Room temperature 90° phase-matching in zirconium and magnesium co-doped lithium niobate crystals

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Laser has been widely used in many aspects, by now it is difficult to get each frequency that we want, and frequency conversion is an effective way to obtain different frequency laser through a nonlinear optical crystal. MgO-doped LiNbO3 (Mg:LN) crystal has usually been used for second harmonic generation (SHG) through temperature-matching configuration with a stove, till now a room temperature 90° phase-matching is still lacking. Here we find that the SHG of Nd:YAG laser is achieved at 26.1 °C while the optical damage resistance is higher than 6.5 MW/cm² in the ZrO2 and MgO co-doped LiNbO3 (Zr,Mg:LN) crystal. Moreover, the monotonic decrease of phase-matching temperature is firstly found with the increase of doping concentration. These unusual properties may be attributed to the formation of MgLi+ + ZrNb− defect pairs. Our work suggests that Zr,Mg:LN crystal may be an attractive candidate for nonlinear optical applications.

Miniature, compact and high-power all-solid-state blue-green lasers are widely applied in ocean exploration, medical treatment, optical communication and laser display, etc.1–4. As one of the most versatile optical crystals, lithium niobate (LiNbO3, LN) plays a key role in the second harmonic generation (SHG) of blue-green light from near-infrared lasers owing to its large nonlinearity and capability of temperature-tuned noncritical phase matching (90° phase-matching)5–8. Unfortunately, optical damage in LiNbO3, also known as photorefractive effect, induced by modest intensities of visible light, sharply decreases the conversion efficiency and hinders its practical usage9,10. A breakthrough came that the optical damage resistance of LiNbO3 could be improved at least two orders of magnitude when 4.6 mol.% MgO was doped into11,12. From then on, MgO-doped LiNbO3 (Mg:LN) has become the often used material in frequency conversion, optical waveguide, optical parametric oscillation and terahertz source13–17. But for infrared-to-visible nonlinear frequency conversion, the phase-matching temperature is usually above 100 °C, so a precise temperature-controlled stove is needed. The extra unit in the laser cavity can increase the complexity of the system and lead to the additional energy loss18. Besides, the elevated operating temperature will also reduce components reliability and shorten service life. Detailed investigations show that the phase-matching temperature of Mg:LN increases with increased MgO concentration, and reaches the maximum near the doping threshold, then decreases with further increased doping concentration19. Therefore, it is possible that phase matching achieves at room temperature (about 25 °C) with a high enough doping concentration of MgO, but such heavily doped Mg:LN crystal is hard to grow with high optical quality20. Later, several ions such as Zn2+, In3+, Sc3+, and Hf4+ were also reported to have the same resistance against optical damage when doped into LiNbO3, but just like Mg:LN, the efficient noncritical phase matching at room temperature is still a problem19,21–23. Therefore, room temperature 90° phase-matching has always been a serious challenge for LiNbO3 at present.

In recent years, ZrO2-doped LiNbO3 (Zr:LN) has attracted great attentions because of its high optical damage resistance in the visible and even ultraviolet region, low doping threshold (2.0 mol.% and distribution coefficient

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close to one\textsuperscript{24–26}. Up to now, investigations on Zr:LN crystals mainly focus on optical waveguide, defect structure and co-doping with photorefractive impurities\textsuperscript{27–29}, but their refractive indices and nonlinear optical properties (e.g., phase-matching temperature) are rarely reported. In fact, no sign of phase matching in Zr:LN crystals was found when they were heated from room temperature to above 200 °C in our pre-experiments, which implies that the phase-matching temperature of Zr:LN crystals may be lower than room temperature. If that is true, we may obtain room temperature 90° phase-matching by doubly doping with ZrO\textsubscript{2} and MgO in LiNbO\textsubscript{3}. And co-doping with two optical damage resistant ions is conducive to finely tune the optical properties of LiNbO\textsubscript{3}\textsuperscript{19,30}.

