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STUDY OF $KNbO_3$ SINGLE CRYSTAL GROWTH BY THE RADIO-FREQUENCY HEATING CZOCHRALSKI METHOD

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16. Abstract

A radio-frequency heating Czochralski technique (rf-Cz) to obtain single-crystal $KNbO_3$ is first presented. The technological parameters of $KNbO_3$ crystal growth by the Czochralski technique and its pulling conditions have been studied in detail. The experiments on second harmonic generation using 1.06 micrometer Nd:YAG laser in $KNbO_3$ have been conducted. The second harmonic efficiency for upconversion of $KNbO_3$ is found to be as high as that of $NaBa_2Nb_5O_{15}$. An automatic scanning measurement for the optical homogeneity of $KNbO_3$ crystal is also described. $KNbO_3$ is revealed to be a potentially useful nonlinear material for optical device applications.

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STUDY OF $KNbO_3$ SINGLE CRYSTAL GROWTH BY THE RADIO-FREQUENCY HEATING CZOCHRALSKI METHOD*

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I. Preface

Potassium niobate crystals (abbreviated KN) have a perovskite type structure. Matthias and others first discovered the ferroelectric properties of KN. In recent years, following developments in laser technology, single domain KN crystals can be used in optical frequency multiplication and optical modulation and iron doped KN crystals can also be used as optical recording medium material [1-5]. SHG tests proved that the second harmonic efficiency of KN crystals is high and they have strong laser damage resistance capabilities. In the near ultraviolet waveband, the optical sensitivity of the KN crystal is better than that of existing crystal materials. It can be said that the KN crystal is an excellent nonlinear optical material. It not only has vast prospects in the field of laser technology applications but it can also provide abundant information on the crystal's defects, structural phase changes and other basic theoretical research.

However, KN crystal growth is relatively difficult. This is

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**Professor Feng Duan proposed many important ideas for this work and also devoted frequent attention to it; Zao Yichun and Qi Ming et al participated in some of the experiments; Xu Ziran, Li Qi and Zhu Jingsun et al gave assistance and support to the physical property testing of KN crystals. We would like to thank them here.

because the KN phase area does not have congruent points in the phase equilibrium of the K_2CO_3-Nb_2O_5 system, it is necessary to have two structural phase changes during the growth process and the domain structure of the KN crystal is relatively complex. Therefore, the Kyropoulos method (abbreviated Ky) or improved Kyropoulos method (such as the top seed crystal method, abbreviated as the TS method) is generally used for growing KN crystals. We summed up and compared the various methods of KN crystal growth [1,6-12] and consider that use of the radio-frequency heating Czochralski method (called the rf-Czochralski method and abbreviated as the rf-Cz method) takes into account the strong points of both the Kyropoulos method and top seed crystal method, shortens the growth period of KN crystals, increases the economic benefits, is convenient for automatic control and it is advantageous for observing and studying the various phenomena during the growth process of KN crystals.

II. The Growth of $KNbO_3$ Crystals

1. Instruments and Equipment

We used the YAG-20 monocrystal furnace to grow KN crystals and both the crystal rotating and Czochralski systems are directly driven by a moment motor. The radio-frequency generator is the ZM-481 model which operates by the FU-22 oscillating tube forming a self-excited oscillating circuit. The highest emissive frequency is 500kC, the maximum output power is 20kW and the usual operating frequency is about 200kC. We used the method of controlling the high frequency power input to control the temperature. Its special feature is that it can very rapidly and accurately derive the heating power signals. The automatic control circuit is shown in Fig. 1. The fiture has programmed automatic control circuit (a) and electron weighing automatic control circuit (b). The two can be used interchangeably. Further, a television monitor can be used to observe the situation of the KN crystal growth.

