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Oxygen vacancies in lithium tantalate

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Lithium tantalate crystals turn "black" when annealed above approximately 850 °C in an argon atmosphere. The resulting optical absorption spectrum has a distinct peak at 460 nm but also extends through the entire visible and near ultraviolet. We attribute this absorption to oxygen vacancies containing two electrons. Optical bleaching near 77 K converts the initial absorption spectrum to a different spectrum having a peak near 570 nm. Electron-spin-resonance results show that the 77-K bleach also produces Ta^{4+} ions. Both Ta^{4+} ions and oxygen vacancies (containing only one electron) contribute to the absorption spectrum after the bleach.

I. INTRODUCTION

The optical properties of ferroelectric materials such as $LiNbO_3$ and $LiTaO_3$ are of interest because of applications in electro-optic devices.[1,2] It has been known for many years that reducing $LiNbO_3$ causes the material to become "black," and recent papers[3,4] have assigned this effect to oxygen vacancies. In the present Brief Report, we describe optical- and magnetic-resonance results that allow us to reach similar conclusions about the role of oxygen vacancies in reduced $LiTaO_3$.

Since $LiTaO_3$ has the same trigonal crystal structure as $LiNbO_3$ and also exhibits similar physical properties, we initially expected the reduction behaviors to be nearly the same for the two materials. However, Chen, Sweeney, and Halliburton[5] did not find any significant blackening in reduced $LiTaO_3$ crystals. We now know that the primary reason for their "failure" was a relatively large oxygen partial-pressure within their reducing atmosphere (i.e., a vacuum) because of the use of a fused-quartz tube. In our present reduction experiments, we used an argon atmosphere contained within a stainless steel tube. Under these latter conditions, we find an intense optical peak near 460 nm in $LiTaO_3$ crystals following reduction, and we observe that subsequent optical bleaching near 77 K converts the initial optical spectrum to a different spectrum which has a peak near 570 nm. The 77-K optical bleach also introduces an electron-spin-resonance (ESR) spectrum due to Ta^{4+} ions.

Optical absorption bands suggestive of our present results were initially reported by Antonov, Arsenev, Linda, and Farstendiker.[6]

II. EXPERIMENT

The acoustic-grade lithium tantalate crystals used in our present investigation were grown by the Czochralski technique at Union Carbide. Reductions were done in an argon atmosphere (approximately 500 Torr pressure) held within a stainless steel tube extending through a small bench-top furnace. Optical data were obtained from a Perkin-Elmer 330 spectrophotometer. The optical samples were approximately $1\times5\times10$ mm^3 plates, oriented such that the *c* axis was within the plane of the plate. Thus, all the absorption spectra were obtained with unpolarized light propagating perpendicular to the *c* axis. We did not distinguish between the *X* and *Y* axes of the crystal, and we did not repole the crystals after heating. During the optical measurements, the samples were mounted on the copper tail of a liquid-nitrogen Dewar.

Magnetic-resonance data were taken with a Bruker ER200D spectrometer (9.45-GHz microwave frequency and 100-kHz modulation frequency). The ESR samples were rectangular in shape, approximately $2\times2\times10$ mm^3, with the *c* axis being one of the smaller dimensions. An Air Products Heli-Tran liquid helium transfer system controlled the sample temperature during the ESR experiments.

III. RESULTS

The optical absorption spectrum taken at 80 K from an as-grown $LiTaO_3$ crystal is shown in trace (a) of Fig. 1. This initial absorption is essentially zero in the infrared but steadily increases through the visible region and into the near ultraviolet. The single distinguishing feature in trace (a), other than the band edge beginning at about 260 nm, is the "small" absorption band peaking near 300 nm. We expect that this visible and near-ultraviolet absorption in the as-grown crystal is due to transition-metal-ion impurities, and that it is possibly enhanced because of incomplete oxidation of the crystal during or after growth.

