The growth and characterization of Rb-doped $KNbO_3$ nonlinear optical crystals

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Abstract

We have successfully grown colorless and transparent Rb-doped potassium niobate (KRN) single crystals using the top seeded solution growth (TSSG) technique. In our crystal growth experiments, the Rb doping concentrations within the melt range from 2 - 15 mol% relative to that of Nb_2O_5. Atomic absorption measurements indicate that the Rb content in the KRN solid solution is rather low; the Rb segregation coefficient is found to be on the order of 0.05. It is believed that this is due to the relatively much larger Rb^+ ionic radius compared to that of K^+, rendering it more difficult for Rb to replace K in the $KNbO_3$ (KN) host lattice. Preliminary single-pass second harmonic generation (SHG) experimental results indicate that there exists marginal improvement in the phase-matching temperature tolerance of KRN compared to that of pure KN single crystals.

1. Introduction

$KNbO_3$ (KN) has been found to possess large nonlinear optical coefficients [1]. The nonlinear optical and electro-optical applications of KN have also been carried out extensively. In recent years, this material has also become one of the most attractive candidates for the fabrication of a solid state blue laser source via second harmonic generation for high-density optical data storage, as well as other applications [2-5]. However, the phase-matching temperature tolerance of pure KN is found to be rather small, i.e., on the order of 0.3°C for single-pass frequency doubling using a 838.5 nm pump beam [6]. A small deviation of 0.5°C from the phase-matching temperature would result in a significant drop of the SHG output power. This makes it necessary to have stringent temperature control to be incorporated into the device.

Analysis of the narrow SHG phase-matching temperature tolerance phenomenon has been carried out; it was proposed that the introduction of Rb dopants into the KN lattice to replace the K host atoms might improve the phase-matching temperature tolerance [7]. The main motivation of this work was to investigate whether the SHG phase-matching temperature tolerance of pure KN can indeed be improved by virtue of the lattice strain effect due to the Rb substitution, and to what extent such improvement can be achieved. To this end, systematic studies on the growth of KRN single crystals using the TSSG technique have been carried out; both pure KN and KRN single crystals grown have been processed and prepared for the SHG experiments. In this report, the findings on the growth of KRN single crystals are first presented; preliminary experimental results on the SHG phase-matching temperature tolerance of both KN and KRN single crystals grown will then follow.

2. Experiment

The K_2O-Nb_2O_5 phase diagram was first reported by Reismann and Holtzberg [8], and was later revised by Flückiger et al. [9] and Murata et al. [10]. It was found that the optimal composition for the starting growth materials in KN crystal growth consists of 52.5% and 47.5% of K_2O and Nb_2O_5, respectively [11]. Reagent grade or better K_2CO_3, Rb_2CO_3 and Nb_2O_5 were used as starting materials in our KRN growth experiments with the following compositions: K_2CO_3:Nb_2O_5 = 52.5%:47.5%, and Rb_2CO_3:Nb_2O_5 was equal to the desired Rb doping level in the growth melt, whereby excess K_2CO_3 served as a flux. Crystal growth was carried out using the TSSG method; the amount of Rb doping concentration within the melt was systematically increased from 2 to 15 mol%.

For the KRN growth experiments, well-mixed and sintered raw materials were heated up in the growth furnace and smelted at a temperature of 20°C to 30°C above the melting point around 1080°C for 24 hours. The furnace was then slowly cooled down to the proper seeding temperature. During growth the furnace was being cooled down at a rate of 0.05-0.2 °C/h. Pulling was commenced when the growing crystals had widened to the desired size. After growth, the crystals were pulled off the melt and the furnace was gradually cooled down to room temperature at a rate of 15-30 °C/h.

The Rb concentration in the KRN crystals grown has been determined using the atomic absorption analysis. KN and KRN single crystals have been prepared for single-pass SHG experiments, using a 865 nm pump source, for the determination of phase-matching temperature tolerance

3. Results and discussion

The proper seeding temperatures are plotted in Fig. 1. It can be seen that the equilibrium coexistence point between the KN seed and KRN melt was dependent on the Rb concentration within the melt. It was found that the higher the Rb concentration, the lower was the seeding temperature.

The starting growth temperatures, defined as when crystal growth was first observed, have also been plotted in Fig. 1. The starting growth temperatures for melts containing different Rb doping levels were found to be consistently lower than the corresponding seeding temperatures in the order of 3°C. This is clearly depicted by the similar gradient of the two curves, obtained by second order polynomial regressions of the experimental data.