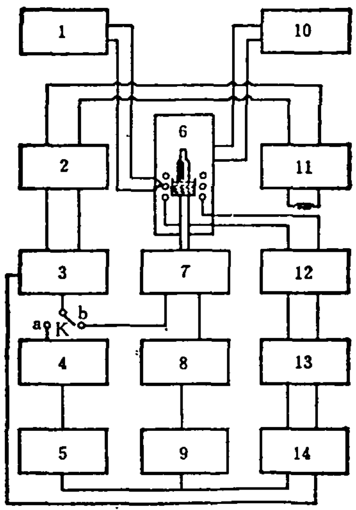


图 1 rf-Cz方法KN晶体生长自动控制系统

Fig.1 Automatic control system for radio-frequency heating Czochralski growth of crystal $KNbO_3$

a——Program-autocontrolled circuit; b——Electronic weighing autocontrolled circuit
1——Temperature recorder; 2——Coreless transformer; 3——Thermocouple vacuum-tube; 4——Temperature program control unit; 5——Millivolt locator; 6——Furnace of crystal pulling; 7——Electronic weighing unit; 8——Linear voltage-generator; 9——Millivolt locator; 10——T.V. monitor; 11——Pick-up coil; 12——Radio-frequency generator; 13——Radio-frequency heating control unit; 14——Microvolt amplifier and PID modulator

2. Proportions of Raw Materials /439

Based on the phase diagram of K_2O-Nb_2O_5, there are no congruent points in the KN phase area. Moreover, there is a peritectic reaction near the composition of K_2O:Nb_2O_5=1:1 [1,13]. Under normal conditions, it is very difficult to use the Czochralski technique in the phase area of the peritectic reaction to grow monocrystals with homogeneous qualities. There, fore, when using the rf-Cz method to grow KN crystals, in order to avoid having the peritectic reaction occur, after many tests and comparative analyses, we considered that use of a 52-53mol% content of K_2CO_3 was relatively suitable when selecting the proportions of the raw materials. Further, we considered that when the temperature of the melt was higher than 1,000°C, the K_2CO_3 volatilized from the surface of the melt and the volatizing speed increased with the rising of the temperature. Therefore, it was suitable that the contents of K_2CO_3 be in slight excess of that of the normal proportion.

3. Heat Treatment of the Raw Materials

The purity of the raw materials K_2CO_3 and Nb_2O_5 are of the A.R. level. After the prepared raw materials were mixed and pressure bound, they were placed in a platinum crucible, the temperature was raised to 800-900°C and the temperature was maintained for 15-24h. Afterwards, the temperature was raised to 1100-1200°C and the temperature maintained for 1-2h so that the raw materials completely reacted and the formed KN polycrystalline phase did not further decompose.

4. The Technical Parameters of KN Crystal Growth

1) Temperature gradient. The selection and determination of a suitable temperature gradient is a very important condition for preventing cleavage of the KN crystal and for obtaining the ideal growth form. After calculations and analyses, when growing the KN crystal, the axial temperature gradient within 2mm above the melt liquid surface in the crucible was less than 10°C/cm. This was able to completely satisfy the requirements in our designed temperature field [14].

2) Growth rate. Each type of crystal had growth rates suitable to themselves. This was mainly determined by the structure, growth characteristics as well as the physical chemistry properties etc. of the crystal. As soon as the growth method of artificial crystals is determined, the growth rate is then closely related to the characteristics of the temperature field. The growth rate of KN crystals is very slow. This is one of the major reasons people mostly use the Kyropoulos method to grow KN crystals. However, there are also those who select relatively large growth rates such as 2.7-6.5mm/h [7,8] and tests prove that if this rate is used for the Czochralski growth of KN crystals, only failure will result. The Czochralski rate which we selected was 0.2-0.5mm/h, the release shoulder stage Czochralski rate was 0.2-0.3mm/h after crystal pulling and the equidiameter growth stage Czochralski rate was 0.4-0.5mm/h after receiving shoulder. The rotating speed of the crystal was 40-60rpm, the pulling crystal stage crystal rotated at 60rpm, the release shoulder stage was 50rpm and the equidiameter growth stage was 40rpm. Its aim was to control the liquid effect of the melt in the crucible so as to keep the shape of the

solid-liquid interface as a flat interface.