After the initial optical characterization, this same sample was subjected to a series of reducing treatments. The crystal was held at 850 °C for 1 h in an argon atmosphere, and the subsequent absorption spectrum is shown in trace (b) of Fig. 1. This treatment caused an increase in absorption throughout the visible and near-ultraviolet region, and a new peak has emerged at 460 nm. The peak near 300 nm in the "as-grown" spectrum is no longer discernible. Additional 1-h reductions were done at 875, 900, and 925 °C.

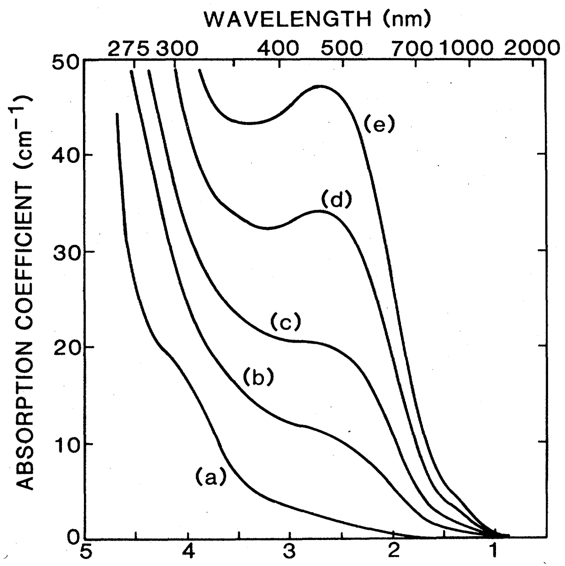

FIG. 1. Optical absorption of $LiTaO_3$ measured at 80 K using unpolarized light propagating perpendicular to the c axis of the sample. Trace (a) represents the as-received crystal, and traces (b), (c), (d), and (e) represent the absorption induced by 1-h reductions in argon at temperatures of 850, 875, 900, and 925 °C, respectively.

These results are presented in traces (c), (d), and (e) of Fig. 1 and they show a steadily increasing 460-nm peak. The crystal was not oxidized between these reduction steps; thus, the results represent an accumulation of reducing effects. As a note of caution, we believe it is unlikely that equilibrium was reached during any of the four reducing treatments, and thus the optical absorptions represented in traces (b)–(e) of Fig. 1 are not expected to be uniform within the volume of the crystal. After the reduction at 925 °C, the crystal was held at 900 °C in air (i.e., an oxidizing atmosphere) for several hours. This treatment removed all traces of the "black" coloration.

It is informative to apply Smakula's equation[7] to the absorption spectra in Fig. 1 and thus calculate the concentration of responsible defects. In doing this, we made several approximations. First, a Gaussian 460-nm band was assumed with a half-width of 1.38 eV (double the width from the center of the band to the lower energy half-intensity point) and second, the oscillator strength was taken to be 1.0. Using $n = 2.18$ and $\alpha_{max} = 45$ cm^{-1} gave a concentration of 2.6×10^{17} cm^{-3} for the 925 °C-reduced sample [represented by trace (e) in Fig. 1]. Although not illustrated, we observed values of α_{max} that were over 135 cm^{-1} in other $LiTaO_3$ samples reduced at higher temperatures, thus indicating concentrations greater than 7.8×10^{17} cm^{-3}. It is important to emphasize that these numbers are lower bounds on the concentrations because of our assumptions. The actual values are possibly an order of magnitude higher in each case because we have neglected much of the induced absorption in the spectral region between the 460-nm peak and the band edge, and the oscillator strength is more likely between 0.1 and 1.0.

