



# **Ternary system Li<sub>2</sub>O-K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>: Re-examination of the 30mol% K<sub>2</sub>O isopleth and growth of fully stoichiometric potassium lithium niobate single crystals by the micro-pulling down technique**

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# **Ternary system $\text{Li}_2\text{O-K}_2\text{O-Nb}_2\text{O}_5$ : re-examination of the 30 mol% $\text{K}_2\text{O}$ isopleth and growth of fully stoichiometric potassium lithium niobate single crystals by the micro-pulling down technique**

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## **Abstract**

Potassium lithium niobate (KLN) single crystals have attractive properties for non-linear optical applications based on frequency conversion of laser diodes in the blue range. Especially, fully stoichiometric  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  crystals would be capable of doubling a laser light in the near UV range. Using powder X-ray diffraction and DSC experiments, we have re-investigated the 30 mol%  $\text{K}_2\text{O}$  of the ternary system  $\text{Li}_2\text{O-K}_2\text{O-Nb}_2\text{O}_5$  in order to explore the possibility of a limited existence field for this phase. From our results, it was shown that the stoichiometric KLN phase exists between 970 and 1040 °C, temperature at which it undergoes a non congruent melting. From this conclusion, compositionally homogeneous a-axis oriented single crystals fibers of stoichiometric  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  were successfully grown by the micro-pulling down technique with pulling rates in the range 0.3-0.7 mm.min<sup>-1</sup>. The crystal length was between 10 and 120 mm for an apparent diameter near 500 μm. The fibers, characterized by optical microscopy, X-ray diffraction and Raman spectroscopy, appeared free of macro-defects and of good quality and their stoichiometric composition was also confirmed.

**Keywords:** A1. Phase diagrams, Crystal structure, X-ray diffraction, Raman spectroscopy, A2. Micro-pulling down technique, A3. Niobates

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## **1. Introduction**

There is an important interest in blue light compact lasers for various applications such as optical data storage, full-color projection displays or high resolution laser printers as well as in medicine or biotechnology. Fiber shaped single-crystals capable of frequency conversion (frequency mixing or non-critical phase-matched second-harmonic generation) are then a potential alternative to blue laser diodes. Among the usable materials, crystals corresponding to the chemical formula:  $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$  ( $x < 0.5$ ) are uniaxial negative materials showing high non-linear coefficients and optical damage threshold [1]. In these crystals, the phase-matching wavelength is adjustable to the composition and decreases with  $x$ . Calculated with the Sellmeier equations, it is practically equal to 762 nm at room temperature for  $x=0$  which corresponds to the stoichiometric compound  $K_3Li_2Nb_5O_{15}$  [2, 3]. The obtention of ferroelectric crystals of that composition would give access to interesting devices operating in the near UV range.

At the beginning, KLN single crystals were grown by conventional techniques (Czochralski, HTTSSG,...), starting melt compositions being based on the only available phase diagram determination of the ternary system  $Li_2O$ - $K_2O$ - $Nb_2O_5$  performed by Scott et al. [4]. This study showed that KLN belongs to a rather large ternary solid solution domain ranging about from 27 to 32 mol%  $K_2O$  and from 50 to 68 mol%  $Nb_2O_5$ . As expected, crystals grown with these techniques from non-congruent melting compositions were not compositionally homogeneous.

In the 90's, several researchers succeeded in growing KLN single-crystal fibers using LHPG (Laser Heated Pedestal Growth) and  $\mu$ -PD (micro-pulling down) techniques with the main advantage to obtain homogeneous crystals all along the growing axis (effective distribution coefficients close to 1) if sufficiently high pulling rates are applied as these two

techniques are characterized by high temperature gradients [5-14]. Several of these works were performed with starting melts belonging to the 30 mol%  $K_2O$  isopleth of the ternary system  $Li_2O$ - $K_2O$ - $Nb_2O_5$ . In this isopleth, at room temperature, the limit of the ternary solid solution range was established to 51.5 or 51.9 mol%  $Nb_2O_5$  [15, 16]. Therefore, the growth of crystals using melts belonging to the isopleth but with less than 51.5-51.9 mol%  $Nb_2O_5$  and at high pulling rates should lead to polycrystalline mixtures containing  $Li_3NbO_4$ ,  $KNbO_3$  and a certain amount of KLN ternary solid solution according to the phase diagram of Scott et al.. It is particularly the case for the stoichiometric melt  $K_3Li_2Nb_5O_{15}$  (50 mol%  $Nb_2O_5$ ).

