

## CRYSTAL GROWTH AND CHARACTERIZATION OF $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$ - SOLID SOLUTIONS

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### SUMMARY

Single crystals of  $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$  with compositions  $0.35 \leq x \leq 1$  have been grown from a solution of molten  $\text{KNbO}_3 + \text{KTaO}_3$  with an excess of  $\text{K}_2\text{O}$ . In order to minimize variations in the Nb/Ta ratio, a method was developed to grow crystals at a small temperature gradient and at a low growth rate.

To characterize the homogeneity of the crystals, the spatial fluctuations of the Nb/Ta ratio were resolved by electron microprobe analysis. The temperature dependence of the dielectric constant of the whole crystals was measured.

The results indicate that the spatial variation of the Nb/Ta ratio cannot explain the dielectric behavior. We suppose that internal stress, caused by the tendency of exsolution in the system  $\text{KNbO}_3 - \text{KTaO}_3$ , must be taken into consideration.

### INTRODUCTION

Solid solutions of potassium tantalate-niobate,  $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$  or KTN, are transparent ferroelectric materials showing very large electro-optic effects. The Curie temperature of these solid solutions varies with composition: Crystals with  $x \leq 0.4$  are cubic at room temperature, thus applicable for quadratic electrooptic effects; those with  $0.4 \leq x \leq 0.57$  and  $x \geq 0.57$  are tetragonal and orthorhombic, respectively, thus exhibiting large linear effects (ref. 1).

Accordingly, KTN is regarded as an attractive material for many applications, e.g. for light modulation and deflection (refs. 2,3) or for holographic storage (ref. 4), pyroelectric detectors, etc.

The difficulties in preparing KTN crystals of sufficient optical quality have been described by several authors and are cited in reference (5). The phase diagram determined by A. Reisman et al. (ref. 6) shows, that it is impossible to grow crystals with a constant Nb/Ta ratio. During the crystal growth process the tantalum content of the melt decreases continuously. Small temperature variations due to thermal convection cause deviations from the mean crystal composition ('striation problem') (ref. 7). For larger crystals of optical quality it is therefore desirable to avoid temperature gradients and temperature fluctuations.

## CRYSTAL GROWTH

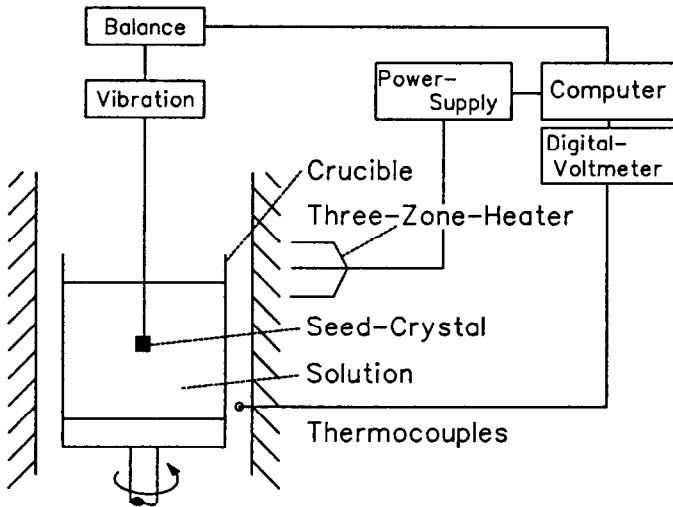
Apparatus

Fig. 1: Crystal-growth apparatus for  $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$ .

A schematic drawing of the crystal growth apparatus used in the present investigation is shown in Fig. 1. The furnace is situated in a room with small fluctuations of the room temperature. Temperature and diameter control are located in a separate room. Four resistance heaters (Kanthal super) are centered around a ceramic tube. The platinum crucible is placed on an alumina pedestal that can be rotated by a mechanism below the furnace. Two additional heaters placed closely above and below the crucible in the tube minimize the vertical temperature gradient to  $\pm 0.1$  K/cm. The two heaters of Kanthal A1 wire are surrounded by alumina crucibles to protect the solution against impurities. The charge is contained in a 100 ml platinum crucible which is placed in another crucible made of high purity alumina to give higher mechanical stability at high temperatures. The temperature is measured using a thermopile of six thermocouples of PtRh6% versus PtRh30% (El 18). These thermocouples combine high sensitivity at high temperatures with low sensitivity of the cold junctions at room temperature. The thermovoltage is measured with a 8 1/2 digit digital multimeter (Solatron, type 7081). Temperature data are transmitted to a computer, which controls the temperature via the power supply. An optimized design of the control and measurement systems allows to achieve a precision of temperature control with a standard deviation of 0.01 K in the solution,

detected during 48 h.