3) The temperature lowering program. The selection of a suitable temperature lowering program is very important for protection of the cleavage of KN crystals. The growth temperature of the KN crystal which decreases to room temperature must go through two phase changes, that is, the phase change process of cubic $\xrightarrow{435^\circ C}$ tetragonal $\xrightarrow{225^\circ C}$ rhombic. When going //440 through phase change temperatures, the changes of the crystal lattice constant were non-continuous [15] and thus produced induction domain boundary, internal stress accumulated and formed along the domain boundary and caused cleavage of the crystal. In order to prevent the effects of structural phase changes on the cleavage of KN crystals, we used the changing temperature lowering program and when above 500°C the temperature lowering rate was 30°C/h. When the temperature decreased to below 500°C and the phase change temperature was above 20-40°C, the temperature lowering rate was 3-5°C/h. When the temperature decreased to 150°C, the temperature lowering rate could be restored to 30°C/h.

5. Seed Crystal Orientation and Growth Form

If the seed crystal orientations are not the same, then the grown KN crystals will have different forms. When the rf-Cz method is employed to grow KN crystals and the above mentioned growth technical parameters are used, if the seed crystal orientation is $\langle 100 \rangle$, the growth form of the KN crystals is generally a cube and formed from the $\{100\}$ crystal face, the released shoulder stage's four crystal edges are clear and visible, the crystal face is a smooth natural surface and the solid-liquid interface is a plane. If the seed crystal orientation is $\langle 110 \rangle$, then the growth form is generally a regular octahedron, the integrity is relatively good and it does not easily have cleavage (see Fig. 2).

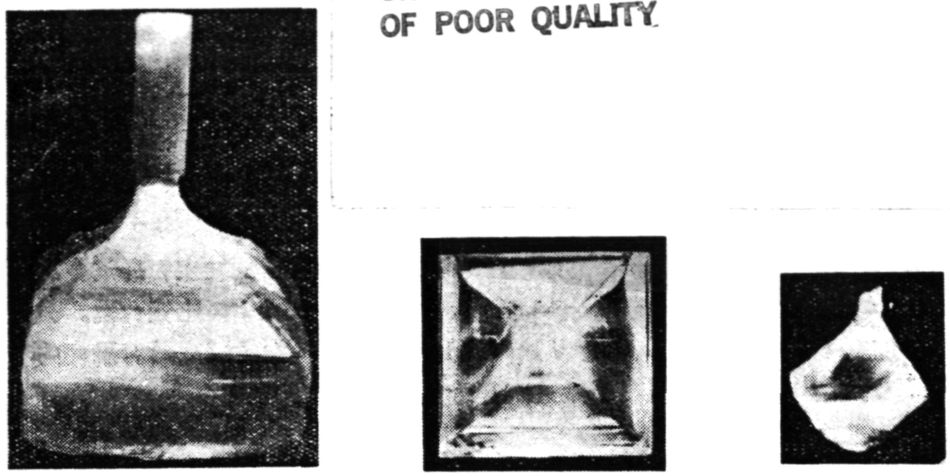

(1) (2) (3)

图 2 用rf-Cz方法生长的KN晶体

Fig.2 $KNbO_3$ crystals grown by method of rf-Cz

(1)—Seed orientation<100>, side view; (2)—Seed orientation<100>, vertical view; (3)—Seed orientation<110>, side view