The optical-absorption spectrum of a heavily reduced $LiTaO_3$ crystal undergoes major changes when the sample is bleached for a few minutes at 77 K with an unfiltered 150-W xenon lamp. These effects are shown in Fig. 2 for a sample that has been reduced at 900 °C. Trace (a) in Fig. 2 was taken after the reduction [and is the same as trace (d) in Fig. 1] while trace (b) in Fig. 2 was taken after the 77-K optical bleach. The peak at 460 nm initially present after the reduction is destroyed by this optical bleach and a new peak appears near 570 nm. Also, the optical absorption throughout the region from approximately 500 nm to the band edge decreases as a result of the bleach. This converted optical-absorption spectrum shown in trace (b) of Fig. 2 is thermally stable as long as the crystal remains near liquid-nitrogen temperature, but it reverts to the before-bleach condition shown in trace (a) when the crystal is returned to room temperature.

A new ESR spectrum, which we assign to Ta^{4+} ions, appears when the reduced $LiTaO_3$ crystals are optically bleached at 77 K or lower temperatures. Conversion of the 460-nm peak to the 570-nm peak, which is described in the previous paragraph, coincides with the appearance of the ESR spectrum. Also, the Ta^{4+} ESR spectrum is thermally stable as long as the sample remains near or below 77 K, as were the changes in the optical spectrum. The Ta^{4+} ESR spectrum disappears upon warming to room temperature.

The Ta^{4+}-ion ESR spectrum is shown in Fig. 3, along with a separate, sharp ESR line at slightly lower field which is due to an unidentified transition-metal-ion impurity. These data were obtained at 17 K with the magnetic field oriented perpendicular to the c axis of the crystal. There are eight hyperfine lines in the Ta^{4+} spectrum, corresponding to the $I = \frac{7}{2}$ nuclear spin of the 100% abundant ^{181}Ta isotope. However, the hyperfine separations within the eight-line Ta^{4+} pattern are not constant. In Fig. 3, the separations vary from about 350 to over 400 G when progressing from the low- to high-field side of the spectrum. Also, the hyperfine-component linewidth increases from the low- to

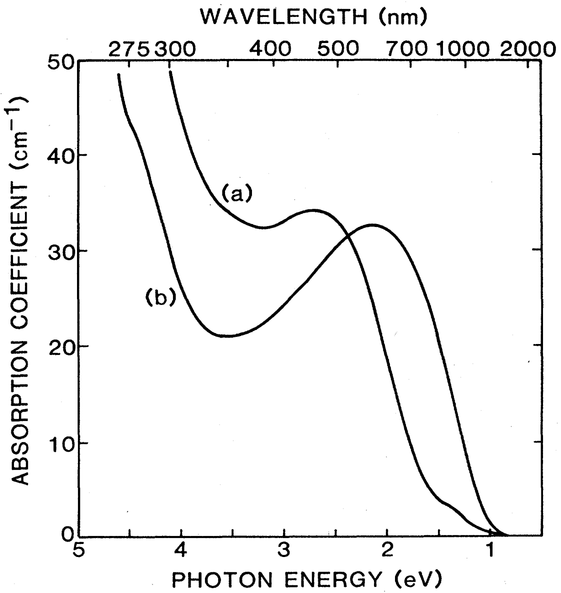

FIG. 2. Effect of a 77-K optical bleach on the optical-absorption spectrum of a $LiTaO_3$ crystal that had been reduced for 1 h in argon at 900 °C. Trace (a) was taken before the bleach and trace (b) was taken after the bleach.

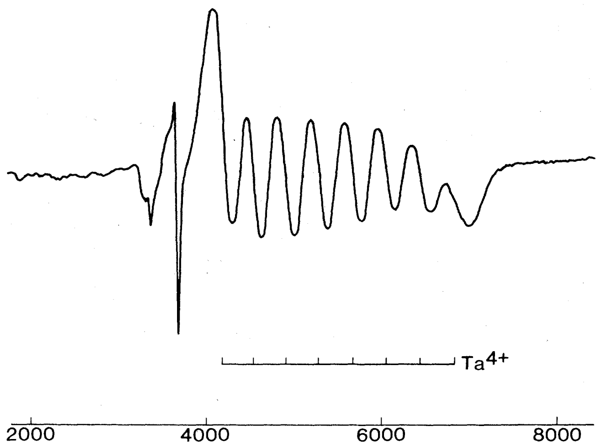

FIG. 3. ESR spectrum of Ta^{4+} ions in $LiTaO_3$. The microwave frequency was 9.449 GHz, the temperature was 17 K, and the magnetic field was oriented perpendicular to the c axis of the crystal.

