Growth and Properties of Ru Doped Lithium Niobate Crystal

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Abstract

Ruthenium (Ru) doped lithium niobate (LiNbO₃) single crystal was grown by the Czochralski method from a congruent melt composition. The color of the Ru: LiNbO₃ was red and darkened with the increasing Ru concentration. The amount of Ru concentrated in the grown crystal gradually decreased along the pulling direction because the effective segregation coefficient of Ru in lithium niobate is greater than one, and also because RuO₂ evaporated during the crystal growth period. However, a solubility limit does exist in Ru: LiNbO₃ crystals, so the maximum amount of Ru doped into LiNbO₃ single crystals is about 0.2 mol%. In addition, the lattice constants of Ru: LiNbO₃ on the A- and C-axis decreased with the concentration of Ru in lithium niobate. The absorption spectra examination of Ru: LiNbO₃ showed that there were two absorption peaks around 370nm and 530nm that is within the UV/VIS region. The absorption coefficients should increase, and the absorption edges shift toward longer wavelength as the Ru concentration increases. The OH⁻ absorption spectra proved that Ru ions would first occupy Nb⁴⁺ Li sites in congruent LiNbO₃.

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1. Introduction

Lithium niobate (LiNbO$_3$) single crystal because of its good electro-optic, acousto-optic, and nonlinear properties has been widely used. The Czochralski (CZ) method is the most common technique for growing bulk lithium niobate single crystal from a congruent melt composition ([Li]/[Nb]=48.6/51.4~0.945) [1]. However, many intrinsic defects can appear in congruent LiNbO$_3$ crystal due to the insufficient amounts of Li. The presence of these defects leads to some restrictions for several of the desired applications. One of the most effective methods for improvement is to add a small amount of dopant into the congruent LiNbO$_3$ melt composition. A variety of dopants have been used in the past, such as Mg, Zn, Sc, and In (for reducing optical damage) [2-5], Nd, Er, Yb and Cr (for laser-host applications) [6-7], and Fe, Mn, Rh, Cu and Ce (for high-density holographic data storage) [8-11]. The material and optical properties of the crystal are also changed by the amount and type of dopant added. Therefore, suitable dopant types and concentration can be selected based on the desired application.

Ruthenium (Ru) and iron (Fe) are both transition elements and are also close to each other in the periodic table. It is therefore suggested that the effects of Ru ion doping in non-linear crystals would be similar to Fe doping. Fe-doped LiNbO$_3$ (Fe: LiNbO$_3$) single crystal has been studied intensively for many years. It has been proven to have great potential for applications in nonlinear optics because Fe ions improve the photorefractive properties of LiNbO$_3$. The Ru ion doping of non-linear crystals, such as Ru: BaTiO$_3$ [12], Ru: Bi$_{12}$TiO$_{20}$ [13], Ru: Bi$_4$Ge$_3$O$_{12}$ [14], Ru: Bi$_{12}$SiO$_{20}$ [15], and Ru: LiNbO$_3$ [16] has recently been investigated, and indeed Ru ions can be helpful to improve the photorefractive properties. Furthermore, although LiNbO$_3$ is a good holographic recording material, it has a serious volatility problem.
when used for holographic data storage: the read-out process usually erases the stored information and amplifies the scattered light. Buse et al. [17] proposed an improved method for the realization at nonvolatile holographic storage by using a double doped Fe: Mn: LiNbO$_3$ crystal. Since then many researches have devoted to effort to using double or triple doped LiNbO$_3$ for non-volatile holographic storage [18-20]. Fujimura et al. [16] have reported on some preliminary optical results related to the sensitivity and diffraction efficiency of single doped Ru: LiNbO$_3$, and have succeeded in recording nonvolatile holographic at a wavelength of 632.8nm. Only a few of researches have studied the optical properties of Ru: LiNbO$_3$. However, research on Ru-doped LiNbO$_3$ crystal growth has not brought up to the best of our knowledge. Hence, it is necessary to first grow Ru: LiNbO$_3$ crystals doped with different Ru concentrations, and then study their physical and optical properties.

In this study, the Czochralski (CZ) method was applied to grow C-axis (the [0 0 1] orientation) Ru: LiNbO$_3$ crystals with different Ru concentrations. The physical properties of the lattice constants of the different Ru concentration crystals were examined. Finally, the optical properties of Ru: LiNbO$_3$ were studied using the ultraviolet-visible (UV/VIS) and OH$^-$ infrared absorption spectra.