However, some papers reported the growth of KLN fibers from melts with less than 51.9 mol%  $Nb_2O_5$  [8-10] with pulling rates up to  $120 \text{ mm.h}^{-1}$ . Unfortunately, no information was given about the chemical composition of the obtained crystals apart an assessment of the crystal structure to the KLN structure by X-ray diffractometry. However, Imaeda and Imai recently gave some indications on the composition of their fibers pulled by  $\mu$ -PD through the determination of the room temperature non-critical phase matching wavelength [10]. Using the Sellmeier equations, it could be possible to determine the  $Nb_2O_5$  content of the considered fibers. When performing this calculation, a large deviation from the niobium oxide amount of the starting melt was found which is inconsistent with the features of the technique if account is taken of the growth rates used. For example, the phase matching wavelength of a fiber pulled at 40 mm/h from a starting melt composition equal to 50 mol%  $Nb_2O_5$ , 30 mol%  $K_2O$  and 20 mol%  $Li_2O$  is found to be 889 nm which corresponds to 52 mol%  $Nb_2O_5$  and 30 mol%  $K_2O$  using the Sellmeier equations [2, 3]. Moreover, in all cases, the phase diagram of Scott et al. does not allow the interpretation of the growth results obtained.

In 1996, Ouwerkerk claimed the obtention of almost stoichiometric KLN:  $(K_2O)_{0.3}(Li_2O)_{0.2+a}(Nb_2O_5)_{0.5+b}$  with  $-0.01 < a < 0.01$  and  $-0.005 < b < 0.005$  by very slow cooling from  $1050^\circ\text{C}$  of a melt with composition: 30 mol%  $K_2O$ , 27 mol%  $Li_2O$  and 43 mol%  $Nb_2O_5$

[17]. The crystals manufactured in this way showed an optimal frequency doubling at room temperature for a fundamental wavelength of 803 nm corresponding to a composition equal to 50.8 mol%  $\text{Nb}_2\text{O}_5$  and 30 mol%  $\text{K}_2\text{O}$  according to Sellmeier equations which is inconsistent with the crystal composition given by Ouwerkerk. Here also, the phase diagram of Scott et al. fails to explain these growth results.

In an attempt to get a better understanding of the literature growth results and to overcome some inconsistencies, we have re-investigated the 30 mol%  $\text{K}_2\text{O}$  isopleth of the ternary system  $\text{K}_2\text{O}$ - $\text{Li}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  and studied the possibility to grow truly stoichiometric KLN crystals by  $\mu$ -PD starting from a melt of stoichiometric composition  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ .

## 2. Experimental methods

For sample preparation,  $\text{Li}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  powders (99.999 % from Cerac) were used. Starting materials were first dried, then weighed and mixed. Generally, the sample preparation consisted of a two step solid phase reaction: sintering in air at 950 °C during 30 h, grinding and sintering again under the same conditions.

Thermal analysis measurements were performed on heating using a PL Thermal Sciences 1500 differential scanning calorimeter (DSC) fitted with data acquisition and evaluation system. All DSC measurements were carried out in platinum crucibles in flowing argon atmosphere ( $10 \text{ cm}^3 \cdot \text{min}^{-1}$ ) with a heating rate of  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  and using calcined high purity  $\text{Al}_2\text{O}_3$  as reference material. The sample weight was about 50 mg; the temperature and heat flow response of the calorimeter were calibrated using 6N purity metal standards (In, Sn, Pb, Zn, Al, Ag, Au, Si).

Powder phase identification was performed using X-ray powder diffraction. At room temperature, an Inel MPD CPS 120 diffractometer was used. At high temperatures, an Anton Paar HTK16 heating chamber coupled with a Philips XPert MPD diffractometer was used. In

all cases, Cu K $\alpha$  radiation in the 2 $\theta$  range 0-120 ° for Inel and 5-60 ° for Philips was generally used.

Crystal growth experiments were performed by the micro-pulling down technique using the resistive heating apparatus recently installed in our laboratory. Typical dimensions of the used Pt crucibles were: 10x5x3 mm. The nozzle was 1.5 mm length and 0.4 mm internal diameter (external diameter: 0.6 mm). The seed was a SBN 60 (strontium barium niobate) crystal oriented along the a-axis with an apparent diameter of 0.5 mm. The fibers were pulled under air atmosphere and with pulling rates between 0.3 and 0.7 mm.min<sup>-1</sup>,

For the crystal structure determination, intensity data were collected with a Xcalibur CCD diffractometer from Oxford Diffraction Ltd, using MoK $\alpha_1$  radiation. The structure was solved with SIR92 [18] and refined with SHELXL [19] programs.

The morphology of crystals was optically investigated with a Leica DM 4000 M transmission/reflexion microscope.

The homogeneity of crystals was investigated with a Labram Aramis Jobin-Yvon Raman spectrometer in a backscattering geometry. The spectra were obtained at room temperature with an incident slit of 150  $\mu$ m, a 10x lens and a 785 nm laser excitation wavelength. The resolution of the Raman spectra was better than 1 cm<sup>-1</sup>.