An electronic balance (Sartorius, type 200s analytic) with a resolution of 0.1 mg is fixed above the furnace to measure the weight of the crystal during the growth process. (This is possible because of a difference in density of about 2 g/cm<sup>3</sup> between the solution and the crystal.) Weight and temperature data are used to control the growth rate automatically by the computer.

Measurements of the density of the solution show that it is difficult to achieve homogeneity of the melt. Stirring techniques like 'ACRT' (accelerated crucible rotation technique) described by H.J.Scheel (ref. 8), are not very effective. Instead, we applied a method of stirring for a period of two days by a vibrating mechanism at 40-80 Hz and an amplitude of 2 mm. By combining this technique with rotation of the crucible no density gradient can be detected in the solution.

The seed crystal was mounted at a thin platinum wire and completely immersed in the solution, a method known for the crystallisation in aqueous solutions (ref. 9).

#### Typical crystal growth conditions

Charges were prepared using potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, Merck optipur), niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>, Starck HCST 7332) and tantalum pentoxide (Ta<sub>2</sub>O<sub>5</sub>, Starck HCST 630). The crystals must be grown from a solution containing an excess of K<sub>2</sub>O. In most cases we used a melt with a composition of 53 mole % K<sub>2</sub>O and 47 mole %  $x(\text{Nb}_2\text{O}_5) + (1-x)(\text{Ta}_2\text{O}_5)$ . The melting point changes from 1333 K to 1650 K depending on composition  $x$ . The concentration of Ta in the seed crystal is chosen about 5% higher than expected for a crystal grown from the solution. This prevents a fast remelting of the seed when being in contact with the solution. The crystallographic orientation is chosen in such manner that all faces of the crystal are from {100}'-type.

The seed is set into position after homogenization of the solution. Then the temperature is increased to dissolve the surface of the seed. This procedure prevents the incorporation of seed perturbations, produced during preparation. Subsequently the temperature has to be decreased until growth occurs with a rate of 0.01 g/h. This corresponds to a growth velocity of 0.01 mm/h. During crystal growth it is important to homogenize the solution continuously to avoid a concentration gradient between melt near the crystal and the remainder of the melt. Crucible rotation and vibration of the seed are used for this.

After 20 days the crystal is lifted out of the solution and cooled down to room temperature during 48h. The crystal diameter is about 12 mm and it shows {100}'-faces.

KNbO<sub>3</sub> shows several structural phase transitions (ref. 10). The cubic phase (Pm3m) at high temperatures changes at 690 K to the tetragonal (P4mm) symmetry. Below 470 K the orthorhombic (Amm2) structure is found. The non-cubic phases show ferroelectricity (ref. 10). In KTaO<sub>3</sub> on the other hand there are no phase transitions. In solid solutions of K(Ta<sub>1-x</sub>Nb<sub>x</sub>)O<sub>3</sub> it

is possible to shift the transition temperatures of the phase transitions lineary with the Ta content to lower temperatures (ref. 1).

The polarization of the crystals in the ferroelectric phases is not uniform and therefore the crystals are opaque. It is possible to achieve single domain crystals by applying an electrical field at elevated temperature. Crystals in the cubic phase look colorless and optically clear.