2. **Experimental procedure**

Congruent lithium niobate (Li/Nb=48.6/51.4) powders were prepared from high-purity Li$_2$CO$_3$ (99.99%) and Nb$_2$O$_5$ (99.995%). They were mixed in a polypropylene (PP) can in an alcohol-wetted ZrO$_2$ ball mill for 24h. After the mixture was dried and calcined at 800$^\circ$C with a 24h de-carbonization and solid state reaction period, different amounts of RuO$_2$ (99.95%) powders (0, 0.05, 0.1, 0.2, 0.4, 1.0, 2.0, and 3.0mol%) were added into the calcined mixture. The mixture was then
mixed once again before being put into a Platinum (Pt) crucible with dimensions of 65mm in diameter and 60mm in height. Single crystals of Ru: LiNbO$_3$ were grown by the conventional Czochralski method using a resistance heating furnace. The heating elements were U-shaped molybdenum disilicide arranged around an Al$_2$O$_3$ ceramic tube (80mm in diameter and 500mm in height). The vertical temperature gradient of the furnace near the growth interface was about $10^\circ$C/cm. A weight load cell under the Pt crucible was used to measure the weight variation of the melt during the crystal growth period in order to control the growth rate. The chosen seed crystal was un-doped LiNbO$_3$ with dimensions of about 5mm×5mm×50mm and orientated along the C-axis (optical axis). These crystals were grown in air with a pulling rate of 1.5mm/h and rotation rates of about 8-12rpm. The weight of the powder was 330g. A 200~220g crystal was grown in each run (about 60%~65% of the melt was crystallized). All the grown crystals were around 30mm in diameter and 50-60mm in length. After being grown, they were cooled to room temperature in air at a rate of 50$^\circ$C/h.

The Ru concentration in the grown crystals was determined by an inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer, SCIEX ELAN 5000). The lattice constants of the Ru: LiNbO$_3$ were analyzed by a single-crystal diffractometer (X-Ray/CCD, Siemens Smart CCD). The Ultraviolet-visible (UV/VIS) absorption spectra of polished C-cut Ru: LiNbO$_3$ crystal samples of 1mm in thickness were measured with a UV/VIS spectrometer (HITACHI U-4100) at room temperature, operated in the 300-800nm range, the precise wavelength was 1nm. The OH$^-$ infrared absorption spectra of the crystals were measured by a Fourier-Transform Infrared Spectrometer (FT-IR) (Bomem, DA8.3), with incident light transmission, the accuracy of this spectrometer was 1cm$^{-1}$. The ferroelectric
domain structure of the sample surface was observed after being etched in an acid solution (HF : HNO₃ = 1: 2 in volume) at 100°C for 40 min.

3. Results and discussion

Lithium niobate crystals doped with different Ru concentrations from 0 to 3.0 mol% were grown by the Czochralski method. Fig.1 shows the grown Ru: LiNbO₃ crystals grown from 0.1 and 0.4 mol% RuO₂ concentrations. These crystals were transparent and crack-free. The color of the as-grown un-doped lithium niobate crystal (RuO₂ concentration is zero) is yellowish. The RuO₂ powder was black in color, but the crystal’s color was changed by the doping of RuO₂ into the lithium niobate. When the RuO₂ doping concentration is less than the 0.1 mol%, the resultant crystal becomes pale orange in color. But with increasing Ru concentrations the color of the Ru: LiNbO₃ gradually changes to red. The coloration increases as the Ru concentration increases.

In the photographs in Fig.1 we can observe that the color of Ru: LiNbO₃ was not uniform along the axial direction in either crystal. The color of the as-grown crystal changed from dark to light along the growth direction indicating that the Ru concentration was not homogeneous in the crystal. As a matter of fact, because the color of the crystal darkens as the RuO₂ doping concentration increases, we know that the RuO₂ concentration is higher in the upper part of the crystal. As increasing the length of the crystal, the red color gradually lightens, the RuO₂ concentration is decreasing.