### **3. Results and discussion**

#### *3.1. Investigation of the 30 mol% K<sub>2</sub>O isopleth of the Li<sub>2</sub>O-K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> ternary system*

##### *3.1.1 DSC measurements*

In a first time, several mixtures located in the composition range corresponding to the stoichiometric formula K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> were prepared according to the procedure described before and analyzed by DSC. Table 1 gives the composition of the mixtures investigated and the temperatures of the different endothermic thermal events identified. The first thermal

event clearly suggests the existence of an invariant reaction at 970 °C as a similar plateau was observed for the isopleths 10, 20 and 25 mol% K<sub>2</sub>O in our previous work on this ternary system [20]. The most reliable interpretation of the second thermal event is also to consider a plateau at about 1040 °C corresponding to a phenomenon to be identified. The third and fourth temperatures recorded can be attributed to solidus and liquidus temperatures. The fifth thermal event, only observed for one sample (45 mol% Nb<sub>2</sub>O<sub>5</sub>), can be assigned to a change of equilibrium domain. The last column gives the Curie point for each composition.

### *3.1.2. X-ray diffraction measurements*

In order to confirm the consistency of our interpretation of thermal analysis results, three mixtures were prepared with the compositions: 47.5, 50 and 52.5 mol% Nb<sub>2</sub>O<sub>5</sub> and 30 mol% K<sub>2</sub>O. As expected, the corresponding X-ray powder diffraction patterns at room temperature revealed a mixture of three phases identified as: Li<sub>3</sub>NbO<sub>4</sub>, KNbO<sub>3</sub> and KLN from the JCPDS data base. KLN was by far the major compound as the mixtures are located in the phase diagram very closer to this compound than to Li<sub>3</sub>NbO<sub>4</sub> or KNbO<sub>3</sub>. Another consequence is that the intensity of their diffraction peaks was weak and decreased when the Nb<sub>2</sub>O<sub>5</sub> amount increased to become not detectable for 52.5 mol% Nb<sub>2</sub>O<sub>5</sub>.

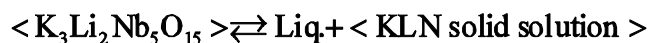
When heated to 980 °C during several hours and slowly cooled to room temperature, the 47.5 mol% Nb<sub>2</sub>O<sub>5</sub> sample underwent a partial melting and the mixture appeared composed of Li<sub>3</sub>NbO<sub>4</sub>, KNbO<sub>3</sub> and KLN whereas the other samples showed apparently only KLN. This indicated that the kinetics for returning to equilibrium on cooling was slow when only solid phases are present. This behaviour suggested that a consistent phase identification could only be performed by high temperature X-ray diffraction.

Then, as the presence of liquid was not compatible with high temperature X-ray diffraction set up, only the spectra of two samples prepared in a different run and containing 50 and 52.5 mol% Nb<sub>2</sub>O<sub>5</sub> could be obtained at 940 and 980 °C. The major lines of KLN could

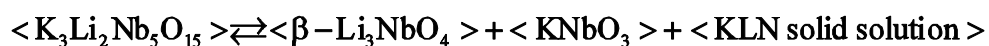
be identified and only the most intense line of  $\text{Li}_3\text{NbO}_4$  could be detected at 940 °C in the 50 mol%  $\text{Nb}_2\text{O}_5$  sample. For the other composition and temperatures, the samples apparently appeared as single phase samples. But it should be kept in mind that other phases in equilibrium can be present even if their concentrations are too low to be detected. Therefore, X-ray diffraction study alone is not sufficient to determine exactly which phases are really present or not.

### 3.1.3 Representation of the 30 mol% $\text{K}_2\text{O}$ isopleth

However, the combination of the thermal analysis and X-ray diffraction results allows to give a reliable picture of the 30 mol%  $\text{K}_2\text{O}$  isopleth of the ternary system by considering that the phase  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  exists with a similar crystallographic structure as the ternary solid solution and in a limited temperature range between 970 and 1040 °C as illustrated by Fig. 1. The plateau at 1040 °C would correspond to the non congruent melting of this ternary compound according to:



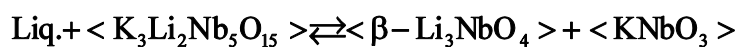
Then, the 970 °C invariant reaction would be an eutectoid one:



rather than the quasi-peritectoid reaction proposed in our previous study [20]. Moreover, our interpretation introduces a miscibility gap between the ternary solid solution and the fully stoichiometric KLN phase. All mixtures located below the eutectoid plateau correspond then to a three-phase mixture involving the KLN ferroelectric solid solution whose stoichiometry varies when the overall mixture composition changes. So, the measured  $T_C$  differs from one mixture to the other (Table 1). It should be recalled that above 55 mol%  $\text{Nb}_2\text{O}_5$  (at room temperature), the crystal structure of KLN becomes orthorhombic which is not ferroelectric [4, 15].