### Results

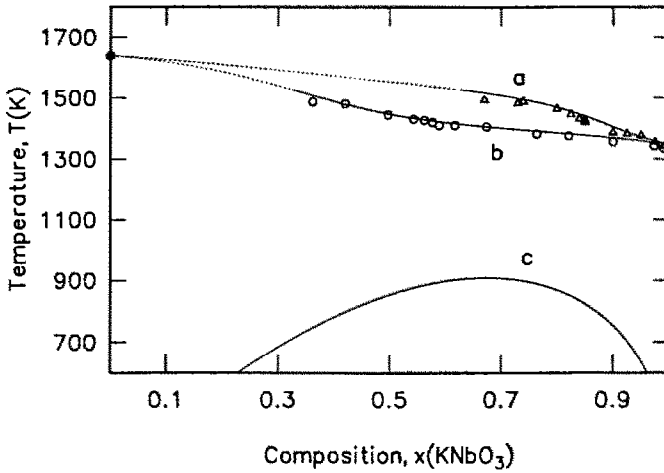


Fig. 2: Phase-diagram of  $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$ .

- a) Liquidus curve
- b) Solidus curve
- c) Calculated miscibility gap in the solid phase (see text).

From the data of our crystal growth experiments ( $\Delta$ ) and a chemical analysis of the crystals by electron-microprobe measurements (o) (for details see later), we derived the phase diagram (Fig. 2). In comparison with the phase diagram determined by A. Reisman et al. in 1955 (ref. 6), a small deviation is seen within the region of  $0.6 \leq x \leq 1$ . Our curves indicate a tendency to exsolution. We suppose that this trend is important for crystal growth as discussed later.

## CHARACTERIZATION

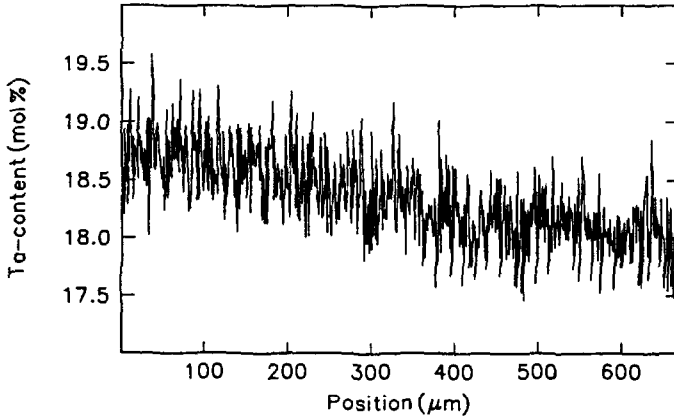


Fig. 3: Electron microprobe analyses of a KTN crystal containing 18.5 mole % Ta.

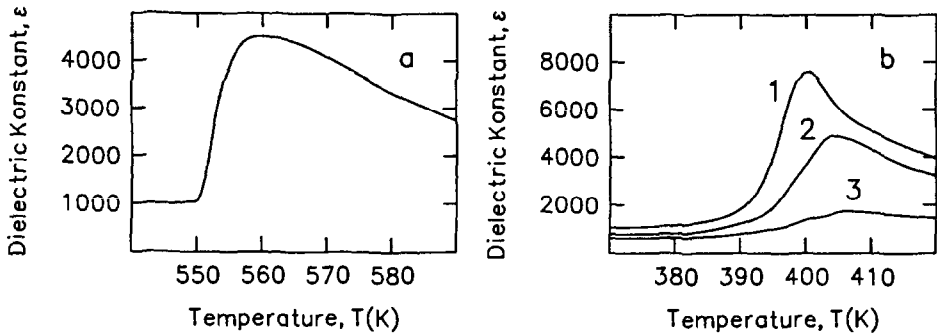


Fig. 4: Temperature dependence of the dielectric constant.

- a) Phase transition cubic to tetragonal, KTN 18.5 mole % Ta.  
 b) Phase transition cubic to tetragonal, KTN 42.8 mole % Ta with external stress (1: no stress, 2: 20 MPa, 3: 40 MPa).

The crystals are analysed by electron-microprobe technique (Cameca SX50). Samples 2-3 mm in size are polished to examine a flat surface. Nearly 700 points with a diameter of  $1\mu\text{m}$  over a distance of  $700\mu\text{m}$  are measured in different crystal directions. The Nb and Ta content

is detected simultaneously. Fig. 3 shows the Ta content of a crystal grown from a solution containing 10 mole % Ta. A maximum amount of  $\pm 0.6$  mole % Ta fluctuations is detected in this crystal.