After this, the doped 2.0 mol% Ru: LiNbO₃ crystal was sliced into 1 mm thick slices both perpendicular and parallel to the C-axis. The ferroelectric domain structure was observed (see Fig. 2) by first etching the crystal slices in an HF: HNO₃
acid mixture. The domain structure of as-grown LiNbO$_3$ can be affected by the thermal history, stress, composition, and dopant distribution [21]. Undoped and Ru doped as-grown LiNbO$_3$ crystals both usually exhibit a multi-domain structure. Fig. 2(A) shows the ferroelectric domain structure of an as-grown C-plane Ru: LiNbO$_3$ crystal. The domain structure is in the shape of concentric circles. In order to eliminate a multi-domain structure to form a single domain, it is necessary to do a poling treatment by raising the temperature to near the crystal’s Curie temperature and then applying some current.

The crystal was also sliced parallel to growth direction (C-axis), and the shape of solid-liquid interface was observed (see Fig. 2(B)). Fig. 2(B) shows that the shape of the solid-liquid interface was convex with the sharp and toward the melt during the crystal growth. It is well known that the shape of the solid-liquid interface influences the quality of the resultant crystal. Kitamura et al. [22] observed the interior structure of such crystals. They found that line defects propagate towards the edge of the crystal if the solid-liquid interface is convex to the melt and that the line defects can easily become concentrated at the center of the crystal to form inclusions and cracks when the interface is concave to the melt. Consequently, to grow high quality lithium niobate the interface should be convex to the melt [23]. If the shape of the solid-liquid interface is not flat during the crystal growth, the temperature at the same level will not be equal. If the segregation coefficient of the dopant in LiNbO$_3$ is greater than one, the concentration of dopant in the crystal is higher than in the melt. Crystal with a higher dopant concentration will solidify in the initial stage. When the shape of the solid-liquid interface is convex to the melt, the temperature at the center of the melt in front of the interface is lower than at the periphery. Therefore, the dopant concentration will not be homogeneous in the
radial of the crystal. A comparatively higher concentration of dopant would appear near the center of the crystal in comparison with that near the periphery at the same level. By the concentration examination of the 2.0 mol% Ru: LiNbO₃ in the radial direction with ICP-MS, the results showed this trend.

In the Ru: LiNbO₃ crystal, the Ru concentration is not homogeneous along the pulling direction as can be seen by the color difference. In order to determine the distribution of the Ru concentration along the axis of each crystal, ICP-MS was used. Fig. 3 displays the Ru concentration variation along the axis of the 0.1, 0.2, 1.0, 2.0, and 3.0mol% Ru: LiNbO₃ crystals. The X-coordinate indicates the ratio of the solidification in the melt (that is the crystallization ratio of the melt), and the longitudinal coordinate shows the actual Ru concentration in the crystal as determined by ICP-MS examination. It can be seen that the Ru concentration is higher in the upper part (lower ratio of the solidification) of each grown Ru: LiNbO₃ crystal decreasing along the pulling direction. The difference in concentration along the axial direction could be caused by two reasons. First of all, Ru ions could segregate since the effective segregation coefficient of Ru in lithium niobate was greater than one. The dopant prefers to remain in the crystal. Thus, the distribution of the dopant gradually decreases along the crystal growth direction. Secondly, the RuO₂ would evaporate at about 800°C, and the RuO₂ evaporation would become more severe as the temperature was raised. There is thus less Ru concentrated in the melt than in the solid state before the temperature was raised. In addition, the RuO₂ in the melt continues to decrease during the crystal growth period. Therefore, evaporation effects would also be another factor heading to the Ru concentration difference. However, the gradually decreasing RuO₂ concentration in each Ru: LiNbO₃ crystal would also have been produced by Ru segregation. It is difficult to estimate
accurately the segregation coefficient of Ru in the lithium niobate due to the RuO$_2$ evaporation factor. Thus, if we want to grow a more uniform concentration of RuO$_2$ doped lithium niobate, RuO$_2$ evaporation during the crystal growth period should be prevented.