In a concern of consistency and to be strict with the phase diagrams construction rules, we have also to consider the existence of a quasi-peritectic reaction:



for  $\text{Nb}_2\text{O}_5$  amounts less than 50% at a temperature between 970 and 1040 °C. No DSC peaks can evidence its existence probably because the amounts of the disappearing phases during the invariant reaction are too small to give a detectable signal according to the mass of the samples investigated. It has also to be accounted for that this side of the phase diagram is not directly under the scope of this work and to confirm our interpretation, a thorough investigation of the ternary phase diagram in this composition range is now in progress.

The proposed interpretation is consistent with the manufacturing of stoichiometric KLN crystals given by Ouwerkerk [17] since it involves a small crystallization field in the ternary system for the phase  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ . Starting from the melt used by Ouwerkerk, (43 mol%  $\text{Nb}_2\text{O}_5$ , 30 mol%  $\text{K}_2\text{O}$  and 27 mol%  $\text{Li}_2\text{O}$ , line A in Fig. 1), a slow cooling will deposit a KLN crystal with stoichiometric composition until the liquid in equilibrium with the solid phase reaches the univariant point B in Fig. 1 where the co-crystallization of  $\text{Li}_3\text{NbO}_4$  and stoichiometric KLN occurs. Considering the small liquidus range for stoichiometric KLN, the amount of single-crystal should be low which is confirmed by Ouwerkerk: “approximately 1 to 2% of the melt was converted to a potassium lithium niobate crystal”. The calculation of the exact yield indeed requires to know the exact position of point B.

However may be, crystal growth methods allowing high growth rates (high temperature gradients) such as LHPG (Laser Heated Pedestal Growth) or  $\mu$ -PD (micro-pulling down technique) can also allow to obtain truly stoichiometric  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  crystals directly by quenching the high temperature phase. In the same way, the verticality of the boundary of the KLN ternary solid solution domain near 55 mol%  $\text{Nb}_2\text{O}_5$  offers the possibility to pull homogeneous fibers with compositions very close to that boundary.

### 3.2 Crystal growth

Starting from a melt with composition: 50 mol%  $\text{Nb}_2\text{O}_5$ , 30 mol%  $\text{K}_2\text{O}$  and 20 mol%  $\text{Li}_2\text{O}$ , several single-crystal fibers were successfully pulled with lengths between 10 and 120 mm (Fig. 2a) and the entire melt was then crystallized. Under the microscope (Fig. 2b), the fibers were clear, transparent and free of cracks and macro-defects such as bubbles or inclusions. The cross section (Fig. 3) was slightly rectangular (length: about 550  $\mu\text{m}$ , width: about 520  $\mu\text{m}$ ). The asymmetry observed is probably due to the fact that perfect growth of KLN requires a very symmetrical temperature field because of different growth kinetics of the faces which was not obtained in this case [5].

In other crystal growth experiments, at the beginning of the growth, a possible misorientation of the seed (key factor for the success of the growth [9]) led to the loss of the a-axis orientation and to strong faceting and growth steps formation on the fiber with, sometimes, the appearance of strong cracks resulting in the breaking of the fiber rendering the growth of KLN fibers very difficult.

### 3.3 Crystal structure and stoichiometry

The crystal parameters and information related to data collection and structure refinement of as-grown crystals are summarized in Table 2. Table 3 gives the atomic coordinates. The structure refinement was successfully performed by taking P4/mbm as space group and  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  for stoichiometry (all occupancy factors equal to 1). The best values of the reliability factors were obtained only with this space group and stoichiometry. Any attempt to solve the structure with another space group (P4bm) or stoichiometry led to poorer reliability factors. So, taking also into account:

- the most higher accuracy of X-ray diffraction technique than other physico-chemical methods such as electron probe micro-analysis (accuracy about 1 at%) or chemical methods to titrate species such as lithium [22]
- the features of the growth method: high pulling rates ensuring effective distribution coefficients very close to 1 [12]
- the stoichiometric composition of the melt
- the extent and limits of the ternary solid solution in the phase diagram [4, 15, 16] and the layout of its 30 mol% K<sub>2</sub>O isopleth

it can be concluded that stoichiometric crystals have been very probably obtained. The paraelectric state (centrosymmetric space group) of stoichiometric KLN crystals was confirmed by the DSC study of both crystals grown by  $\mu$ -PD and stoichiometric reacted powder used for the growth. Fig.4 shows clearly that the crystal fiber does not undergo any ferro-paraelectric transition. Only a very weak exothermic peak is observed at 427 °C ( $\Delta H = -0.07 \text{ J.g}^{-1}$ ) followed by a slight endothermic deviation of the baseline. This behaviour and the absence of ferro-paraelectric transition is consistent with the conditions of existence of the phase given by the phase diagram since the crystals obtained correspond to the quenching of a high temperature phase existing only in a paraelectric tungsten bronze-type structure [21] which should return to stable equilibrium (mixture of the three phases: KNbO<sub>3</sub> + Li<sub>3</sub>NbO<sub>4</sub> + KLN ternary solid solution) if proper conditions of thermal treatment are applied.

A long-time (85 hours) annealing of crystals at 350 °C (below the Curie temperature of this material [21]) showed no evolution of the sample and the space group remained P4/mbm. Treated under air at 930 °C during a similar time (80 hours), a part of a K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> crystal became very brittle and Fig. 5 reveals deep changes in the microstructure of both the surface and core of the crystal fiber, characteristic of the occurrence of an eutectoid reaction as proposed in 3.1. The observed evolution of the DSC curve (Fig. 4 up)

and its slow endothermic deviation could be related to the occurrence of the eutectoid decomposition reaction, slow in this temperature range and the kinetics of which being a complete research topic to be performed in a next future.

However may be, we demonstrate here the possibility to obtain crystals of the high temperature phase  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  and the obtained results reinforce our interpretation of the 30 mol%  $\text{K}_2\text{O}$  isopleth of the phase diagram.

### *3.4 Compositional homogeneity by Raman spectroscopy*

Raman microspectroscopy is a powerful non-destructive technique to investigate crystal fibers. Firstly, it allowed to determine and confirm the crystallographic orientation of the fibers. Placed in the proper orientation, a KLN fiber placed horizontally with its growth axis aligned with the polarization direction and vertically illuminated exhibited characteristic spectra as previously demonstrated [23].

In a second step, we observed that all Raman spectra recorded along the growth axis showed no evolution both in intensity and frequency for all the bands within measurement uncertainties. Fortin et al. showed earlier that the frequency of the Raman band near  $650\text{ cm}^{-1}$ , corresponding to  $\nu_1$  internal modes of niobium octahedra  $[\text{NbO}_6]^{7-}$ , was very sensitive to the niobium content of the crystals and then, to their stoichiometry [24] as a result of the modification of strains (octahedra more or less compressed) when the environment changes due to stoichiometry modifications. On this basis and for a-axis fibers, the invariability (within measurement uncertainties) of the corresponding Raman frequency (Fig. 6) indicates no compositional evolution. So, the as-grown fibers can be considered as homogeneous in composition all along the growth axis. However, the calibration curve given by Fortin et al. cannot be used to deduce or confirm the composition of our crystal fibers since the authors do not give any information about Li and K contents in their crystals. Then, their curve can only

be used as a qualitative tool to characterize the homogeneity of the fibers. Performed along the cross section, the same measurements confirmed also the homogeneity of the crystals (Fig.7). The decrease in intensity observed is due to the increasing absorption of the Raman signal as the exciting beam enters in the crystal.

#### **4. Conclusion**

Truly stoichiometric potassium lithium niobate  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  crystals have been grown as fibers by the micro-pulling down technique. This was possible owing to the re-examination of the 30 mol%  $\text{K}_2\text{O}$  isopleth of the ternary system  $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{Nb}_2\text{O}_5$ . The crystals have the expected tetragonal tungsten bronze-type structure but with the space group  $\text{P4}/\text{mbm}$  consistent with the quenched state of the paraelectric high temperature phase and its structural evolution in accordance with the phase equilibria in the ternary system.

The results obtained do not yet allow to explain the literature results having motivated the present work. Some questions remain about the so-called stoichiometric crystals obtained by Ouwerkerk and the  $\mu$ -PD crystals grown from stoichiometric melts as they have phase-matching properties, however not in good accordance with the relation given by the Sellmeier equations between phase-matching wavelength and composition. A larger determination of the ternary phase diagram  $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{Nb}_2\text{O}_5$  in this composition range is required and is now in progress. In particular, the research of possible metastable phenomena will be engaged.

