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# Solute distribution in $KNbO_3$ melt-solution and its effect on dendrite growth during rapid solidification*

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This paper reports that the rapid solidification of mixed $Li_2B_4O_7$ and $KNbO_3$ melted in a Pt loop heater has been performed experimentally by the method of quenching, and various morphologies of $KNbO_3$ crystals have been observed in different regions of the quenched melt-solution. Dendrites were formed in the central region where mass transfer is performed by diffusion, whereas polygonal crystals with smooth surface grew in the marginal region where convection dominates mass transport. Based on measurement of $KNbO_3$ concentration along crystal interface by electronic probe analysis, it finds the variety of crystal morphologies, which is the result of different solute distributions: in the central region the inhomogeneity of solute concentration is much sharper and morphological instability is easier to take place; nevertheless in the marginal region the concentration homogeneity has been greatly enhanced by convection which prevents the occurrence of morphological instability. Additional solute distribution in the melt along the primary dendrite trunk axis as well as that in mushy zones has also been determined. Results show that the solute concentration in the liquid increases linearly with distance from the trunk tip and more solutes were found to be concentrated in mushy zones. The closer the mushy zone is to trunk tip, the lower the solute concentration will be there.

**Keywords:** rapid solidification, $KNbO_3$ melt-solution, solute distribution, dendrite growth
**PACC:** 6150J, 6870, 8110D

## 1. Introduction

Single crystals are usually obtained under the condition of low growth rates, which inevitably improve the cost. Recently scientists are endeavouring to promote the growth rate to reduce the cost of growth for commercial demand.[1,2] However, physical properties of the as-grown crystal will become deteriorated if the growth rate is high due to the occurrence of morphological instability.[3,4] In general the morphology of crystal has relation not only to the crystal structure and anisotropy, but also to the process of heat and mass transport including diffusion and convection. In order to well understand the heat or mass transport during rapid growth, the information of solute concentration distribution is extremely necessary because it is in close relationship to the interfacial mass flux, which however has been seldom concerned in most rapid growth researches due to the measuring difficulties.

Our previous works[5,6] have shown that, for oxide melt morphological instability will occur and skeletal or dendritic shape will be obtained during rapid growth. In this work, using an *in situ* observation system, we distinguished diffusive and convective effects on crystal morphological stability in case of high cooling rate. Particularly, the distribution of solute in the melt has been investigated by electronic probe analysis for the purpose of thoroughly comprehending mass transport during unsteady growth of crystals. Potassium niobate ($KNbO_3$) crystal is chosen for experimental study here on account of its excellent piezoelectric and optical properties as well as its high transparency, which permits direct observation.

## 2. Experimental procedure

The crystal growth was performed in a high-temperature *in situ* observation system developed previously.[7] The crystal grows in a growth cell with a loop-shaped Pt wire heater as shown in Fig.1. The di-

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ameter of the loop is about 1.6 mm and the V-type of electrodes are used to defend the loop-shaped heater from deformation. The temperature of the heater was measured by a Pt-10%Rh thermocouple ($\phi$0.08 mm) with the resolution of $\pm 1$°C.

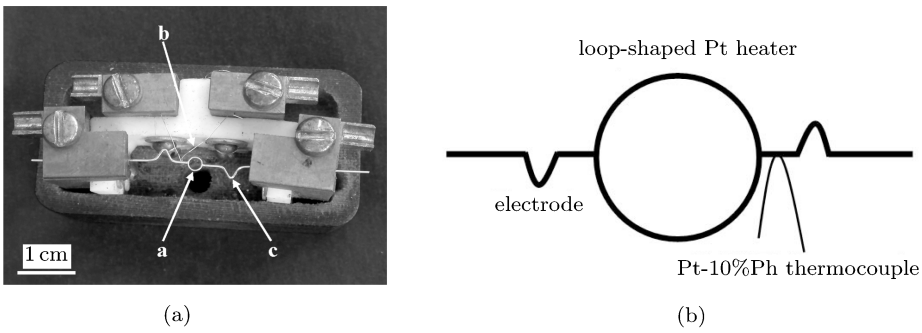



**Fig.1.** (a) Picture of crystal growth cell: a- loop-shaped Pt wire heater; b- Pt-10%Rh thermocouple; c- V-typed electrode. (b) Schematic diagram of the heater.