high-field side. The g value for the Ta^{4+} ion is approximately 1.2 when the magnetic field is perpendicular to the c axis. Except for the larger hyperfine splitting and increased g shift, the Ta^{4+}-ion ESR spectrum is similar to that of Nb^{4+} in $LiNbO_3$.[3,8] A more detailed investigation of the ESR spectrum of the Ta^{4+} ions, including additional production methods and an angular dependence study, is in progress and will be reported in a future paper.

IV. DISCUSSION

The primary question raised by our present investigation concerns the identities of the defects responsible for the observed optical-absorption spectra in reduced $LiTaO_3$. There are three specific results reported in the present paper which help determine the appropriate models of these defects. First, we have found that the intense "blackening" introduced during the reducing treatments can easily be reversed by heating the crystal in an oxygen-rich atmosphere. Second, the defect concentrations estimated from our 460-nm optical-absorption data are greater than 7.8×10^{17} cm^{-3}, which corresponds to more than 60 ppm (relative to either the Li or Nb sites) and is well above expected transition-metal-ion impurity levels for these undoped materials. Third, we have observed major changes in the optical spectra, and the simultaneous appearance of an intense Ta^{4+} ESR spectrum, when a reduced crystal is optically bleached near or below 77 K.

These results are most easily interpreted in terms of oxygen vacancies in the $LiTaO_3$. The removal of the black coloration when the reduced samples are reheated in an oxygen-rich atmosphere provides the initial suggestion that oxygen vacancies may be involved. However, this observation alone is not conclusive. The concentration of observed defects is significantly greater than the 1–20 ppm level that is expected for transition-metal-ion impurities, and this eliminates the possibility that the absorptions arise simply from valence changes of such impurities. Other possibilities for the source of the optical absorption are vacancies and interstitials of the constituent metal ions of $LiTaO_3$, or valence changes of these ions. Trapped electrons on the tantalum ions can be eliminated from consideration for the 460-nm peak because these ions are not present immediately after reduction but instead require a subsequent optical bleach to be formed, and we do not expect either Li^0 or Li^{2+} ions to be stable within the lattice. Strong evidence in favor of oxygen vacancies comes from the low-temperature optical conversion and the associated appearance of the Ta^{4+} ESR spectrum. The Ta^{4+} ion represents a trapped electron, and is formed when the bleaching light releases an electron from a donor defect. The oxygen vacancy containing two electrons would be an obvious choice for such a donor.

In summary, we offer the following explanation of the results presented in this paper. Reducing a $LiTaO_3$ crystal in an argon atmosphere causes oxygen vacancies to be formed. Each oxygen vacancy contains two electrons initially and is a neutrally charged defect which is responsible for the optical-absorption peak at 460 nm. Subsequent optical bleaching at or below 77 K removes one of the electrons from the oxygen vacancy. The oxygen vacancy with its remaining electron has an effective positive charge relative to the lattice. The electron that was removed from the vacancy becomes trapped at a Ta^{5+} ion, thus forming a Ta^{4+} ion. Both the single-electron oxygen vacancies and the Ta^{4+} ions may contribute to the optical-absorption spectrum (i.e., containing the 570-nm peak) which is present after the bleach. This general description of defect behavior in $LiTaO_3$ during reductions and subsequent bleaching is directly analogous to the assignments made as a result of similar experiments in $LiNbO_3$.[3,4] As was the case in $LiNbO_3$, an ESR spectrum arising from the one-electron oxygen vacancies was not observed during our investigation of $LiTaO_3$.

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