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## **FIGURE CAPTIONS**

**Fig. 1** – The 30 mol% K<sub>2</sub>O isopleth of the ternary system Li<sub>2</sub>O-K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> drawn from DSC and X-ray phase identification experiments (Liq: liquid, L3N: Li<sub>3</sub>NbO<sub>4</sub>, KLNst: K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub>, KN: KNbO<sub>3</sub>, ss: KLN ternary solid solution)

**Fig. 2** – Examples of KLN crystal fibers grown from a melt corresponding to the stoichiometric KLN composition (a) and typical microscope pictures (Gx50) (b)

**Fig. 3** – Typical cross section of a KLN crystal fiber obtained during this work

**Fig. 4** – Compared DSC traces of a stoichiometric KLN fiber and the stoichiometric reacted powder used for the growth

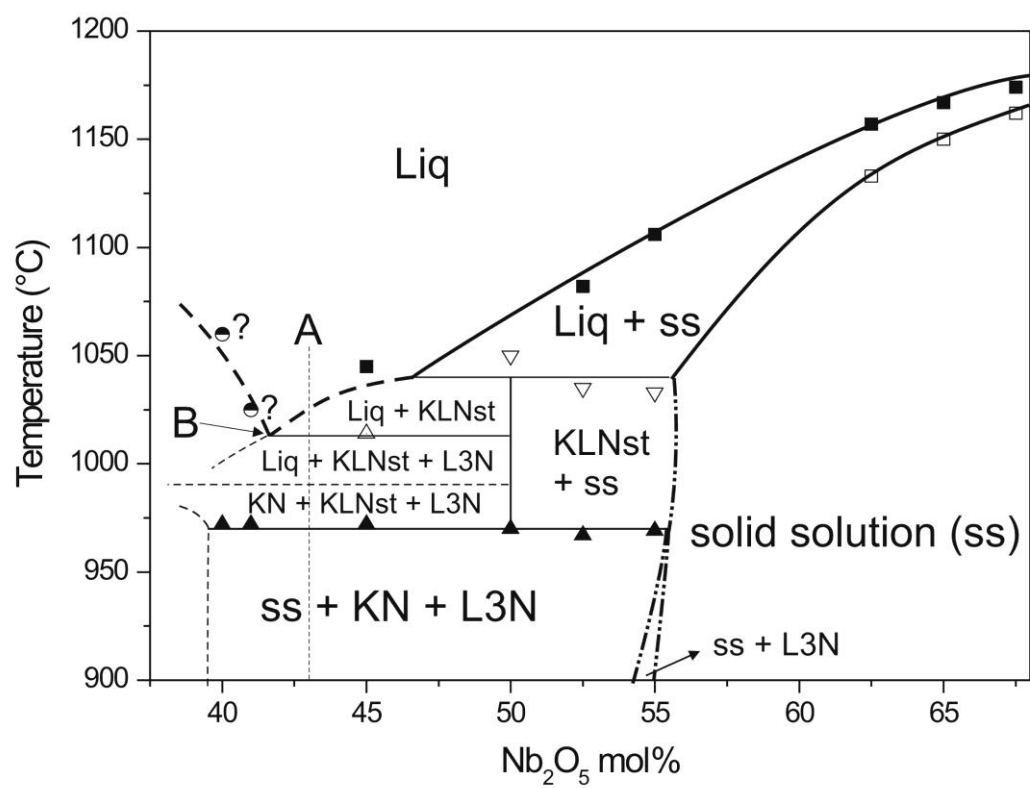
**Fig. 5** – Microstructure of an annealed stoichiometric KLN crystal fiber at 930 °C ((a): surface (Gx1000), (b): core of the fiber (Gx1000))

**Fig. 6** – Evolution of the frequency of Raman band near 650 cm<sup>-1</sup> along the growth axis of a a-axis oriented stoichiometric KLN fiber

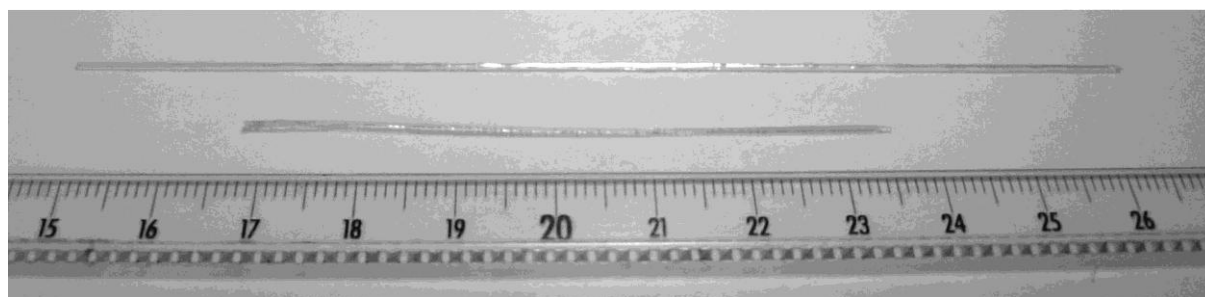
**Fig. 7** – Evolution of the Raman spectra along the cross section of a a-axis oriented stoichiometric KLN fiber