Furthermore, when the RuO$_2$ doping concentration in lithium niobate is small (less than about 0.05 mol %), the Ru segregation and RuO$_2$ evaporation conditions are not serious. Thus, the crystal composition becomes more uniform with smaller amounts of dopant. Increasing the RuO$_2$ doping content causes the effects of the two factors to become gradually more severe. The variation of the actual Ru concentration in the crystal along the axial direction is raised. The difference with Ru concentration of the 0.2 mol% Ru: LiNbO$_3$ crystal is greater than that of the in 0.1 mol% Ru: LiNbO$_3$. However, when the initial RuO$_2$ doping content is attained to 1.0 mol%, the variation in the actual Ru concentration is smaller than that in the 0.2 mol% Ru: LiNbO$_3$. This is due to the fact that RuO$_2$ doping in lithium niobate has a definite solubility limit. The 1.0 mol% RuO$_2$ concentration is close to this solubility limit, so that the Ru dopant is hard to get into the lithium niobate crystal. Thus, we can clearly see in Fig.3 that the 1.0 mol% Ru: LiNbO$_3$ crystal is more uniform than the 0.2 mol% one. The trend of the concentration variation in the 2.0 mol% Ru: LiNbO$_3$ crystal is similar to that of the 1.0 mol% Ru: LiNbO$_3$ crystal, but the actual concentration in the 2.0 mol% Ru: LiNbO$_3$ is slightly higher than that in the 1.0 mol% Ru: LiNbO$_3$ crystal. In addition, the Ru concentration in every part of the 3.0 mol% Ru: LiNbO$_3$ crystal is similar to that in the 2.0% mol% crystal. This is because the RuO$_2$ doping concentration has reached to the solubility limit. In our given conditions for crystal growth, no matter how much the initial doping RuO$_2$ increases, the maximum concentration of Ru in the Ru: LiNbO$_3$ crystal was about 0.2 mol%.
Afterwards, we would study the properties of Ru: LiNbO$_3$ with the actual Ru concentration in the crystals.

XRCCD was used to confirm that all the crystals were single crystals and also to determine the lattice constants with the variation of the amount of Ru doped in lithium niobate. Fig. 4 demonstrates that the A and C-axis lattice constants varied with the actual RuO$_2$ doped into lithium niobate. When an impurity is doped into the lithium niobate, the lattice constants change with the valence and ion radius of the dopant. For instance, when Fe doped into lithium niobate, the lattice constants decrease with the Fe concentration because the Fe ion radius is smaller than that of Li$^+$ and Nb$^{5+}$ [24]. According to reference [25], the radius of an Ru ion is smaller than the Li$^+$ or Nb$^{5+}$. Thus, when Ru is doped into lithium niobate, Ru ions are substituted for Li$^+$ or Nb$^{5+}$. Irregardless of whether the Ru is substituted for cation ion in lithium niobate or not, the lattice constants of Ru: LiNbO$_3$ would be reduced. Fig. 4 shows that the lattice constants of un-doped lithium niobate (0 mol% RuO$_2$ concentrations) are 5.1499Å on the A-axis and 13.8947Å on the C-axis. Both the A and C-axis lattice constants decrease linearly with increasing Ru content.

An HITACHI U-4100 was used to measure the absorption coefficient within the ultraviolet and vision (UV/VIS) region from 300 to 800nm with different actual concentrations of Ru in Ru: LiNbO$_3$ crystals (0, 0.017, 0.03, 0.08, 0.12mol%Ru: LiNbO$_3$). Samples with various concentrations of as-grown Ru: LiNbO$_3$ were cut into sections about 1mm thick perpendicular to the C axis and polished. The incident light source was along the C direction. Fig. 5 shows the absorption spectra of un-doped and Ru doped lithium niobate crystals. In addition, it indicates that the un-doped congruent lithium niobate can transmit in the visible region; the absolute absorption of light is below about 320nm. When some impurities are doped into the
lithium niobate, the absorption spectra will be changed by the property of dopant ions. For example, when Fe was doped into lithium niobate, the absorption peak would occur at 480nm by the Fe$^{2+}$ [26]. Fujimura [16] measured the transmission spectra of the Ru: LiNbO$_3$ crystal and observed only one absorption peak around 530nm. However, our measurement (in Fig. 5) of 0.03 mol% Ru: LiNbO$_3$ absorption spectra showed two clear absorption peaks around 370nm and 530nm within UV/VIS region, one more absorption peak than in Fujimura’s report. According to the reference [15], Ru ions have three valences Ru$^{3+}$, Ru$^{4+}$, and Ru$^{5+}$. If the Ru: LiNbO$_3$ crystals have three different valences, there would be three absorption peaks at different wavelength. In Fig. 5, there are at least two absorption peaks within the measurement region, perhaps caused by the different valences of Ru ions in our grown crystals. What valence causes which peak can only be clarified by other measurements, such as electron paramagnetic resonance (EPR). However, as a result of the different concentration of Ru valence in the crystal, the peak position would remain the same while the intensity changes. When the RuO$_2$ content in the lithium niobate is small, such as 0.017mol%Ru: LiNbO$_3$, there is no clear observed peak within the UV/VIS region. And the absorption spectra is similar to that of the undoped lithium niobate. But as the RuO$_2$ dopant concentration increases, the absorption coefficient peaks center around 370 and 530nm would increase, and the absorption edges shift towards longer wavelengths.