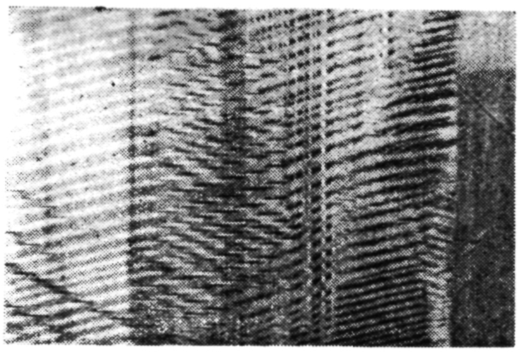
6. Color of Crystal

During the KN crystal growth process, the KN crystal assumes different colors. There are two major empirical phenomena: one is if the bubble material temperature is different when the raw material proportion is the same, then the color of the grown crystal is different. When the temperature of the melt is lower than 1050°C, the crystal is blue or deep blue in color; when the temperature of the melt is higher than 1150°C, the crystal is light yellow or nearly colorless. What is of interest is that if the same piece of crystal tends to have low temperature during crystal pulling then the seen crystal's surrounding is blue and it gradually becomes colorless following the enlargement of the crystal. On the contrary, if the axial temperature gradient of the melt in the crucible is relatively large, then the upper half of the grown KN crystal is basically colorless and the lower half is blue. Another situation is that if the K_2CO_3 contents of the raw material proportions are different, the color of the grown KN crystals are different. Tests showed that when the K_2CO_3 contents were greater than

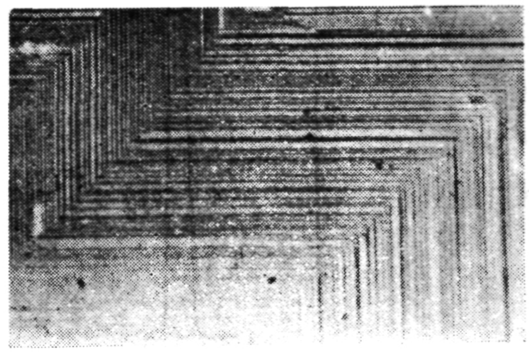
54mol% and the bubble material temperature was higher than 1150°C, the grown KN crystal was still blue; if the K_2CO_3 contents were less than 51mol%, the grown crystal was yellow, or light blue. In order to prevent the crystal from assuming color, we could raise the bubble material temperature, lengthen the constant temperature time as well as select suitable K_2CO_3 contents. B.A. Timofeeva etc. [7,8] consider that the color of KN crystals is caused by the color center and propose the use of /441 annealing to eliminate the color of the crystal. We used this method but did not attain anticipated results. T. Fukuda and Y. Uematsu [10] carried out absorption spectrum tests on KN crystals and attempted to explain the causes of the color. However, we have to date still not seen their test results. Therefore, the reason why the different bubble material temperatures and K_2CO_3 contents can affect the color of KN crystals still awaits further research.

7. Polarization of Crystals

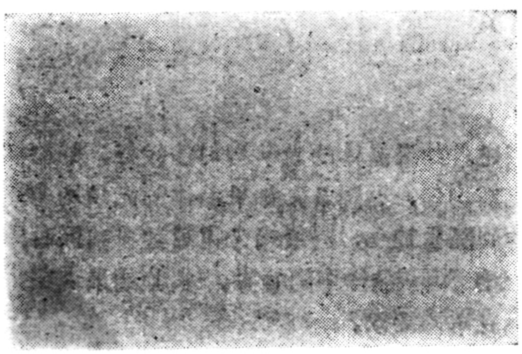
At room temperature, KN crystals assume pseudocubic crystalized forms but are really rhombic crystal systems possessing complex domain structures. We used a polarization microscope to observe the natural surface of the KN crystal and aside from the 90° domain, the 120° and 60° domains always appeared (see Fig. 3(1). The 180° domain could be observed after erosion processing. The type of domains of KN crystals with good optical qualities are relatively simple, the distributions are uniform and they predominantly use 90° domains (see Fig. 3(2)). In order to obtain the single domain KN crystal, it is necessary to carry out polarization processing. However, if we use conventional polarization technical conditions, the polarizing level is often incomplete and the aim of making the KN crystal single domained cannot be attained. Therefore, in our experiments, we placed the KN crystal specimens in a thermal field with a zero temperature gradient and we used double electrodes. At the same time, we carried out polarization processing by applying mechanical stress on the KN crystal [16] and obtained different sized single domain KN crystals with dimensions of 5x7x7mm to 10x10x10mm etc. We used a polarization microscope to observe the KN crystal after polarization and discovered that the side angular area of a minority of the specimens still had remaining 60° domains and the polarizing level was basically complete (see Fig. 3(3)).