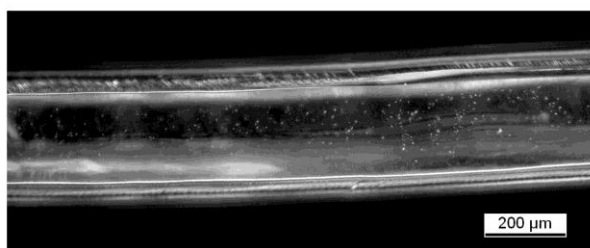
**Figure 1**



**Figure 2**

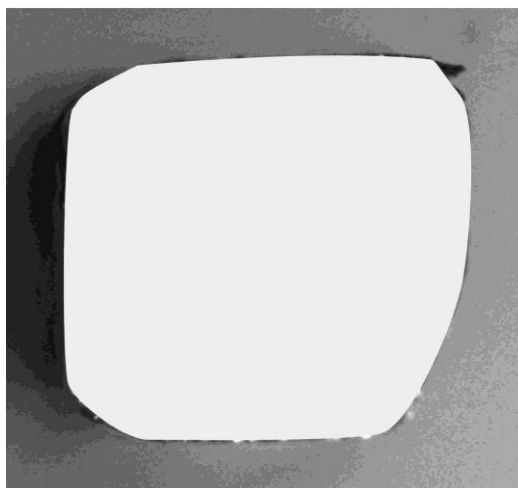


(a)

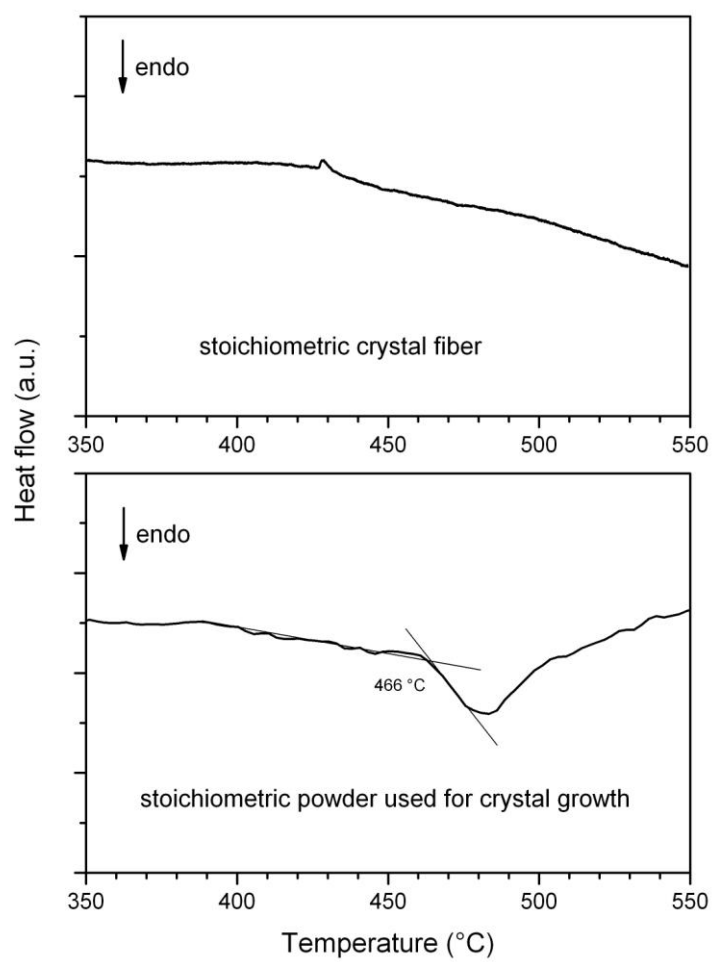


(b)