The dielectric constant  $\epsilon$  as a function of temperature  $T$  was measured to examine phase transitions of KTN crystals (ref. 11). Capacity, electrical conductivity and the temperature of the crystal are measured by a Hewlett Packard bridge (4270A) and a digital multimeter (Prema 6030). The values are taken every 0.2 K at 1 KHz, 10 KHz, 100 KHz, 1 MHz and stored by a computer.

From (ref. 1), a function can be derived to obtain the Nb/Ta ratio of KTN from the dielectric constant of a solid solution. At the phase transition temperatures of  $\text{KNbO}_3$  pronounced peaks are very sharp increases of  $\epsilon$ . In KTN broadening is caused by a statistical distribution of Ta and Nb in the crystals. Fig. 4a shows the dielectric behavior of the same crystal shown in Fig. 3. The dielectric constant increases over a range of 9 K and this corresponds to a variation of about 1.4 mole % Ta content, calculated from the values given by S. Triebwasser (ref. 1). A quantitative comparison of the variations of the Nb/Ta ratio shows, that the values analysed by electron microprobe technique are always considerably smaller than the values detected by  $\epsilon$  measurements.

We propose that internal stress influences the dielectric behavior. To check this suggestion we applied external uniaxial stress to a KTN crystal and measured  $\epsilon$  at the phase transition cubic-tetragonal. The results of Fig. 4b clearly demonstrate the influence of stress: The decrease of  $\epsilon$  at the transition temperature is broadened and the maximum value is lowered.

## DISCUSSION

To explain the spatial fluctuations of the Nb/Ta ratio a thermodynamic analysis of the binary system was performed. The specific heats  $C_P$  of the components being known we were able to calculate the phase diagram.

The GIBBS energy of  $\text{KNbO}_3$  and  $\text{KTaO}_3$  were obtained by numerical integration  $C_P$  data compiled by Spencer (ref. 13). The excess GIBBS energy of both the solid and liquid solution were estimated by the following procedure:

The simplest model explaining asymmetric miscibility gaps (i.e. gaps with a critical point lying on either side of the  $x = 0.5$  isopleth) is the subregular solution model. The molar enthalpy of the mixing of a subregular solution A-B is given by:

$$\Delta_{mix}H_m = x_A x_B (h_A x_A + h_B x_B)$$

where  $x_A$  and  $x_B$  are the molar fractions of the respective components;  $h_A$  and  $h_B$  are the so called subregular interaction parameters. In a subregular solution the entropy of mixing is virtually ideal and  $\Delta_{mix}H_m$  is taken to be independent of temperature. If values of  $\Delta_{mix}H_m$  are unknown they can be derived from the boundaries of the phase regions in the phase diagram.

By microprobe analysis of KTN crystals grown from a solution of known composition we obtained experimental data of the solidus and liquidus curves. By fitting the calculated solidus and liquidus curves to the experimental data points we obtained for the solid (s) the interaction parameters:

$$h_{KTaO_3}^{(s)} = 17kJmol^{-1}$$

$$h_{KNbO_3}^{(s)} = 8kJmol^{-1}$$

and for the melt:

$$h_{KTaO_3}^{(l)} = 17kJmol^{-1}$$

$$h_{KNbO_3}^{(l)} = 12kJmol^{-1}$$

An extrapolation of these data valid at the solidus liquidus interface towards lower temperatures leads to a broad asymmetric miscibility gap with critical point located at  $x = 67$  mole %  $KNbO_3$  and a critical temperature of 908 K.

The existence of a miscibility gap, already reported by V.G. Hill et al. (ref. 12), could be the reason for the concentration fluctuations and for the internal stress of the crystals observed during microprobe experiments and dielectric constant measurements. The critical point of the gap reported by Hill is very close to the solidus curve. This is unlikely, because miscibility gaps usually distort the solidus especially when being located very near to it. The solidus curve of the KTN system shows only small deviations from ideality which can be adequately described by the interaction parameters given above.

## ACKNOWLEDGEMENTS

We thank E. Krätzig and K. Betzler for helpful discussions. This work has been performed within the program of the SFB 225. We thank the Deutsche Forschungsgemeinschaft for financial support.

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