In this paper, we grew a series of ZrO\textsubscript{2} and MgO co-doped LiNbO\textsubscript{3} (Zr,Mg:LN) crystals with various ZrO\textsubscript{2} dopants, and the doping concentration of MgO was chosen as 5.0 mol.% because Mg:LN has high phase-matching temperature in this doping level. Our experimental results demonstrate that the phase-matching temperature of Zr,Mg:LN monotonically decreases with increased ZrO\textsubscript{2} concentration. And the efficient 90° phase-matching is achieved in Zr,Mg:LN crystal at room temperature without a stove, meanwhile it also has a very high optical damage resistance.

**Results**

**Temperature tuned 90° phase-matching.** Temperature tuned 90° phase-matching was achieved by using a Q-switched Nd:YAG laser with a wavelength of 1064 nm. The dependence of the phase-matching temperature $T_{\text{PM}}$ on the ZrO\textsubscript{2} concentration in the melt for Zr,Mg:LN crystals is depicted in Fig. 1(a). From this figure, we can see that the $T_{\text{PM}}$ decreases as the ZrO\textsubscript{2} concentration increases, and a straight line can be fitted well to the experimental data. For comparison, the $T_{\text{PM}}$ versus the doping concentration of MgO for Mg:LN crystals is presented in Fig. 1(b), and the data are referenced from the previous literature\textsuperscript{19}. The relationship between the $T_{\text{PM}}$ and the impurity concentration is similar to a parabola going downwards, and the maximum temperature stays within the concentration range of 4–6 mol.%. Generally, the $T_{\text{PM}}$ versus the doping concentration exposes a more or less expressed threshold behavior corresponding to the sharp change of optical properties, and this similar behavior can be found in other mono or dual doped LN crystals, such as Zn:LN\textsuperscript{21}, Sc:LN\textsuperscript{22} and Zn,In:LN\textsuperscript{30}. In contrast, Zr,Mg:LN crystals exhibit a significant monotonic, and a simple linear extrapolation from existing data holds over a wider concentration range.

Please note that the phase-matching temperature in Zr\textsubscript{1.7},Mg\textsubscript{5.0}:LN crystal is 26.1 °C, which is close to room temperature (25 °C). Figure 2 clearly shows its normalized temperature-tuning curve for doubling 1064 nm using 90° phase-matching. The dots are the measured second harmonic output power, and the solid curve is a fit to the $\text{sinc}(x)$ function, which almost perfectly overlaps the experimental data. The full width at half maximum (FWHM) of the temperature-tuning curve is 1.2 °C. Moreover, the conversion efficiency is plotted as a function of the incident fundamental power density in Fig. 3. An average second harmonic power of 91.5 mW is obtained with a conversion efficiency of 28.6% at the peak-power density of 50 MW/cm\textsuperscript{2}, and maintaining this conversion efficiency for two hours, there is no significant degradation. Overall, we should point out emphatically that if considering the temperature increase (about 2–3 °C) in the continuous harmonic output\textsuperscript{31,32}, Zr\textsubscript{1.7},Mg\textsubscript{5.0}:LN crystal is particularly well-suited for practical application of laser frequency doubling at room temperature.

**Optical damage resistance.** In order to measure the optical damage resistance, the distortion of the transmitted light beam through the wafer was observed with a 532 nm laser. Figure 4 shows the transmitted laser beam spots after 5 min of irradiation. As the concentration of ZrO\textsubscript{2} increases from 0.5 to 1.7 mol.%, none of Zr,Mg:LN crystals appears noticeable beam smeared, even under the highest focused intensity of 6.5 × 10\textsuperscript{8} W/cm\textsuperscript{2} in our laboratory, and the optical damage resistance is the same magnitude as that of Zr\textsubscript{2.0}:LN. However, Mg\textsubscript{5.0}:LN crystal can only withstand a maximum intensity of 4.1 × 10\textsuperscript{8} W/cm\textsuperscript{2} under the same conditions. The above results indicate that the optical damage resistance of these Zr,Mg:LN crystals is improved by at least an order of magnitude than that of Mg\textsubscript{5.0}:LN.