Firstly, a slice of $Li_2B_4O_7$ and $KNbO_3$(65wt%) solid mixture was placed on the loop-shaped heater and was melted to form a thin film of solution. After keeping the temperature of the solution at 960°C for three minutes, it was cooled to 840°C and kept the temperature for about 50 s. During this process, some small $KNbO_3$ grains nucleated in the melt, which can be clearly observed by a differential interference microscope as shown in Fig.2. Finally the melt was

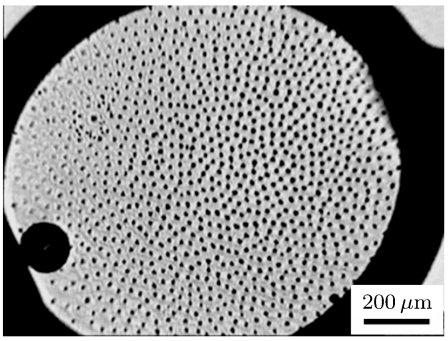


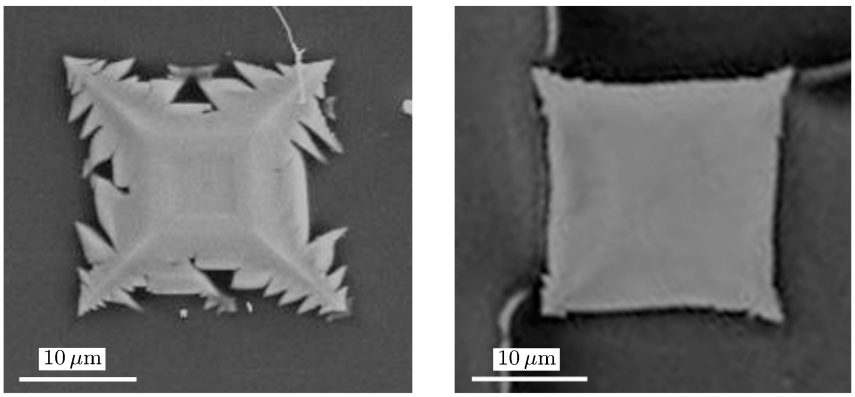

**Fig.2.** Nucleation of $KNbO_3$ solute grains in the melt-solution observed by optical microscope.

quenched to room temperature with cooling rate of 220°C/s. The x-ray diffraction (XRD) results of the quenched sample of $Li_2B_4O_7$ and $KNbO_3$ mixture demonstrated that the crystals grown in high temperature were $KNbO_3$ crystals. Since solidification is rapid, the quenched solution retained their situations in the high temperature. The solute concentrations in the quenched melt near the $KNbO_3$ grains were examined microscopically by the electron-microprobe analyses (EMPA).

# 3. Results and discussion

## 3.1. Effect of solute distribution in the melt-solution along solid-liquid interface on the stability of interfacial morphologies

In general, the solid-liquid interface during $KNbO_3$ crystal growth from high temperature melt-solution is flat and smooth for its high melting entropy, and the shape of single crystal is usually polygonal in two dimensions.[8,9] However, it was found that in condition of high cooling rate the morphology of $KNbO_3$ solid-liquid interface varies. Figure 3 shows the typical microscopic morphologies of $KNbO_3$ single crystals achieved under the condition of rapid solidification. Dendrites grew in the central region of the melt as shown in Fig.3(a) indicating the appearance of morphological instability, whereas crystals with smooth surface were observed in the quenched melt adjacent to the periphery of the loop heater as illustrated in Fig.3(b).




(a) (b)

**Fig.3.** Morphologies of $KNbO_3$ grains in (a) the central region and (b) the marginal region of the melt-solution observed by electron-microprobe.

According to the temperature distribution in the radial direction of the thin liquid film measured by a non-contact method,[10] in the central portion of the loop ($\sim \phi 1$ mm) the melt temperature gradient can be negligible. This means that the mass transfer is dominated by solute diffusion (named diffusive region). Nevertheless, in the melt adjacent to the periphery of the loop heater convective transport is significant due to the large temperature gradient (named convective region). Then one can conclude that the difference of crystal morphologies in different regions is correlated with the varied conditions of mass transfer at high temperature.