（1）原生晶体的表面电畴(KN晶体的扩肩部分)
(1)Surface electrical domains of primary crystals (shoulder area of KN)



（2）(010)面90°畴
(2)90° electrical domains in surface (010)



（3）经极化处理而得到的单畴的KN晶体
(3)Single domain KN crystals are obtained through polarizing procedure

图 3　在正交偏光下KN晶体的电畴结构
Fig.3 Photograph of electrical domains structure of KN under polarizing microscope 200×

III. SHG Test and Measurement of Optical Homogeneity /442

1. SHG Test

We used the acousto-optic Q modulated Nd:YAG laser with output of 1.06μm to carry out second harmonic generation tests (generally called the SHG test) on KN crystals which have gone through polarization processing. The test results showed that the conversion efficiency of the KN crystal was not lower than that of barium-sodium nicobate and lithium niobate and yet the anti-laser damage capabilities of the KN crystals was far superior to those of the latter. See Fig. 4 for the scanning curve of the second harmonic strength versus angle of the KN crystal. The half width is between 0.45-0.75° and this shows that the optical quality of the KN crystal is very good.

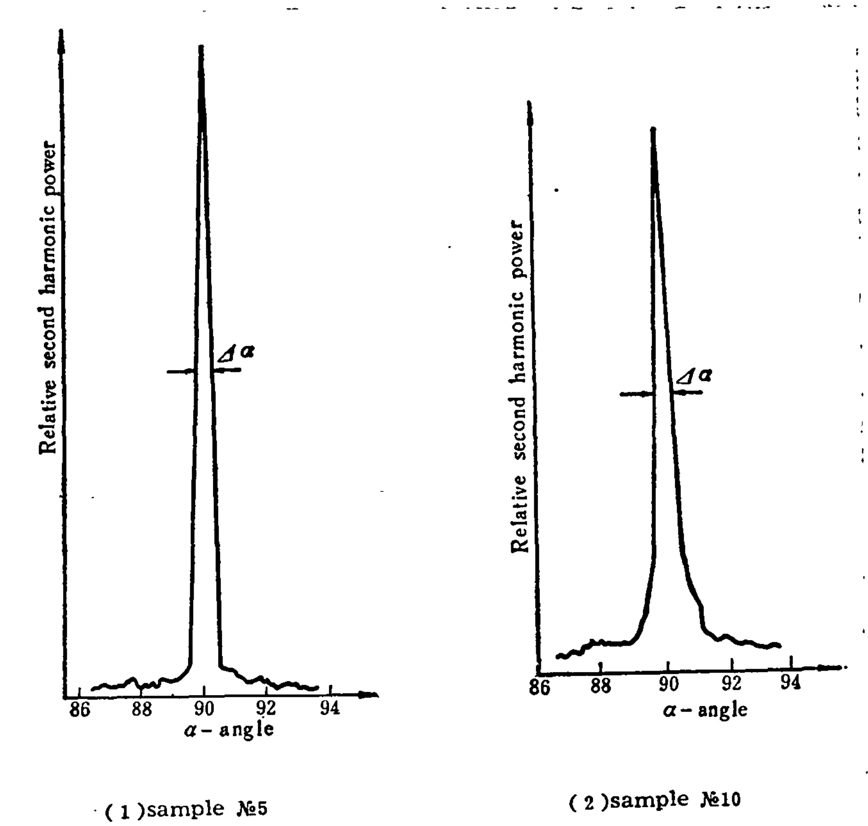
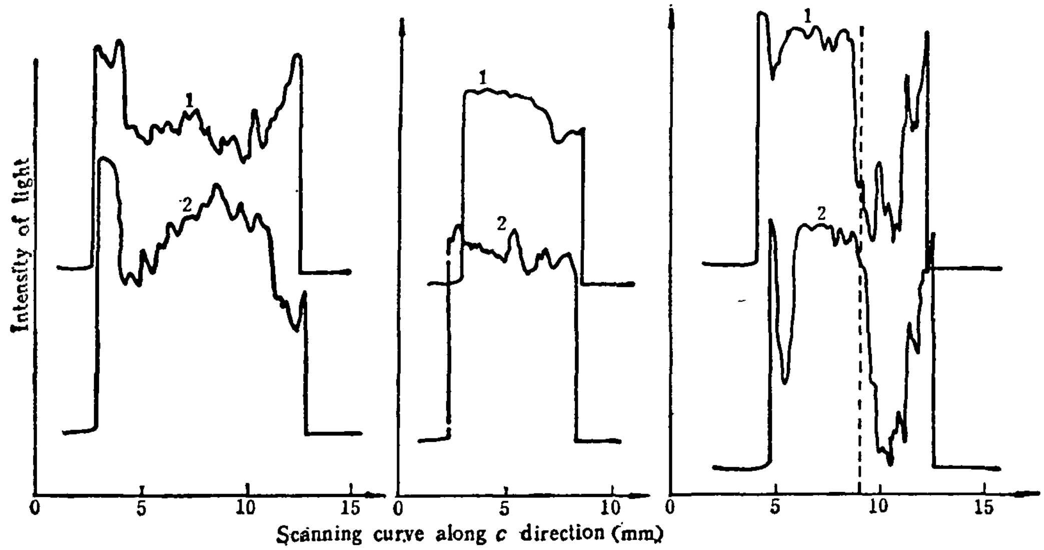