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**Figure 1.** Phase-matching temperature $T_{\text{PM}}$ versus the doping concentration in the melt of (a) Zr,Mg:LN and (b) Mg:LN crystals. The dotted symbols represent the experimental data, and the red guided line is a function fitting.
To quantitatively characterize the optical damage resistance, the light-induced changes of the refractive index $\Delta n$ of these crystals were measured by two-beam holography. Two $e$-polarized coherent beams at 532 nm were intersected in the wafers with equal intensity of 400 mW/cm$^2$. The change of refractive index $\Delta n$ was calculated by the equation $\eta \lambda \theta_{max} = \pi \Delta n \sin(\theta_{cry}^2 / 2c_{cry})$. Here, $\eta_{max}$ is the maximum diffraction efficiency; $\lambda$ is the wavelength, 532 nm; $d$ is the crystal thickness, 3.0 mm; and $\theta_{cry}$ is the intersection half-angle of the two coherent beams outside the crystal, $2\theta_{cry} = 30^\circ$. The photoconductivity $\sigma_{ph}$ was also estimated through the relationship, $\sigma_{ph} = \sigma_0 / \tau_e$, where $\sigma_0$ is the vacuum dielectric constant, $\varepsilon = 28$ is the relative dielectric constant of the crystal [35], and the erasure time constant $\tau_e$ is defined as the time when the diffraction efficiency decays to $1/e$ of its initial value.

The change of refractive index $\Delta n$ and the photoconductivity $\sigma_{ph}$ versus the ZrO$_2$ concentration for all samples are presented in Fig. 5. We can see that the change of refractive index reduces rapidly with doping 0.5 mol.% ZrO$_2$ into Mg$_{5.0}$:LN, then changes slightly as the ZrO$_2$ concentration increases. Moreover, the $\Delta n$ of Zr,Mg:LN is considerably less than that of Mg$_{5.0}$:LN but close to that of Zr$_{2.0}$:LN. In addition, the $\sigma_{ph}$ of Zr,Mg:LN is larger than that of Mg$_{5.0}$:LN but close to that of Zr$_{2.0}$:LN. It is well known that the increase of the photoconductivity is primarily responsible for the increase of the optical damage resistance[36]. Therefore, the results demonstrate again that adding some ZrO$_2$ into Mg$_{5.0}$:LN can further enhance the optical damage resistance, which is consistent with the results of the transmitted light beam distortion.

**Infrared absorption spectra.** The infrared absorption spectra, referring mainly to OH$^-$ absorption spectra, sensitively reflect the change of defect structure in LiNbO$_3$, which have become an important tool in studying the properties of dopant-related defects. Figure 6 shows the OH$^-$ absorption spectra of CLN and Zr,Mg:LN crystals. As no obvious OH$^-$ band shift is observed, a three-peak model [37] is employed by Lorentz fitting, and the results are listed in Table 1. For comparison, that of Mg$_{5.0}$:LN and Zr$_{2.0}$:LN crystals are also listed. It can be seen from the
table that the component peaks of Zr_{2.0}:LN are located at 3475, 3485, and 3495 cm\(^{-1}\), respectively, which agree with the previous results\(^{38}\), and the shift in component peaks is connected with the formation of OH\(^{-}\)-Zr Nb clusters. Moreover, with increased doping concentration of ZrO\(_2\), the relative intensity of OH\(^{-}\)-Zr Nb band will increase\(^{39}\). As shown in the table, the peak of 3476 cm\(^{-1}\) appears in Zr_{0.5},Mg:LN and moves to 3478 cm\(^{-1}\) with increased concentration of ZrO\(_2\). Based on these analyses, the total content of 0.5 mol.% ZrO\(_2\) and 5.0 mol.% MgO in LiNbO\(_3\) has reached the doping threshold.

