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Investigation on p-type lithium niobate crystals

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Till now it is difficult to obtain a p-type lithium niobate crystal. Here the carrier types in various doped and oxidized LiNbO3 crystals have been investigated by holographic technique. The experimental results show tetravalent ions (Zr4+ and Hf4+) with doping concentrations just above optical damage resistant thresholds is helpful to increase the concentration of holes. And 3.0 mol% ZrO2 doped LiNbO3 can be used as a p-type crystal. The dominant carrier of iron doped LiNbO3 crystal can be changed to holes when treated by thermo-electric oxidization. Then the possible mechanism on how to obtain a p-type LiNbO3 was discussed.

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I. INTRODUCTION

Lithium niobate (LiNbO3, LN) has many important properties for both research and applications, such as electro-optic, acousto-optic, thermoelectric, piezoelectric and photorefractive effects. As a strong contender for “optical silicon”, LiNbO3 is now applied for optical waveguide, electro-optical modulation, holographic storage, optical parametric oscillators, etc. However, all the above applications act as passive components. Till now there is rare report of LiNbO3 as an active component. If we can integrate passive and active components on one LiNbO3 substrate, a real all-light photonic chip will be accomplished. To fabricate an active component, the basic unit is to make a p-n junction. By now the main obstacle of a LiNbO3 p-n junction is the lack of p-type LiNbO3.

As we have known, there are electrons and holes in nominally pure LiNbO3 as the electrical charge carries. And the amount of electrons and holes changes with different dopants and doping concentrations. For example, electron is the primary carrier in iron doped LiNbO3 (Fe: LN) as excited by visible light, and hole is the main carrier in MgO doped LiNbO3 (Mg: LN) crystal when the concentration of MgO exceeding the doping threshold (4.6 mol%). However, our recent experimental results show the main carrier is still electron even the doping concentration of MgO is up to 6.5 mol%. And it was reported that the main carrier is hole when LiNbO3 was irradiated by ultraviolet light, but unfortunately, our results show the main carrier of LiNbO3 is still electron even in ultraviolet region. Therefore, finding p-type LiNbO3 is the first step for the realization of optical active components such as an ultraviolet laser and LiNbO3 based integrated photonic circuit.

In fact, many researchers have tried to find p-type oxide materials. Narushima et al. discovered a p-type amorphous oxide ZnO · Rh2O3, which shows controlling the state of matter is a way to gain p-type materials. Copper-based transparent conducting oxides such as CuAlO2, CuGaO2, SrCu2O2, and LaCuOCh (Ch=S, Se, Te) are p-type materials for their copper energy level structure, which shows another way to achieve p-type materials. And the usual method is to dope with different impurities in materials, for example, CuInO2 is p-type when doped with Ca and n-type while doped...
TABLE I. List of the lithium niobate crystals used in our experiments.

| Abbreviation | Dopants | Oxidation       |
|--------------|---------|-----------------|
| 4.0 Mg: CLN  | 4.0 mol% MgO |
| 6.5 Mg: CLN  | 6.5 mol% MgO |
| 6.5 Mg: CLN-air | 6.5 mol% MgO | 700°C, air, 24 h |
| 6.5 Mg: CLN- O₂ | 6.5 mol% MgO | 700°C, O₂, 24 h |
| 1.0 Zr: CLN  | 1.0 mol% ZrO₂ |
| 2.0 Zr: CLN  | 2.0 mol% ZrO₂ |
| 3.0 Zr: CLN  | 3.0 mol% ZrO₂ |
| 5.0 Zr: CLN  | 5.0 mol% ZrO₂ |
| 2.5 Hf: CLN  | 2.5 mol% HfO₂ |
| 4.0 Hf: CLN  | 4.0 mol% HfO₂ |
| 6.0 Hf: CLN  | 6.0 mol% HfO₂ |
| 1.0 Zr: 0.03Fe: CLN | 1.0 mol% ZrO₂; 0.03 wt% Fe₂O₃ |
| 3.0 Zr: 0.03Fe: CLN | 3.0 mol% ZrO₂; 0.03 wt% Fe₂O₃ |
| 0.025 Fe: CLN | 0.025 wt% Fe₂O₃ |
| 0.025 Fe: CLN-air | 0.025 wt% Fe₂O₃ | 700°C, air, 10 h |
| 0.025 Fe: CLN- O₂ | 0.025 wt% Fe₂O₃ | 700°C, O₂, 10 h |
| 0.025 Fe: CLN-TEO | 0.025 wt% Fe₂O₃ | thermo-electric |
| 0.1 Fe: CLN-TEO | 0.1 wt% Fe₂O₃ | thermo-electric |

with Sn. In this paper, we grew various doped LiNbO₃ crystals by Czochralski technique, heat-treated Fe: LN with different degree of oxidization, judged the carrier types of these samples, and discussed the possible ways to find p-type LiNbO₃.

