THE SILVER NIOBATE SINGLE CRYSTALS — TECHNOLOGY AND PHASE TRANSITIONS

By M. Łukaszewski and A. Ratuszna

Institute of Physics, Silesian University, Katowice*

(Received January 11, 1979; revised version received March 9, 1979; final version received May 17, 1979)

Single crystals of silver niobate have been obtained by molten salt methods. At room temperature $AgNbO_3$ possesses a pseudocubic perovskite type structure with distortion from monoclinic symmetry. X-ray examinations indicate the presence of phase transitions at 230°C and 330°C. Enclosed DTA and permittivity data for $AgNbO_3$ are discussed from the phase transition point of view.

1. Introduction

The least examined compound of the niobate group is silver niobate, $AgNbO_3$. Properties of this material, that are known so far, have been investigated for polycrystalline samples only [1, 2]. In these papers the authors mentioned some technological difficulties in preparing ceramics, as well as the presence of free silver inside them.

The authors of this paper have obtained different results concerning both the number of observed phase transitions and their temperatures. In the above papers the presence of the hysteresis loop and the simultaneous presence of the super lattice effect are mentioned.

The purpose of this investigations was to obtain the $AgNbO_3$ single crystals and to give more specific information about the properties of the compound, particularly about phase transition that occur in it.

2. Technology

Single crystals of silver niobate have been obtained by the molten salt method. The largest crystals have been obtained from a high temperature solution of the following ingredients: Ag_2O, Nb_2O_5 and AgCl as a solvent, in a 1 : 1 : 1 molar proportion. The mixture was heated to 1200°C. After all of it had melted in a period of 1 to 3 hours the mixture was subsequently cooled at the rate of 10° − 17°C/h. The length of the edges of the largest crystals was up to 20 mm. The obtained crystals were of light brownish colour. However,

* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

after heating the crystals for a few hours in open air, their colour faded and they became pale brown. The crystals are semitransparent and they darken slowly when exposed to daylight. Spectral analysis confirmed the chemical composition of crystals. The atomic spectrum shows the presence of a trace quantity of the cruicible material.

3. X-ray examination

The single crystals were powdered and examined in an *X*-ray diffractometer. The measurements were carried out on the *X*-ray diffractometer DRON-1 using monochromatic radiation $K_\alpha Fe$ and $K_\alpha Cu$. Operating conditions of the X-ray generator were as follows: 35 kV, 20 mA.

At room temperature $AgNbO_3$ has pseudocubic symmetry. The best numerical fitting of the diffractogram gives the following monoclinic parameters of the unit cell: $a = c = 3.9403$ Å± 0.0005 Å, $b = 3.9076$ Å± 0.0005 Å, $\alpha = \gamma = 90°$, $\beta = 90°34' \pm 6'$.

Later on measurements of the lattice constants versus temperature were carried out. The experiment was carried out using a high temperature camera GPWT 1500. The high

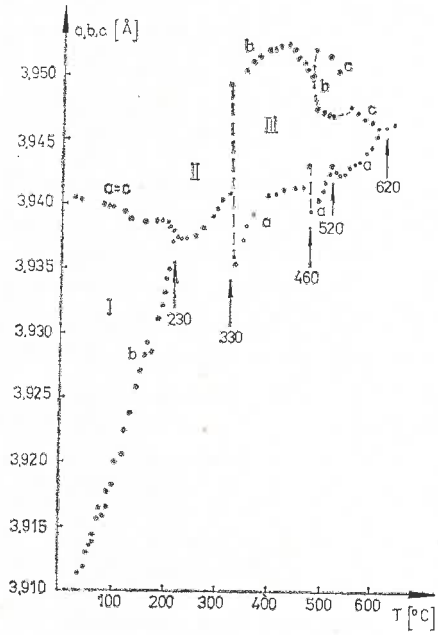

Fig. 1. Lattice constants vs temperature. The lattice parameters were determined with an accuracy of $\mp 5 \cdot 10^{-4}$ Å. The temperature of the sample was kept constant to within ∓ 0.5°C

angular reflection {400} and {310} were chosen for the measurements. The changes in lattice parameters in measured temperature range are shown in Fig. 1. The arrows show the temperatures of the observed structural phase transitions. In figure 1 the observed particular phases have been described by Roman numerals. On the base of the obtained

data one can suppose that in phase I the unit cell has a distortion toward monoclinic symmetry with $a = c \neq b$ and in phase II with $a = b = c$. In phase III distortion is orthorhombic and at 520°C the transition to the tetragonal symmetry is observed. Above 620°C the crystal undergoes a transition to the cubic ideal perovskite symmetry [3].