Next, FTIR was used to examine the OH$^-$ spectra of Ru: LiNbO$_3$ from 3400 to 3600 cm$^{-1}$. The OH$^-$ absorption spectra were measured at room temperature by an FT-IR Spectrometer with light being transmitted along the C-axis. As in LiNbO$_3$, the OH$^-$ absorption spectra have usually been utilized to probe the crystal’s defect structure. The main intrinsic defects in LiNbO$_3$ are the Li vacancy ($V_{Li}$) and the
antisite Nb ion \((\text{Nb}^{4+}_{\text{Li}})\). Most doping ions occupy Li-sites when the doping concentrations are below the thresholds [27]. The reported thresholds for divalent and trivalent ions are about 5.5 and 2.5 mol\%, respectively [28]. The absorption peak does not shift when the doping concentration is below the threshold. Fig. 6 shows the OH\(^-\) absorption spectra of Ru: LiNbO\(_3\) with different Ru concentrations compared with un-doped congruent LiNbO\(_3\). In Fig. 6, it can be observed that the OH\(^-\) absorption peak of un-doped lithium niobate is about 3482 cm\(^{-1}\). As the Ru concentration increased, the OH\(^-\) absorption coefficient at 3482 cm\(^{-1}\) also increased, but there was no apparent peak shift observed in these absorption spectra. Therefore, it is found that when the actual Ru concentration was below the 0.2 mol\% Ru: LiNbO\(_3\) maximum concentration in our grown crystals, it did not exceed the threshold concentration, and Ru ions would prefer to occupy \(\text{Nb}^{4+}_{\text{Li}}\) in the lithium niobate.

4. Conclusions

In this study, different concentrations of RuO\(_2\) doped lithium niobate crystals were successfully grown by the Czochralski method. The Ru: LiNbO\(_3\) crystals were red in color, transparent, apparently uncracked, and darkened with an increasing Ru content. Due to the fact that the effective segregation coefficient of Ru in lithium niobate is greater than one and that RuO\(_2\) evaporates during the crystal growth period, the Ru content decreases gradually along the pulling direction. No matter what amount of RuO\(_2\) was doped into melt, the actual Ru concentration in the LiNbO\(_3\) crystals grown in the air had a solubility limit of about 0.2 mol\%. Furthermore, the lattice constants were decreased by the addition of Ru ions into lithium niobate. The absorption spectra measurements of the crystal showed two absorption peaks around 370nm and 530nm within the UV/VIS region. The absorption coefficients increased,
and the absorption edges shifted towards longer wavelengths as the Ru concentration increased. In the OH\textsuperscript{−} absorption spectra, the absorption coefficient also increased with the Ru concentration, but the absorption peak did not shift because the Ru doping concentration in the grown Ru: LiNbO\textsubscript{3} crystals may not have exceeded the threshold concentration. It has been proven that Ru ions would be first to occupy Nb\textsuperscript{4+}\textsubscript{Li} sites in congruent LiNbO\textsubscript{3}.

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References


**Figure Captions:**

Fig. 1 As-grown Ru : LiNbO₃ crystals with (A) 0.1mol% and (B) 0.4mol% RuO₂ doping

Fig. 2 Etched slices of the 2.0 mol% Ru: LiNbO₃ samples (A) perpendicular to the C-axis, and (B) parallel to the C-axis

Fig. 3 Variation of Ru concentrations in 0.1, 0.2, 1.0, 2.0, and 3.0mol% Ru: LiNbO₃ crystals

Fig. 4 Variation at lattice constants with different Ru concentrations

Fig. 5 Absorption spectra of Ru: LiNbO₃ with different Ru concentrations in the UV/VIS region

Fig. 6 OH⁻ absorption spectra of Ru: LiNbO₃ with different Ru concentrations
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