Atomic absorption analysis of the Rb content in the KRN single crystals are given in Table 1. The segregation coefficient of Rb, k_o, was found to be rather small. The Rb segregation coefficient being less than unity is consistent with the experimental observation, whereby the addition of Rb into the growth melt had lowered the melting point of the growth melt.

The small Rb segregation coefficient can be explained as follows: Based on energy considerations, the most probable location of Rb^+ is the lattice site of K^+ cation. Pauling's values for the ionic radii of Rb^+ and K^+ are 1.48Å and 1.33Å, respectively, with the former being relatively larger [12]. Therefore, it can be deduced that the substitution of K^+ by the larger Rb^+ cation is likely to introduce lattice strain in the KRN bulk crystals, thereby contribute to the total crystal free energy. The small effective Rb segregation coefficient in the KRN crystals grown may therefore be attributed mainly to the lattice strain due to the substitution of K^+ by Rb^+.

Optimal growth parameters have been obtained for the growth of colorless and transparent KRN single crystals. Some as-grown KRN single crystals grown from the melt with up to 15 mol% of Rb_2O are shown in Fig. 2.

Our preliminary single-pass SHG experimental results are plotted in Fig. 3. The phase-matching temperature tolerance, ΔT_{pm}, of pure KN sample is found to be around 0.4°C; and there exists a marginal increase for the doped samples, with ΔT_{pm} being 0.43°C and 0.6°C for the KRN (5 mol%) and KRN (15 mol%) samples, respectively. Notice that the improvement in ΔT_{pm} is only marginal even for the KRN sample grown from melt with 15 mol% of Rb doping concentration within the melt. This is not unreasonable since, as pointed out before, the Rb segregation coefficient is rather small. Whether more Rb can be incorporated into the KRN solid solution by adding more Rb into the melt, leading to further improvement of the phase-matching temperature tolerance remains to be ascertained.

4. Conclusion

Using the TSSG technique, colorless and transparent KRN single crystals have been successfully grown from melts comprising up to 15 mol% of Rb concentration. The Rb content in the KRN solid solution determined by atomic absorption analysis revealed that the Rb segregation coefficient in the KRN solid solution was rather small. This could be explained by the fact that segregation phenomenon tends to reduce the lattice misfit in the bulk crystal so as to minimize the total crystal energy. The preliminary single-pass SHG experimental results indicated that there exists marginal improvement in the phase-matching temperature tolerance of KRN single crystals compared to that of pure KN. The not so significant an improvement observed is not unreasonable in view of the low Rb content found in the KRN solid solution. In order to ascertain whether more Rb dopants can be incorporated into the KN host lattice, it is necessary to perform further crystal growth with higher Rb doping concentrations within the melt; and subsequent SHG experiments need to be carried out to find out if this would lead to further improvement of the SHG phase-matching temperature tolerance.

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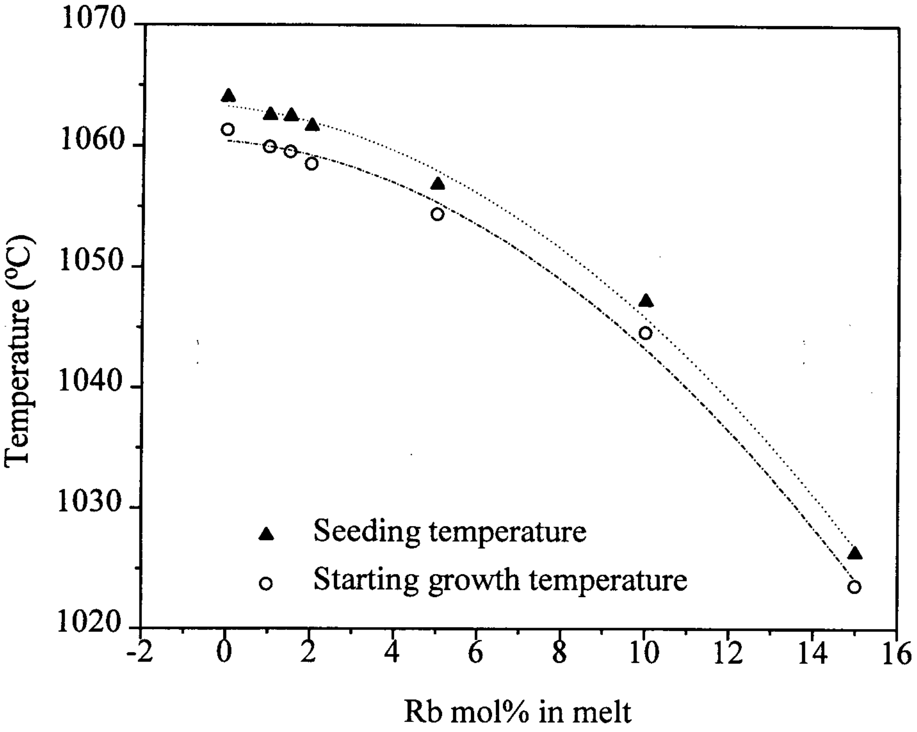

