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Flux Growth of KNbO₃ Crystals by Pulling-Down Method

The crystals of KNbO₃ have been grown by the micro-pulling-down method. Colorless, transparent, and crack-free crystals were produced from the melts containing excess of K₂O as a flux. Growth of relatively large size (up to 2 mm in diameter and up to 30 mm in length) single crystals was found possible using the crucibles with corresponding nozzle size (up to 2.0 mm in outer diameter). Second harmonic generation was observed in the crystals irradiated by fundamental beam with wavelength about 860 nm.

Keywords: potassium, niobate, fibers, flux, growth, pulling-down

1. Introduction

Potassium niobate (KNbO₃ or KN) is a well known ferroelectric material for electro-optic, nonlinear optic, and photorefractive applications (FUKUDA; FLÜCKIGER). It is efficient material for doubling the frequency of near-infrared (Ga, Al)As diode lasers used for recording and reading data from optical compact discs. The information density of optical systems arranged with KN crystal is expected to be four times greater than those of non-arranged ones.

However, it is difficult to grow these crystals because KNbO₃ melts incongruently at temperature above 1000°C (IMAI; IRLE; REISMAN; ROTH). Therefore the crystals have to be grown from a K₂O rich, non-stoichiometric melts. Moreover KNbO₃ is known to exist in three phases. High temperature phase crystallizes in the cubic perovskite structure. Within the temperature range 225-435°C KNbO₃ has tetragonal structure. At room temperature it is isostructural with the distorted perovskite form of BaTiO₃ and has an orthorhombic structure with two formula units per unit cell. Therefore it is also difficult to obtain high quality crystals because of structural reordering that occurs during the crystal cooling.

The flux growth technique is widely used to grow KNbO₃ crystals from the melts containing K₂O excess (FUKUDA; FLÜCKIGER). However reproducibility of growth results is difficult to control because of non-stoichiometry of the starting mixtures and easy volatilization of K₂O from the melt and crystal surface (FLÜCKIGER; IMAI).

It was reported also (IMAI), that single crystal fibers of K(Ta,Nb)O₃ solid solutions were grown by the laser heated pedestal growth method (LHPM). The source rods were enriched with K₂O to prevent formation of K₄Nb₆O₁₇ phase which is stable in the KNbO₃ stoichiometric melt without excess of K₂O (IRLE; REISMAN; ROTH). The temperature gradient in this method is steep enough to prevent constitutional supercooling and therefore to avoid spontaneous nucleation on the liquid-solid interface. In the case of K(Ta,Nb)O₃

mixed crystals (IMAI) the addition of a gas blower to the apparatus was necessary to increase and to control the gradient in the vicinity of the molten zone.

Micro-pulling-down (μ -PD) technique (YOON) is reported in the present paper to be a versatile method of preparation of high quality KNbO_3 fiber crystals starting from the melts of non-stoichiometric composition. We discuss the experimental procedure and the growth parameters which allow us to produce relatively large KNbO_3 crystals.

2. Growth procedure

The starting materials with various compositions were made using K_2CO_3 (Rare Metallic Co.) and Nb_2O_5 (High Purity Chem. Lab.), both of 99.99% purity. Desired quantities of compounds were carefully weighed and mixed by grinding in ethanol with an agate mortar and pestle, and dried at 100°C during 5-10 hr. Special attention was paid to prepare water-free K_2CO_3 . Therefore preliminary annealing of starting K_2CO_3 at temperature 350 - 400°C during 5-10 hr was necessary. The compositions of the melts used in our experiments are summarized in Table 1.

No.	K_2O	Nb_2O_5	Nozzle	Seed	Pulling rate	Length
12-2	40	60	1.2x1.0	Pt wire	0.35	35
1-2	50	50	1.2x1.1	Pt wire	0.11	32
4-2	50	50	1.2x1.0	Pt wire	0.10	8
3-3	52	48	1.2x1.0	Pt wire	0.08	10
7-1	54	46	1.2x1.0	Pt tube	0.30	50
7-2	54	46	1.4x1.3	No. 7-1	0.15	34
6-1	55	45	1.2x1.0	Pt wire	0.13	25
8-1	56	44	1.2x1.0	Pt wire	0.09	22
8-2	56	44	1.2x1.0	Pt tube	0.20	45
8-3	56	44	1.4x1.3	Pt tube	0.12	30
8-4	56	44	1.4x1.3	KTN (flux)	0.13	37
15-1	57	43	1.7x1.6	Pt tube	0.10	30
15-3	57	43	2.0x1.9	Pt tube	0.10	19
11-1	58	42	1.2x1.0	Pt wire	0.11	13
11-2	58	42	1.2x1.0	Pt tube	0.16	27
11-4	58	42	1.2x1.0	Pt tube	0.30	70
11-5	58	42	2.0x1.9	Pt tube	0.10	20
13-1	62	38	1.2x1.0	Pt tube	0.15	18