**UV-visible absorption spectra.** The UV absorption edge of LiNbO\(_3\) is sensitive to the crystal composition and defect\(^{40}\), especially the absorption edge has a maximum violet-shift when the doping concentration reaches the threshold. The UV-visible absorption spectra of Zr,Mg:LN crystals are shown in Fig. 7. The inset clearly shows the position of absorption edges. Here, the absorption edge is defined as the wavelength where the absorption coefficient is equal to 20 cm\(^{-1}\). From this figure, we can see that the absorption edge of Zr_{0.5},Mg_{5.0}:LN crystal has a maximum violet-shift, and with the doping concentration of ZrO\(_2\) increasing from 0.5 to 1.7 mol.%, the absorption edge has an obvious red-shift. Therefore, we can conclude that the total doping concentration of 0.5 mol.% ZrO\(_2\) and 5.0 mol.% MgO in LiNbO\(_3\) reaches the threshold level, which is in agreement with the results of OH\(^{-}\) absorption spectra.
The absorption spectra of Zr,Mg:LN crystals demonstrate that the total content of 0.5 mol.% ZrO₂ and 5.0 mol.% MgO has reached the doping threshold, which implies that impurity ions enter normal Nb sites after all Nb₄⁺ ions have been substituted. Moreover, the three-peak fitting analysis of OH⁻ absorption spectra indicates that the peak shifts are related to the formation of OH⁻–Zr Nb complexes, and 3535 cm⁻¹ absorption peak attributed to the OH⁻ stretching vibration of MgLi–OH⁻–Mg Nb complex is not observed. These results indicate that the additional ZrO₂ can directly influence the threshold level of MgO, namely, Zr⁴⁺ ions affect the site occupation of Mg²⁺ ions. So it can be deduced that the appearance of MgLi⁺–Zr Nb⁻⁻⁻⁻ pairs leads to no obvious OH⁻ absorption band shift. And the amount of MgLi⁺–Zr Nb⁻⁻⁻⁻ complexes will increase with increased concentration of ZrO₂. Considering the MgLi⁺–Zr Nb⁻⁻⁻⁻ pairs without charge compensation, electron trap centers will dramatically reduce in crystals, which brings about the great increase of photoconductivity then results in strong optical damage resistance.

Table 1. The position of component peaks of the OH⁻ absorption spectra.

| Sample            | Position of peaks (cm⁻¹) |
|-------------------|---------------------------|
| CLN               | 3468 3481 3490            |
| Mg₅₀:LN           | 3535                       |
| Zr₂⁺:LN           | 3475 3485 3495             |
| Zr₁₊,Mg₅₀:LN     | 3476 3484 3493             |
| Zr½,1₀,Mg₅₀:LN    | 3477 3485 3493             |
| Zr₁⁺,1₀,Mg₅₀:LN   | 3478 3486 3495             |
| Zr₁⁺,1₂,Mg₅₀:LN   | 3478 3487 3495             |

Figure 6. The OH⁻ absorption spectra of Zr,Mg:LN crystals. For comparison, that of CLN is also drawn. The dashed arrow marks the position of absorption peaks.

Figure 7. The UV-visible absorption spectra of Zr,Mg:LN crystals and of CLN and Mg₅₀:LN for comparison.
Our results on SHG of Nd:YAG lasers have shown that the additional ZrO₂ doping can significantly influence the phase-matching temperature of Mg₀.₅ LN. In particular, the monotonic decrease of phase-matching temperature on ZrO₂ concentration is found for the first time, which is different from the previous reports on doped LiNbO₃. As we know, so-called optical damage resistant impurities in visible region such as Mg, Zn, In and Hf can enhance the UV photorefractive effect⁴³, but Zr exhibits excellent optical damage resistance in both visible and UV region. It is thought that the enhanced UV photorefractive effect has direct relationship with doped ions occupying Nb sites⁴¹, which means that Zr⁺⁺ ions in Nb sites can greatly alter defect structures and properties of LiNbO₃. In Zr,Mg:LN crystals, Mg⁺⁺ + Zr⁻⁻₉ neutral pairs may play an important role in this monotonic decrease relationship. However, further investigation is greatly needed to clarify the micro-mechanism.