Fig. 1. Seeding and starting growth temperatures for KN and KRN crystal growth experiments.

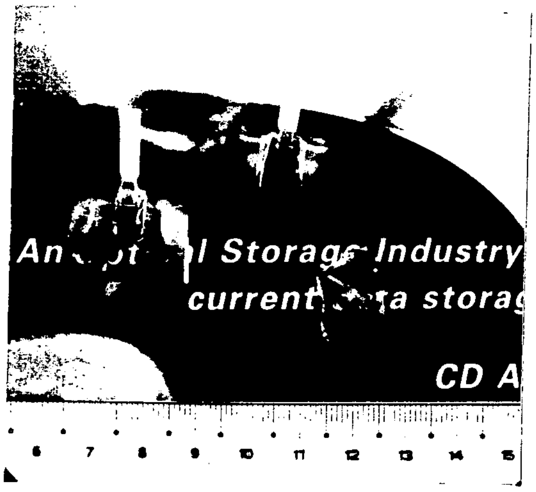

Fig. 2. KRN single crystals grown from melt with Rb concentrations ranging from 2-15 mol% by using the TSSG method.

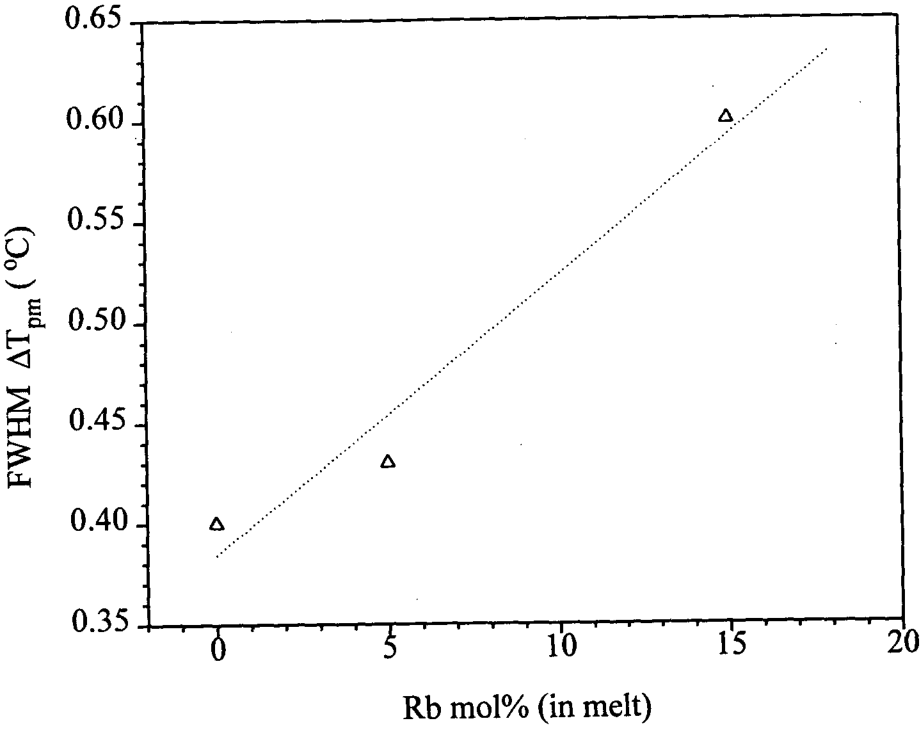

Fig. 3. Phase-matching temperature tolerance, ΔTpm, of KN, KRN (5 mol%) and KRN (15 mol%) samples; mol% refers to Rb doping concentrations in melt.

Table 1. Rb segregation coefficient for Rb-doped $KNbO_3$ crystals grown.

Sample No.	Rb doping level in melt (mol%)	Segregation coefficient k_o
KRN#1-2	1	0.037
KRN#1-3	1.5	0.040
KRN#1-5	2	0.078
KRN#1-6	5	0.064