Increased photorefractive sensitivity in double-doped KTa$_{1-x}$Nb$_x$O$_3$:Fe,Ti

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Double-doped KTN:Fe,Ti exhibits increased photorefractive sensitivity compared with single-doped KTN:Fe and KTN:Ti. Absorption and photoconductivity measurements correlate the increase with an increased concentration of Fe in the reduced Fe$^{2+}$ valence state and to an increased fraction of Fe incorporated into the crystal from the flux.

Photorefractive materials have received increased interest as volume holographic storage media. Material limitations, including low photorefractive sensitivity, remain to be overcome. In ferroelectric materials, including low photorefractive interest as volume holographic storage media. Photorefractive materials have received increased interest as volume holographic storage media. Material limitations, including low photorefractive sensitivity, remain to be overcome. In ferroelectric materials, including low photorefractive interest as volume holographic storage media. Photorefractive materials have received increased interest as volume holographic storage media. Material limitations, including low photorefractive sensitivity, remain to be overcome. In ferroelectric materials, including low photorefractive interest as volume holographic storage media. Photorefractive materials have received increased interest as volume holographic storage media. 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compared with the KTN:Fe,Ti sample. The addition of Ti significantly increases the Fe that enters the crystal in the reduced Fe\(^{2+}\) state. The effect is even more pronounced when one considers that the flux used to grow the KTN:Fe,Ti crystal had half as much Fe as the flux used to grow the KTN:Fe crystal. In addition, assuming that Fe enters primarily in the 2+ and 3+ valence states, the fraction of Fe incorporated into the crystal from the flux is increased by codoping with Ti. Transition-metal impurities substitutionally occupy lattice sites in perovskites. The bias of Fe into the 2+ valence state when it is codoped with Ti may be a result of charge compensation of the lattice. Compensation occurs when a Ti\(^{4+}\) ion occupies a (Ta, Nb)\(^{5+}\) site and a Fe\(^{2+}\) ion occupies a K\(^{+}\) site.

The photocurrent of each sample was measured under 514-nm illumination. Values for the products \(\alpha_\text{ef} \mu \tau_R\) and \(\mu \tau_R\) determined from the measurements are given in Table 1, where \(\alpha_\text{ef}\) is the coefficient for absorption that results in a free carrier and is proportional to the concentration of absorbing ions, \(\mu\) is the electron mobility, and \(\tau_R\) is the free-carrier lifetime (recombination time) that is inversely proportional to the trap concentration.\(^5\) The KTN:Fe,Ti sample exhibits an increased photocurrent compared with the KTN:Fe and KTN:Ti samples, while the mobility lifetime products vary little. The results are consistent with the relative Fe\(^{2+}\) and Fe\(^{3+}\) concentrations determined from the absorption measurements.

Holographic diffraction measurements were made on each sample in the paraelectric cubic phase, which required the application of an external field. Diffraction gratings were written by using two expanded beams from a 514-nm Ar laser. The beams had intensities of 20 and 110 mW/cm\(^2\) (intensity modulation \(m = 0.2\)) and were ordinarily polarized in order to limit photorefractive wave coupling. A field of 1820 V/cm was applied to the samples, and the writing beams were adjusted to form a 5.1-\(\mu\)m grating period. The diffracted intensity of an extraordinarily polarized weak probe beam from a He–Ne laser aligned at the Bragg angle monitored the strength of the grating.

For weak coupling the diffraction efficiency \(\eta\) is given by that from a thick plane holographic grating:  

\[
\eta = \exp(-\alpha I) \sin^2 \left( \frac{\pi \Delta n}{\lambda \cos(\theta/2)} \right),
\]

where \(\alpha\) is the total absorption, \(I\) is the thickness of the sample, \(\Delta n\) is the magnitude of the index grating, \(\lambda\) is the wavelength of the illuminating radiation, and \(\theta\) is the angle between the writing beams. We determined the erase time \(\tau\) by monitoring the exponential decay of \(\Delta n\) under 110-mW/cm\(^2\) illumination after one of the writing beams was blocked. The photorefractive sensitivity, defined as the refractive-index change per absorbed unit of energy, is given by\(^10\)

\[
S = \frac{dn}{d(\alpha I t)} = \frac{\Delta n}{\alpha I \tau},
\]

where \(I\) is the intensity.

We placed the samples on a thermoelectric mount and measured the refractive-index change and the erase rate at several temperatures above each sample's Curie temperature. Both the diffraction efficiency and the response time increase as the Curie temperature is approached. The photorefractive sensitivity has a much weaker temperature dependence than do \(\Delta n\) and \(\tau\) near the phase transition, which allows for comparisons among samples with differing transition temperatures. Results for the temperature dependence of the photorefractive

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Fe(^{2+})] (a.u.)</th>
<th>[Fe(^{3+})] (a.u.)</th>
<th>(a \mu \tau_R) [cm/(V s), (\times 10^{-10})]</th>
<th>(\mu \tau_R) [cm(^2)/(V s), (\times 10^{-10})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KT(<em>{0.87})Nb(</em>{0.30})O(_3):Fe,Ti</td>
<td>3.7</td>
<td>1</td>
<td>6.24</td>
<td>4.99</td>
</tr>
<tr>
<td>KT(<em>{0.86})Nb(</em>{0.39})O(_3):Fe</td>
<td>1</td>
<td>1.3</td>
<td>1.02</td>
<td>2.72</td>
</tr>
<tr>
<td>KT(<em>{0.86})Nb(</em>{0.39})O(_3):Ti</td>
<td>–</td>
<td>–</td>
<td>0.86</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Fig. 1. Absorption spectra of the KTN:Fe,Ti, KTN:Fe, and KTN:Ti samples.

Fig. 2. Difference in the absorption spectra of the KTN:Fe,Ti, KTN:Fe, and KTN:Ti samples.
sensitivity for each sample are given in Fig. 3. The KTN:Fe,Ti sample exhibits more than a factor-of-3 increased sensitivity compared with the single-doped samples. The higher sensitivity is due mainly to a faster response time for the double-doped sample. The photoconductivity measurements indicate that the faster response is due to a larger absorption from the increased concentration of the Fe$^{2+}$ ions rather than to an increased free-carrier lifetime. An increased photorefractive sensitivity is also observed in samples in which the photorefractive center is reduced through the creation of oxygen vacancies. The double-dopant approach described here does not require any postgrowth processing. It can also be applied to other host crystals, including KNbO$_3$, LiTaO$_3$, and LiNbO$_3$, in which the effect has been observed in Ti-indiffused waveguides.

The photorefractive properties of Fe-doped, Ti-doped, and Fe- and Ti-double-doped KTN samples were investigated. Absorption measurements indicate that the double-dopant combination of Fe and Ti increases the fraction of Fe in the reduced Fe$^{2+}$ valence state and increases the fraction of Fe that enters the crystal from the flux compared with that of single-doped Fe sample. The double-dopant combination of Fe and Ti leads to a factor-of-3 increased photorefractive sensitivity compared with single-doped samples.

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References