图 4 KN晶体的倍频强度对角度的扫描曲线

Fig.4 Scanning curve of SH power versus angle of KN crystal

2. Scanning Measurement of KN Crystal's Optical Homogeneity

The optical homogeneity of crystals can be described by the fluctuations of the refracting power. If the optical homogeneity of the crystal is relatively good, then the fluctuation changes of the scanning curve will be homogeneous and the double refraction power gradient of the crystal will be homogeneous (see Fig. 5). If the optical homogeneity of the crystal is relatively poor, then the up and down fluctuations of the scanning curve will be relatively small. This situation generally occurs when the light beam passes through many domain areas (see the right side of the dotted line in Fig. 5 (3)). The dotted line in the figure shows the domain boundary of the KN crystal. Test results show that the optical homogeneity of KN crystals grown with the rf-Cz method can attain the requirements for actual usage.



(1)Sample №4 (2)Sample №5 (3)Sample №10

图 5 KN晶体光学均匀性的扫描曲线

Fig.5 Automatic scanning measurmement for optical homogeneity of KN crystal

IV. Conclusions

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1. The use of the rf-Cz method to grow KN crystals was successful. The seed crystal orientation was ⟨100⟩ or ⟨110⟩, the K_2CO_3 content was 52-53ml%, we selected suitable technical parameters and we were able to grow KN crystals with different dimensions such as 15x15x10mm to 30x30x20mm etc. After polarization processing, we were able to obtain KN crystals with 5x5x7mm to 10x70x10mm single domains which could be provided for

actual usage.

2. The color of KN crystals is determined by the proportions of raw materials and the temperature of the melt. We selected suitable K_2CO_3 contents, appropriately raised the temperature of the bubble material and were able to effectively control the color of the KN crystals and grow colorless and transparent KN crystals.

3. The scanning measurement results of the double refracting power of KN crystals showed that KN crystals grown by the rf-Cz method had relatively good optical homogeneity. We used the acousto-optical Q modulated Nd:YAG laser with output of 1.06μm to carry out SHG tests on the KN crystals. The second harmonic efficiency was not less than that of barium-sodium niobate and lithium niobate crystals yet its anti-laser damage capabilities were much stronger than those of the latter two crystals. KN crystal is a very good type of nonlinear optical crystal material.

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