4. DTA investigations and changes in domain structure

DTA curves have been obtained with the use of the derivatograph OD-102. The curves have distinct anomalies at temperatures of about 340°C and 450°C. Considering the results of Holtzberg and Reisman [2], the derivatographic investigation of compounds containing Nb_2O_5 as their initial ingredient do not always show the presence of all phase transitions. The anomaly of the DTA curve at 450°C does not determine univocally the presence of the phase transition at this temperature. Close to this temperature the solvent AgCl melts and to separate the solvent from the crystals is very difficult. It is a generally known imperfection of this method of growing crystals. The DTA anomaly near 330°C indicates the presence of a real phase transition at this temperature. The phase transition at about 330°C is also noticeable while observing the domain structure changes. In investigating domain structure versus temperature one can observe a change of the form of the domain structure at about 230°C and its change and disappearance near 330°C.

5. Dielectric investigations

The $\varepsilon(T)$ dependence for $AgNbO_3$ single crystals is shown on Fig. 2. The curve is similar to the results of papers [1, 4]. The above dependence has a small local maximum at 60°C and a broad peak between 200°C and 300°C with the maximum somewhere

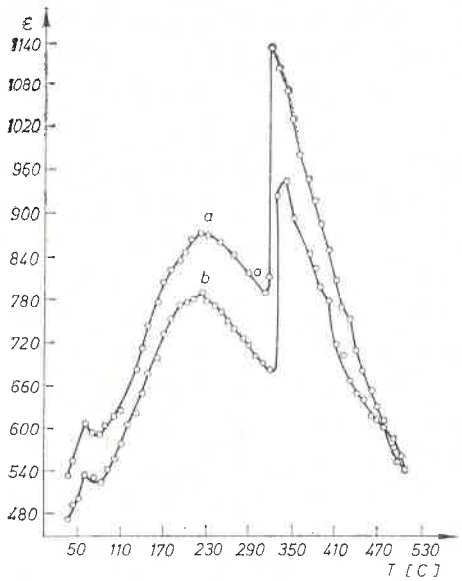

Fig. 2. The $\varepsilon(T)$ dependence for a $AgNbO_3$ single crystal. *a* — cooling process, *b* — heating process

between 220°C–230°C. It reaches maximum value at 330°C in the heating process. Above this temperature $\varepsilon(T)$ decreases similarly as in the paraelectric phase. However $\varepsilon(T)$ is not a straight line, which may suggest the presence of further phase transitions above the temperature of 330°C. For some samples, an anomaly of permittivity, has been noticed at the mentioned temperature of 450°C. It should be mentioned that the last maxima are characterized by great diversities of temperatures which may increase towards higher temperatures by as much as 15° depending on the growth of the crystals. It is most probably caused by defects and strains which accompany the growing process.

6. Summary

In summing up the above description, it should be ascertained that in $AgNbO_3$ single crystals examined with the above methods one can trace, without any doubt the existence of phase transitions at the temperatures of 225°C–230°C and 330°C. Moreover X-ray investigation indicates the presence of the phase transitions in heating process at 460°C, 520°C and 620°C. Taking into account the results of the investigations it may be supposed that the maximum of $\varepsilon(T)$ at 60°C most probably is not connected with the structural phase transition.

More detail data concerning the changes of symmetry of $AgNbO_3$ crystals at particular points of phase transition will be obtained by further X-ray investigations. The recognition of the presence of the ferro or antiferroelectrical property areas in investigated crystals also needs further examination.

REFERENCES

[1] M. Francombe, B. Lewis, *Acta Cryst.* **11**, 175 (1958).
[2] A. Reisman, F. Holtzberg, *J. Am. Chem. Soc.* **80**, 6503 (1958).
[3] E. G. Fesenko, *Semeistvo perovskita i segnetoelektrichestvo*, ed. Atomizdat, Moskva 1972 (in Russian).
[4] M. Łukaszewski, A. Maciążek, *Prace fizyczne UŚl. Katowice* **4**, 145 (1976) (in Polish).