Table 1.: Crystal growth conditions: melts composition (mol.%) outer and inner diameters of the crucible nozzle (mm), seed material, pulling rate (mm/min), and crystal length (mm)

Schematic diagram of the μ -PD system and the details of the experimental technique are described in the above-mentioned paper (YOON). The crystals were grown under air atmosphere. The melt was contained in a crucible, which was made of Pt plate of 0.1 mm thickness and Pt pipe of 1.0-2.0 mm in outer diameter and a wall thickness of 0.05-0.01 mm, as it is shown in Fig. 1. We will call the modified arrangement (large nozzle diameter) as pulling-down (PD) technique to separate it from the conventional (μ -PD) system.

In the main two variations of the seeding technique were used in the experiments described here; solidification of the melt was started on Pt wire of 0.5 mm in diameter or Pt pipe of 0.4 mm in outer diameter and a wall thickness of 0.05 mm. Using of KNbO_3 single

crystal seed was also possible, but it was difficult because of cracking which occurred during heating or seeding. Extremely high temperature gradient under the crucible nozzle and phase transitions mentioned above are considered to be main causes of the cracking. $\text{K}(\text{Nb},\text{Ta})\text{O}_3$ seed crystals grown by conventional flux technique were used also to prevent these disadvantages. The crystal grown on $\text{K}(\text{Nb},\text{Ta})\text{O}_3$ seed (sample No. 8-4 of Tables 1 and 2) was crack-free.

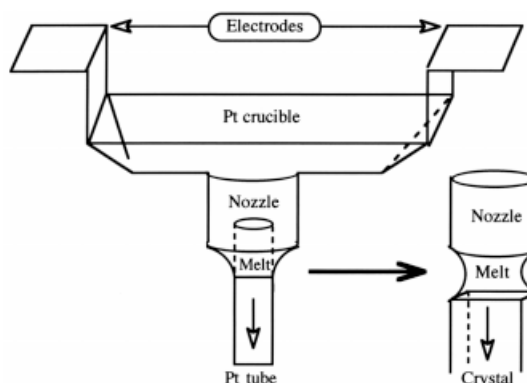


Fig. 1. Schematic diagram of seeding procedure using Pt pipe as a seed.

In case of seeding on Pt wire one crystallographic direction of high growth rate was developed by pulling down rate of 0.50-1.00 mm/min and necking procedure. Further orienting of the crystal was made during the growth process by manipulations of micro X - Y stage. It was possible due to faceting of the crystals observed in situ by optical microscope.

No.	W (mg)	D (mm)	Color	Crystal	Remain Melt	Cracks
12-2	150	1.0	colorless	$\text{K}_4\text{Nb}_6\text{O}_{17}$	$\text{K}_4\text{Nb}_6\text{O}_{17}$	Yes
1-2	-	1.0	colorless	$\text{K}_4\text{Nb}_6\text{O}_{17}$	$\text{K}_4\text{Nb}_6\text{O}_{17}$	-
4-2	-	1.1	blue	KNbO_3	-	-
3-3	39	1.1	colorless	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	Yes
7-1	206	1.1	colorless	KNbO_3	-	Yes
7-2	171	1.3	dark blue	KNbO_3	-	Yes
6-1	94	1.1	colorless	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	No
8-1	77	1.1	light blue	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	No
8-2	207	1.1	colorless	KNbO_3	-	No
8-3	177	1.3	colorless	KNbO_3	-	No
8-4	236	1.4	light blue	KNbO_3	-	No
15-1	246	1.8	colorless	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	No
15-3	239	2.1	light blue	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	No
11-1	52	1.2	light blue	KNbO_3	$\text{K}_4\text{Nb}_6\text{O}_{17}$	Yes
11-2	93	1.1	colorless	KNbO_3	KNbO_3	No
11-4	255	1.1	light blue	KNbO_3	-	No
11-5	231	2.1	colorless	KNbO_3	-	No
13-1	57	1.0	blue	KNbO_3	KNbO_3	Yes