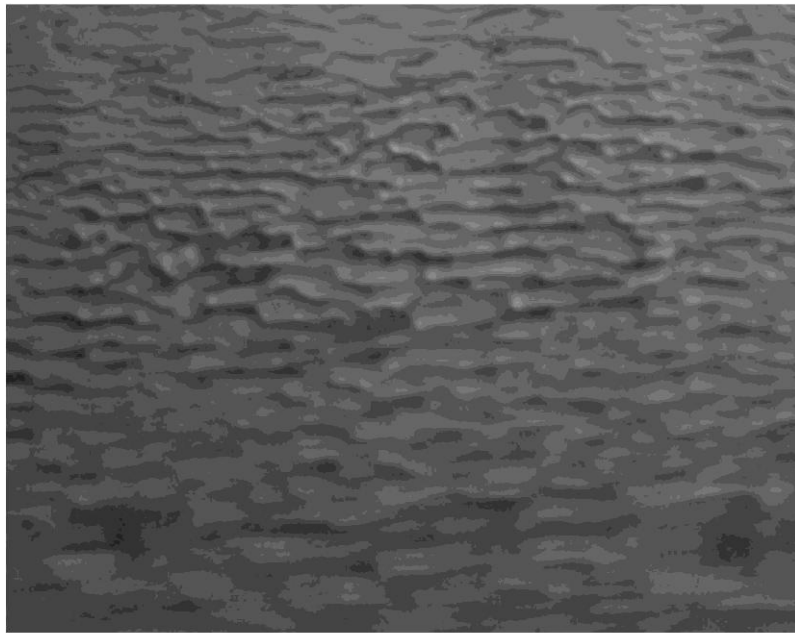
**Figure 3**



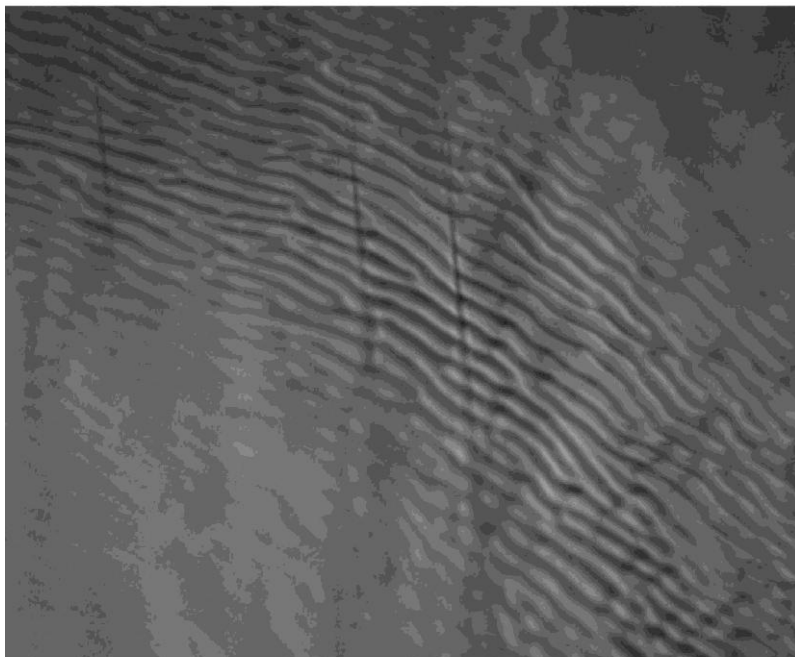
**Figure 4**



**Figure 5**

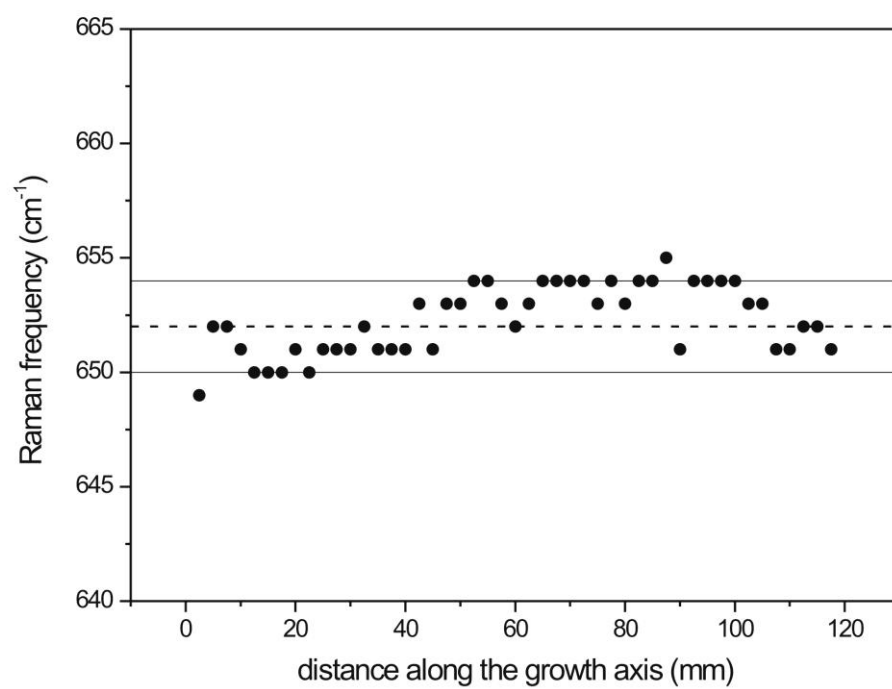


(a)



(b)

**Figure 6**



**Figure 7**