II. EXPERIMENTS

Several series of doped LiNbO₃ crystals were grown for this investigation: they are Mg-, Zr-, Hf-, and Fe-doped, and Zr and Fe co-doped LiNbO₃, all these crystals are collected in Table I. The doped LiNbO₃ crystals were grown in air by the Czochralski method along the c-axis. The congruent composition was selected as [Li]/[Nb]=48.38/51.62. MgO, ZrO₂, HfO₂, or/and Fe₂O₃ were doped into the melt of LiNbO₃. The doping concentrations of Mg, Zr, and Hf were selected below and above their thresholds for optical damage resistance. After annealing and artificial polarization, crystal sheets with a thickness of 3.0 mm were cut along y-faces and optically polished.

There are several methods can be used to judge the carrier type, such as Hall effect, fanning scattering, and holography. Because the dark conductivity of LiNbO₃ is very low, optical methods are usually employed. In this paper, we used the holographic method to determine the photo-induced carrier type. The experimental setup for holography is schematically shown in Fig. 1. A diode-pumped frequency-doubled Nd:YAG laser operating at 532 nm with an intensity of 250 mW/cm² was used as the light source. The laser beam passed through a half wave plate to make the electric field vector parallel with the incident plane, was divided into two equal beam via a beam splitter, then reflected by two reflectors and formed object beam (S beam) and reference beam (R beam). S beam located in the +c direction of y-cut LiNbO₃ crystals and R in the opposite direction. In the measurement, opened the two shutters and let R beam and S beam interfere in the crystal then record the phase grating, after an observation that the diffraction efficiency of the grating increased to a certain degree, blocked S beam and read the diffraction efficiency values (η) varying with time (t) with R beam, and the η-t curve of this erasing process was named as R curve. Chose another point in the crystal to record the grating again, blocked R beam then read with S beam, the η-t curve of the erasing process was named as S curve.

The principle how to judge carrier type in LiNbO₃ crystals by holographic technique can be described as follows: If hole carriers are the main carriers, when read the grating with R beam, the R beam will interference with its diffraction light and form a light intensity distribution mode.

with Sn. In this paper, we grew various doped LiNbO₃ crystals by Czochralski technique, heat-treated Fe: LN with different degree of oxidization, judged the carrier types of these samples, and discussed the possible ways to find p-type LiNbO₃.
Then light induced free hole will accumulate in the low light intensity region via diffusion. The newly formed charge distribution mode has a $\pi$ phase shift with the original one, which results in the decrease of the phase grating. So a rapid decay will be shown in this R curve. While read the grating with S beam, the diffraction light grating has no phase difference then increases the origin phase grating, and we will get a slower decay in the S curve. So we can judge carrier type by comparing R curve with S curve. If S curve decay is slower than R curve, the main carriers are holes. On the contrary, electrons hold the leading position.

### III. RESULTS AND DISCUSSION

Figure 2 shows the holographic erasing curves of Mg-doped congruent LiNbO$_3$ (CLN) crystals, where Fig. 2(a) is for 4.0 mol% Mg doped CLN and Fig. 2(b) for 6.5 mol% Mg doped CLN. We can see that the R curve and S curve of 6.5 Mg: CLN are closer than that of 4.0 Mg: CLN. This phenomenon illuminates that the concentration of electrons and holes get closer with increasing of Mg contents. But electrons always held the leading position even though LiNbO$_3$ doped above the threshold. It was reported that the concentration of hole carriers in Mg: LN increases with increased Mg contents, because Nb$_2$O$_5$, which made the material n-type, disappeared gradually as the doping concentration of MgO increased above its threshold (4.6mol%). But as shown in Fig. 2, the leading carrier in 6.5 Mg: CLN is still electron. This result conflicts with Wang’s but agrees with Qiao’s. As we know, oxidization can improve the concentration of holes meanwhile decrease the concentration of electron, so several 6.5 Mg: CLN crystals were oxidized. Figure 2(c) shows the erasing curve of 6.5 Mg: CLN oxidized at 700°C in air for 24 hours, while Fig. 2(d) shows the one oxidized in O$_2$ environment. Comparing Figs. 2(b)–2(d), we can see that the deeper the sample oxidized the closer of the R and S curves, but the electron carriers take the leading position of all samples. Therefore, the conventional oxidization is hard to change the carrier type in Mg-doped LiNbO$_3$.