The instability of interfacial morphology is close by relating to the solute distribution in front of the solid-liquid interface. Figure 4 shows the concentrations of solute $KNbO_3$ in the quenched melt–solution near $KNbO_3$ grains examined by EMPA. Here, $W_{KN}$ is the mass fraction of the solute distribution in the solution and $r$ refers to the distance in the direction parallel to the interface with origin of $x$-coordinate axis being at the face centre. The point "▲" is for the grain obtained in the central region while point "●" is for the grain obtained in the marginal region of the melt.

It is obvious that the solute concentration along the interface is uneven both for diffusive and convective regions which is related with the specie supplies. In terms of the Berg effect,[11] the apexes of a polyhedral crystal are the best supplied regions and the concentration along the crystal surface varies, being the lowest at the face centre. This is the shape destabilizing factor. The shape stabilizing factor is connected with the anisotropy in the surface growth kinetics. If the kinetic coefficient with its anisotropy is not sufficient to compensate for the inhomogeneity in the concentration distribution over the growing crystal face, morphological instability in the crystal faces takes place. The curves in Fig.4 indicate that not only the concentration difference between the centre and corner of a $KNbO_3$ grain face but also the concentration gradient along the face in the convective region are lower than those in the diffusive region. This is attributed to the enhanced mass transport and thus the improved homogeneity of solute concentration by convection. As a result, morphological instability occurs more easily in the diffusive region where dendrites are found whereas crystal in the convective region conserves a polyhedral shape. This result indicates that, even underlying a very high cooling rate, flat interface may still keep its shape in case of existence of certain convection.

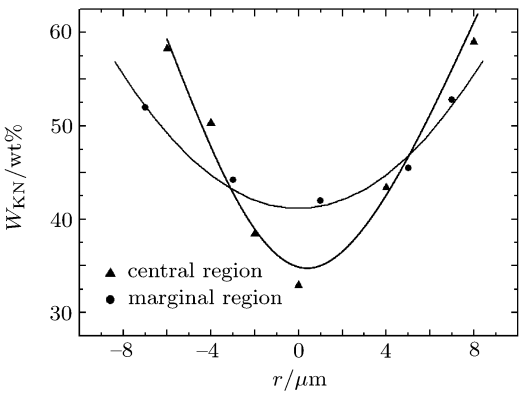



**Fig.4.** Solute concentration in the melt-solution along the solid-liquid interface of $KNbO_3$ grains.

It is noted that the shape of a $KNbO_3$ single crystal in the diffusive region is quadrilateral at the initial

stage of growth and four dendrites comes into being firstly on the corners where there are higher supersaturations when the crystal size gets larger as shown in Fig.3(a). Besides, the side branches spread away from the primary dendrite stems with an opening angle from about 90 degree because of its cubic crystallographic symmetry.

## 3.2. Solute distribution in the melt-solution ahead of the primary dendrite tip

In the absence of temperature gradient the mass transport is carried out by solute diffusion which is closely correlated with the gradient of solute concentration, so it is extremely important to know the distribution of $KNbO_3$ in the melt-solution near the front of dendrite tip for further understanding the mechanism of dendrite growth. Figure 5 shows the distribution of $KNbO_3$ concentration in the melt before primary dendrite front. Here the $x$-coordinate '$d_T$' is the distance between the trunk tip and any point within the liquid phase along the orientation of primary dendrite trunk. As can be observed, the amount of $KNbO_3$ in the melt-solution varied with the position, with the lowest value of 43.5wt% or so near the trunk tip. This can be well interpreted by taking into account of the micro-segregation during solution growth. In general, for a binary system in the solution growth, the solvent is quantitatively rejected at the interface and therefore a lower concentration of solute will be found in the liquid in front of the interface.

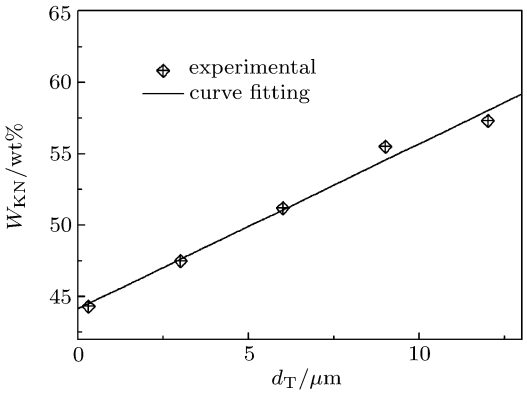



**Fig.5.** Distribution of $KNbO_3$ concentration in the liquid in front of the dendrite primary trunk ($d_T$ means the distance from the trunk tip into the liquid phase along the direction of dendrite primary trunk).