Conclusion

We grew a series of LiNbO₃ co-doping with 5.0 mol.% MgO and various ZrO₂ concentrations. The experimental results indicate that the phase-matching temperature of Zr,Mg:LN decreases with increased ZrO₂ concentration for the first time. And 90° phase-matching of 1064 nm radiation is achieved at room temperature in Zr₁.₇,Mg₅.₀:LN crystal, while it holds a high resistance of optical damage at 532 nm, and does not suffer any dark trace damage when exposed to high power laser irradiation for two hours, which will be greatly valuable for engineering applications in compact and efficient high-power green lasers. These excellent properties of Zr,Mg:LN may be attributed to the formation of Mg⁺⁺ + Zr⁻⁻₉ neutral defect pairs.

Methods

Samples preparation. A series of doubly doped LiNbO₃ crystals were grown along the c-axis by the conventional Czochralski method in air. 0, 0.5, 1.0, 1.5 and 1.7 mol.% ZrO₂ were added, respectively, to the congruent melt (Li/Nb = 48.38/51.62) doping with 5.0 mol.% MgO, labeled as Mg₀.₅ LN, Zr₀.₅,Mg₀.₅ LN, Zr₁.₀,Mg₀.₅ LN, Zr₁.₅,Mg₀.₅ LN and Zr₂.₀,Mg₀.₅ LN. After annealing treatment and artificial polarization, the crystals were cut into 3.0 mm and 1.0 mm thick y-plates for the characterization of photorefractive and absorption. Choosing crack-free and uniform bulk crystals were cut into 9.0 × 10.0 × 9.0 mm³ (X × Y × Z) for second harmonic generation, where y-axis was the transmission direction. All samples were optical grade polished on both faces perpendicular to y-axis of the crystal. For comparison, congruent LiNbO₃ and 2.0 mol.% ZrO₂-doped congruent LiNbO₃ crystals were also prepared, labelled as CLN and Zr₂.₀ LN, respectively.

Spectra characterization. The infrared absorption spectra and UV-Visible absorption spectra of 1.0 mm thick y-plates were measured at room temperature with a Magna-560 Fourier transform infrared spectrophotometer and a U-4100 spectrophotometer, respectively. The resolution value of this infrared spectrometer was 4.0 cm⁻¹, and the step-length of the UV-Vis. spectrometer was 1.0 nm.

Second harmonic generation. The experiments for second harmonic generation were performed with a Q-switched Nd:YAG laser 1064 nm at a 1 Hz repetition rate, 8 ns pulse width. The laser facula diameter was 5.0 mm, and the maximum average output energy was 320 mJ. The fundamental light was directed to the crystal in a geometry with the c-axis of the crystal perpendicular to the polarization direction of the light, so-called 90° phase-matching. The second harmonic energy was detected with a band-pass filter and a pulse laser energy meter. The bulk crystal was mounted in an oven thermally controlled to a temperature better than ±0.2°C. The temperature was measured with a Pt-100 thermistor placed in direct contact with the crystal, and a slow heating rate was used about 0.5°C/min to minimize temperature gradients with the sample. In addition, the distance between the entrance and the exit windows of the crystal surfaces was at least 5.0 cm to minimize the possible temperature gradients along the crystal y-axis. The formula for the conversion efficiency was η = E₂/E₁, where E₁ was the energy of the fundamental wave and E₂ was that of the second harmonic wave.

Data availability. The datasets generated during the current study are available from the corresponding author on reasonable request.

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Author Contributions
Y.K., H.L. and J.X. conceived the study. S.L., L.Z. and T.K. contributed to crystal growth. S.C. and T.K. prepared the samples. T.K. performed the experiments. X.G. and D.Q. measured the spectra. R.R. discussed the results. T.K. and Y.K. wrote the manuscript. All authors reviewed the manuscript.

Additional Information
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