Recently, ZrO$_2$ doped LiNbO$_3$ (Zr: LN) crystals were reported having high resistance not only in visible but also ultraviolet region, so their photoinduced carrier type was investigated. Figure 3 shows the holographic reading curves of 1.0, 2.0, 3.0, and 5.0 mol% ZrO$_2$ doped LiNbO$_3$, respectively. From Figs. 3(a) and 3(b), we can see that the R curve and S curve get closer as the concentration of Zr increases when it lower than the threshold (2.0 mol%). This means the concentration of hole carriers becomes closer with electron carriers. When doped with 3.0 mol% Zr, as shown in Fig. 3(c), the S curve is above the R curve, meaning that hole carriers have conquered electron carriers and hold the leading position. Figure 3(d) shows that the hole carriers have little advantage over the electron carriers, this may be caused by excessively doped with Zr.
It was reported that Zr and Fe co-doped LiNbO$_3$ crystals have a higher photoconductivity than Fe-doped or other optical damage resistant elements, such as Mg, Zn, In, and Hf, codoped LiNbO$_3$ with Fe,$^{18}$ so their photoinduced carrier type was investigated. Figure 4 shows the holographic reading curves of 1.0 and 3.0 mol% Zr and 0.03 wt% Fe codoped LiNbO$_3$. We can see that the R curve is above the S curve for 1.0 Zr: 0.03 Fe: CLN while the S curve is slightly above the R curve for 3.0 Zr: 0.03 Fe: CLN, which shows that the concentration of hole carriers is just larger than that of electron carriers in 3.0 Zr: 0.03 Fe: CLN. These results illustrate that doping 3.0 mol% ZrO$_2$ into LiNbO$_3$ is helpful to get a p-type crystal.

Hf doped LiNbO$_3$ (Hf: LN) was reported as an optical damage resistant crystal like Mg: CLN but has a lower doping threshold,$^{19,20}$ therefore the carrier types of series of Hf: CLN crystals were also investigated. Figure 5 shows the holographic reading curves of 2.5, 4.0, and 6.0 mol% Hf doped LiNbO$_3$. From this figure we can see that electron is the dominant carrier in 2.5 Hf: CLN crystal. When the doping concentration becomes more above the threshold value (about 2.5 mol%), the R curve and S curve get entangled, which illuminates that the concentration of hole and electron carriers is close.

The above experimental results indicate that p-type LiNbO$_3$ is difficult to obtain by highly doped with optical damage resistant ions. It was reported that the dominant carrier could be controlled from electron to hole by changing the Fe$^{2+}$/Fe$^{3+}$ ratio in Fe-doped LiNbO$_3$. So the carrier types of Fe: CLN with different degree of oxidization were investigated. The holographic reading curves of Fe: CLN crystals are shown in Fig. 6. Figure 6(a) shows that the concentration of electron is much higher than that of hole in as-grown 0.025 Fe: CLN. Figure 6(b) shows the oxidization in air at 700°C for 10 hours has slight influence on the carrier concentration of 0.025 Fe: CLN. But as shown in Fig. 6(c), the oxidization in O$_2$ at 700°C for 10 hours apparently increases the concentration of holes, which causes the entanglement of R curve and S curve or the S curve is slight above the R curve.
This result shows oxidation in O₂ is indeed an effective way to increase the concentration of holes in Fe: CLN but it is difficult to let the concentration of holes much higher than that of electrons.

In order to obtain a very strong oxidized Fe: CLN, the thermo-electric oxidation was employed, the detailed description about this technique can be seen elsewhere.²¹⁻²³ It was considered that electrons and lithium can be cemented out in the same time, and the crystals be nearly completely oxidized by this extreme method. In our experiments, the Fe: CLN crystals were heated to 700°C for 6 hours with the max electric field of 125 V/mm while the max electric current of 0.01 mA/mm². In Fig. 6(d) we can see apparently that hole is the dominant carrier in 0.025 Fe: CLN-TEO. Figure 6(e) illustrates the erasing time of 0.1 Fe: CLN-TEO is much shorter than that of 0.025 Fe: CLN-TEO,
FIG. 5. Holographic reading curves of Hf-doped LiNbO₃ crystals. (a) 2.5 Hf: CLN, (b) 4.0 Hf: CLN, (c) 6.0 Hf: CLN.

which indicates the concentration of hole is much higher than that of 0.025 Fe: CLN-TEO. The above results show us that p-type LiNbO₃ can be obtained by thermo-electric oxidation technique.