As a first approximation, the respective data in Fig.5 have been fitted with a straight line. Within the range of investigation, the solute concentration in $KNbO_3$ melt-solution is proportional to the distance from the trunk tip along the dendritic orientation into the liquid. Based on a stability analysis under the diffusive solute bulk transport, Chernov has pointed out that the solute concentration in the solution in front of a flat interface increases linearly with distance from the growing facet.[12] The fitting curve in Fig.5 indicates that such method of analysis is still valid for the growth of dendrite despite the appearance of morphological instability. This should attribute to the fact that only solute diffusive transport operates during dendrite growth in present experiment. Then, some important physical parameters for understanding mechanism about dendrite growth, such as the equilibrium concentration at high temperature or the kinetic coefficient for dendrite growth, can be possibly obtained based on the quantitative examination of solute's linear distribution. This is especially helpful for the control of fine structure formation in dendrite growth under extraordinary conditions.

## 3.3. Solute distribution in mushy zones

The solute distribution in the liquid between two neighbouring side branches (the so-called mushy zone) is also an important source of information because it is directly related to the mass transfer during dendrite coarsening,[13] such as the time-dependent crystallization of secondary side branch and the formation of tertiary or even quartus arms.

In our experiments, the concentration of $KNbO_3$ within the mushy zones has been examined. The position of mushy zones investigated is illustrated in the inlet picture of Fig.6. Here '①', '②', '③' and '④' indicate four adjacent mushy zones respectively, with '①' being the nearest to the trunk tip and '④' being the farthest one. The measured results are shown in Fig.6 by the column chart. Only an average value is given for one specific mushy zone here due to the limitation of measurement technique.

As can be seen from Fig.6, more $KNbO_3$ were found in the mushy zones than that ahead of the trunk dendrite tip. These concentrated solutes are usually difficult to exchange with those in the bulk fluid. Nevertheless, they are helpful for the developing of tertiary arms due to the abundance of growing specie supply there. Meanwhile, the solute concentration has an increasing trend when the mushy zone goes farther from the trunk tip as indicated in Fig.6. This fact is

in good agreement with the result calculated by numerical simulations for dendrite growth.[14,15] It may be the result of less solute consumption at the site far from the trunk tip where the velocity of dendritic arm is slower. However, as to the problem on how the mass transfer driven by concentration nonuniformity in the mushy zone affects the performance of dendrite coarsening, much more thorough work will be required.

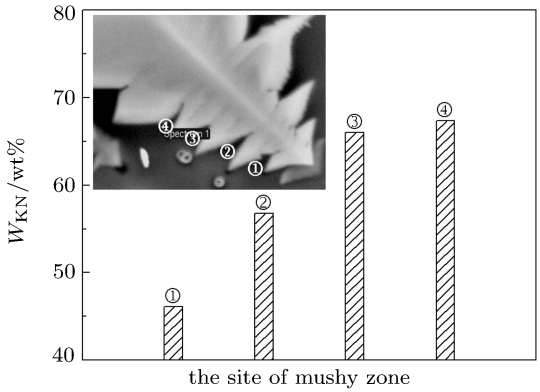



**Fig.6.** Distribution of solute $KNbO_3$ in the melt-solution in the mushy zones between adjacent secondary arms.

# 4. Conclusions

The crystal morphologies and solute concentration distributions in the quenched melt of $Li_2B_4O_7$ and $KNbO_3$ mixture have been investigated experimentally. $KNbO_3$ dendrites were found to be formed in the central region of the melt-solution in a loop-shaped heater where solute diffusion predominates the mass transfer due to the negligible temperature gradient. However, crystals with polyhedral shape were observed in the marginal region of the melt-solution where convection governs the mass transport due to the significant temperature gradient. The morphological difference of crystals in different regions has been found, the result of enhanced homogeneity of solute concentration along the growing interface in the convective region has been examined quantitatively by EMPA. The measurement of $KNbO_3$ concentration along the primary dendrite trunk axis demonstrates that the amount of solute in the melt increases linearly with distance from the trunk tip. Moreover, mushy zones are found to have regions where solutes are highly concentrated.

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