Table 2. : Crystal growth results: weight (W), diameter (D), color and phase of the crystals grown and remain melts

Best results were achieved in the runs where Pt tube was used as a seed similar to that of described earlier (KIMURA) for the crystal growth by Czochralski method. Schematic

illustration of the seeding technique used is illustrated by Fig. 1. As a first step the tube was inserted into the crucible nozzle and kept there about 1 min. At that time overheating of the crucible was necessary to prevent solidification of the melt inside the nozzle because of high thermoconductivity of platinum. Thereafter pulling down was started with a rate close to that of used for crystal growth as it is given in Table 1.

All growth processes were stopped after observation of any kind of crystal imperfection. After that the crystals were disconnected from the molten zone and pulled down with the rate corresponding to cooling rate of about $30^\circ\text{C}/\text{min}$. Thereafter the crystals were removed from the seed holder. As a second stage of each experiment the remain melt was removed from the crucible using the same seeding material with a pulling rate of about $0.50\text{ mm}/\text{min}$. Deposition of small drops of a flux (K_2O) was sometimes observed on the surface of the crystals. Therefore the crystals were washed in warm water.

3. Growth results and discussion.

Fig. 2 shows the as grown KNbO_3 crystals. The fibers grown had a habit corresponding to published data (FUKUDA). The crystals showed simple crystallographic $\{100\}$ faces because of presence of flux. In the main the rod-like crystals had four-fold symmetry corresponding to $[100]$ orientation of pseudo-cubic high temperature phase (ZENG). Similar to the crystals grown by top-seeded solution growth, the ones reported here had very flat cubic faces because the progressive nucleation on cubic planes is quite difficult (HULLIGER).

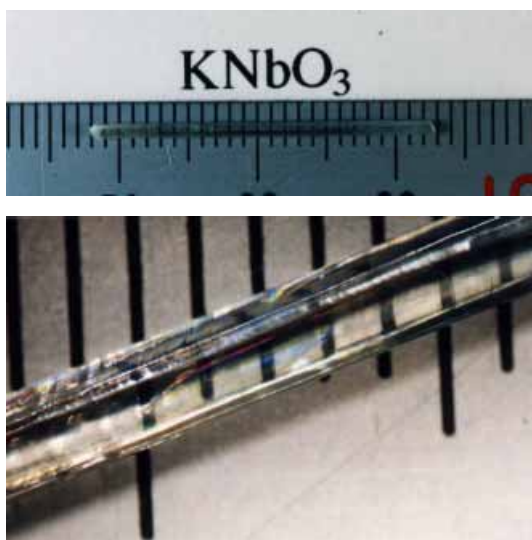


Fig. 2. View of KNbO_3 crystals (sample No. 11-2 above and sample No. 15-1 below) grown by PD technique (scale in mm).

The crystals were blue and colorless depending on melt composition and pulling rate. In general optimization of crystal growth conditions was necessary for all of the melts reported here, because at least light blue coloration following from presence of some amount of oxygen vacancies (FUKUDA; IMAI) was observed in all crystals grown at relatively high pulling rate. Almost all crystals were transparent, as shown in Fig. 2. The typical size of crystals was about 1-2 mm in cross-section depending on diameter of the nozzle and few centimeters in length. In the main about 70-80 vol.% of the melt was crystallized into KNbO_3 single crystals. Maximum yield achieved (crystal/melt volume ratio) was about 90

vol.% for the melts containing insignificant excess of K_2O .

It was also possible to grow the $KNbO_3$ single crystals with an extremely high pulling rate of about 1-2 mm/min. In such a case the crystals also were single phase and had typical four-fold symmetry. However these crystals were dark blue in color.

Phase homogeneity of the crystals grown and the melts remain after growths were studied by X-ray powder diffraction analysis. In the main the crystals grown were $KNbO_3$ single phase (JSPDS data card No. 32-822) as it is given in Table 2. The remain melts were found crystallized as either $KNbO_3$ or $K_4Nb_6O_{17}$ depending on composition of starting mixture.

