This result is in agreement with the orthorhombic symmetry above the ferroelectric Curie temperature. The tests of optical nonlinearity carried out on ground crystals at 423 K, in the paraelectric region, showed the absence of a second harmonic generation and led us to adopt the centrosymmetric point group *mmm* for the ferroelastic–paraelectric phase.

5. FERROELASTIC–FERROELECTRIC COUPLING

The relatively low values of the ferroelectric Curie temperature ($T_C = 371$ K) and of the spontaneous strain ($e_S = b - a/b + a = 8 \times 10^{-4}$, at 298 K) led us to expect a ferroelastic–ferroelectric coupling with an applied electric field lower than the breakdown field of the material.

Therefore we carried out an examination under polarized light of a crystal showing initially a multi-domain structure to which an electric field was applied in the [010] direction. The results obtained are shown on Figure 5, where we can see the progressive development of the domains with increasing electric field from 0 to $17 \text{ kV} \cdot \text{cm}^{-1}$. However it is very important to note that the same effect can be achieved with much lower fields applied during correspondingly longer periods of time (a few minutes under $7 \text{ kV} \cdot \text{cm}^{-1}$ for example). This switching field could probably be reduced also in better quality crystals. The application of an electric field implies a 90° rotation of some domains; and at last, the crystal becomes a single domain with its polarization axis parallel to the field along the [010] direction.

We have demonstrated also that this [010] polarization could be subsequently changed to the [100] direction by the application of a field of $17 \text{ kV} \cdot \text{cm}^{-1}$ between freshly applied electrodes.

These experiments prove that the ferroelastic–ferroelectric properties are partially coupled. Such crystals could find possibly applications as optical memories or optical windows.

6. CONCLUSIONS

A single crystal $\text{Pb}_{2.07}\text{K}_{0.56}\text{Nb}_{0.91}\text{Ta}_{4.15}\text{O}_{15}$ has been grown by the flux method. It crystallizes with the

tetragonal tungsten bronze structure. Two transitions have been determined by dielectric, pyroelectric and birefringence measurements: ferroelastic–ferroelectric phase 371 K , ferroelastic–paraelectric phase 658 K , paraelastic–paraelectric phase. Spontaneous polarization and spontaneous strain are respectively equal to $29 \mu\text{C} \cdot \text{cm}^{-2}$ and 8×10^{-4} at room temperature. Polar axis is along the [010] direction.

Electrical switching of the ferroelastic domains at room temperature shows clearly the existence of a ferroelastic–ferroelectric coupling.

ACKNOWLEDGMENTS

It is a pleasure for us to thank Dr. R. Von Der Mühl (L.C.S. CNRS) for helpful suggestions during the pyroelectric measurements; Dr. L. Rivoallan (CNET) who carried out the non-linear optical test; Dr. J. C. Toledano and J. Schneck (CNET) with whom we had fruitful discussions. We are also indebted to Professor A. K. Jonscher (Chelsea College, London) for help with the editing of the manuscript.

REFERENCES

1. S. C. Abrahams, *Mat. Res. Bull.* **6**, 881 (1971).
2. S. C. Abrahams and E. T. Keve, *Ferroelectrics* **2**, 129 (1971).
3. J. C. Toledano, *Ann. Telec.* **29**, 249 (1974).
4. L. G. Van Uitert, H. J. Levinstein, J. J. Rubin, C. D. Capio, E. F. Dearborn and W. A. Bonner, *Mat. Res. Bull.* **3**, 47, (1968).
5. E. A. Giess, B. A. Scott, G. Burns, D. F. O'Kane and A. Segmuller, *J. Amer. Cer. Soc.* **52**, 276 (1969).
6. B. Elouadi, J. M. Reau and J. Ravez, *Bull. Soc. Chim. Fr.* **3**, 467 (1975).
7. J. M. Reau, B. Elouadi, J. Ravez and P. Hagenmuller, *J. Solid State Chem.* **15**, 18 (1975).
8. J. Ravez and B. Elouadi, *Mat. Res. Bull.* **10**, 1249 (1975).
9. M. H. Francombe and B. Lewis, *Acta Cryst.* **11**, 696 (1958).
10. J. Nakano and T. Yamada, *J. Appl. Phys.* **46**, 2361 (1975).
11. J. Ravez, A. Perron and J. P. Chaminade, *C.R. Acad. Sc.*, **274**, 1450 (1972).
12. J. P. Chaminade, A. Perron, J. Ravez and P. Hagenmuller, *Bull. Soc. Chim. Fr.* **10**, 3751 (1972).
13. F. Galasso, G. Layden and G. Ganung, *Mat. Res. Bull.* **3**, 397 (1968).
14. P. W. Whipp, *J. Solid State Chem.* **4**, 281 (1972).
15. J. C. Toledano and J. Schneck, *Sol. State Comm.* **16**, 1101 (1975).