Our experimental results indicate that highly doping of optical damage resistant ions is helpful to increase the concentration of hole and decrease the concentration of electron in the mean time. When the doping content is above threshold, the concentration of hole can be near or slight higher than that of electron. Especially, 3.0 mol% ZrO₂ doped CLN is a stronger contender for p-type LiNbO₃. It seems that tetravalent ions are more effective in increasing the concentration of hole than bivalent ions. As we know, there are plenty of intrinsic defects in congruent LiNbO₃, the deficiency of Li₂O induces Li-site vacancies (V_{Li}⁻) and charge compensated anti-site Nb⁵⁺ (NbLi⁵⁺) ions.²⁴ Part of the NbLi⁵⁺ ions form small polarons (NbLi⁴⁺) by trapping electrons and some NbLi⁵⁺ ions with neighboring normal-site Nb ions (NbNb⁵⁺) form bipolarons (NbLi⁴⁺NbNb⁴⁺) by trapping a pair of electrons with opposite spins. These polarons act as donors and improve the concentration of photoinduced electrons of LiNbO₃ as illuminated by suitable light. The optical damage resistant dopants will substitute anti-site Nb⁵⁺ ions as the doping concentration below threshold, which decreases the concentration of photoinduced electrons from bipolarons and small polarons and causes the approach of R and S curves. As the doping concentration above the threshold, these dopants will substitute normal Li⁺ and Nb⁵⁺ ions in the mean time, because the valances of these dopants is below +5, the valance of Nb ions, these doping ions will let their neighbor O²⁻ become easier to lose electrons thus product holes, which induces the increasing of hole concentration and the S curve more close to the R curve. However, if the lost electrons from O²⁻ enter conductive band, there will product pairs of holes and electrons in the valance and conductive bands, so the concentrations of holes and electrons almost equal and the S and R curves entangle. Whether the electrons excited from O²⁻ enter conductive band is depended on the ability of bonding electrons of the doping ions in Nb-sites. Obviously tetravalent ions, such as Zr⁴⁺ and Hf⁴⁺, have higher ability to bond electrons than divalent ions like Mg²⁺, which causes a smaller concentration of photoinduced electrons in Zr and Hf doped CLN than that in Mg: CLN, and as
shown in our experimental results, Zr and Hf doped CLN are more suitable p-type crystals than Mg: CLN.

Our results also illuminate electron carriers can be reduced by different oxidization methods. But to fabricate p-type LiNbO₃, the normal oxidization is difficult to give a satisfied result. It is obvious that a larger concentration of holes can be obtained if we improve the heating temperature and time. As we know, long time heating treatment in 800~900°C will cause the component segregation of LiNbO₃. Therefore, if we want to improve the heating temperature, this region should be avoided, so a temperature more than 1000°C had to be employed. But in such high temperature, O₂ is very active, the heating treatment will be harmful to the equipment, and most importantly, the Li⁺ ions in LiNbO₃ are also very active, they can diffuse out of the crystal, which cause the further deficiency of lithium in LiNbO₃.
Our experimental results show hole carriers will take the dominant place in Fe: CLN after thermo-electric oxidization, this is an effective way to get p-type LiNbO$_3$. It should be pointed out that though thermo-electric oxidization can strongly force Fe$^{2+}$ ions to lose their electrons and become Fe$^{3+}$ ions, just as introduced above, Li$^+$ ions are pushed out of the crystal in the mean time, which also cause the further deficiency of lithium in LiNbO$_3$, and especially near the cathode, lithium forms and the Fe: CLN crystal becomes brittle and cracks usually appear. The affect of thermo-electric oxidization on the crystal need be further investigated.

IV. SUMMARY

We investigated the carrier type in series of doped LiNbO$_3$ crystals. The experimental results show that tetravalent ions (Zr$^{4+}$ and Hf$^{4+}$) with doping concentrations just above thresholds is helpful to increase the concentration of hole carriers. Especially, 3.0 mol% Zr doped CLN can be used as a p-type crystal. By now thermo-electric oxidization may be an effective way to fabricate p-type crystals. However intensive investigation is greatly needed to find more applicable methods on the fabrication of p-type LiNbO$_3$ in the future.

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