In the melts corresponding to the vicinity of stoichiometric composition of $KNbO_3$ crystallization of the second phase was often observed. It was assumed that the phase is $K_4Nb_6O_{17}$. However the phase identification was difficult because X-ray diffraction data for $K_4Nb_6O_{17}$ compound found in JSPDS data cards are very different (cards No. 14-287, 21-1295, 31-1063, and 31-1064). Therefore it was necessary to prepare this material by ourselves. The $K_4Nb_6O_{17}$ compound was produced by solid state reaction technique. Moreover the $K_4Nb_6O_{17}$ single crystals were grown by the PD method from stoichiometric melt of the above composition using the procedure similar to that of described above. The $K_4Nb_6O_{17}$ crystals were transparent, colorless, and were well developed in shape. X-ray diffraction pictures of the poly- and single-crystalline samples were very similar. X-ray diffraction data are given in Table 3. The results of Table 3 show relatively high correlation with the data found in JSPDS data card No. 14-287.

2θ	d_{obs}	I/I_0
9.15	9.66	100
13.95	6.35	20
16.58	5.35	16
19.63	4.52	13
21.20	4.19	13
23.00	3.87	16
27.58	3.23	46
29.90	2.99	33
31.55	2.84	77
35.95	2.50	17
38.10	2.36	15
40.28	2.24	21
45.30	2.00	16
46.20	1.96	26
51.20	1.78	15
58.60	1.58	16

Table 3: X-ray powder pattern of the single crystal grown from $K_4Nb_6O_{17}$ stoichiometric melt in the range of $2\theta = 6-60^\circ$ (sample No. 12-2 of Tables 1 and 2)

The KN crystals were cut and polished. Second harmonic generation (SHG) was observed in the samples with fundamental laser beam irradiated along the growth axis (a-axis).

4. PD and related growth methods

Comparison of most common features of PD and related growth techniques is given in Table 4. Two most important advantages of the μ -PD technique modified by increasing of

the diameter of capillary channel (PD) are discussed below briefly.

Methods	μ -PD and LHPM*	PD	Flux Growth
Crystal Diameter	~ 0.5 mm	≥ 2.0 mm	≥ 10 mm
Segregation Coefficients	$K \approx 1$	$K \approx 1$	$K \approx 1$
Flux Growth	Difficult because $K \approx 1$	Possible	Possible
Growth Rate (mm/min)	Very high (0.1-1.0)	Very high (0.1-1.0)	Very low (< 0.01)
Growth control	Easy	Easy	Difficult

LHPM* - laser heating pedestal method

Table 4: Comparison of PD and related techniques

4.1. Flux growth

One of the most important result of this study seems to be related with presence of considerable amount of flux in the starting melts. For example, recalculation of the melts used for the growth of the crystals No. 11-5 and No. 13-1 (Table 1) results KNbO₃ : K₂O = 84 : 16 and KNbO₃ : K₂O = 76 : 24 molar ratios, respectively.

In the case of conventional μ -PD growth reported earlier (YOON) the crucibles were fabricated with a nozzle diameter less than 1 mm. In such a case the segregation phenomena was not observed because of low mass transport inside the narrow capillary channel. Therefore intensity of the cations exchange between the liquid and solid phases was very low. Same phenomena is usually observed in the LHPM crystal growth (IMAI). In both these methods the segregation coefficients reported were close to unity: $K \approx 1$. However, in the modified PD arrangement reported here the diameter of capillary channel has been increased considerably up to 2 mm that is close to size of the crucible (about 10 x 5 x 2 mm, as it is shown in Fig. 1). This way, the rate of natural convection has been increased also, and the segregation on the liquid/solid interface was observed become possible ($K \approx 1$). Thus the modification discussed here results unusual possibility of flux growth with high pulling rate (0.1-1.0 mm/min).

4.2. Growth of macro-crystals

Another important result is related with examination of macro-limitations of the μ -PD system. In all previous reports concerning oxide crystal growth by μ -PD technique the diameter (or cross-section) of the fibers reported did not exceed 1 mm. The maximal size of the KNbO₃ crystals grown in this study was greater than 2 mm. Therefore fields of application of the PD technique and the crystals reported is assumed increase considerably.

5. Conclusions

KNbO₃ single crystals were grown by the pulling-down technique. The crystals were SHG active. It was found that combination of the conventional pulling-down system with the crucible arranged with large capillary channel can be used to produce relatively large macro-crystals with diameter greater than 2 mm by flux method.

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