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1989 J. Phys.: Condens. Matter 1 10015

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High-energy electron irradiation of stoichiometric LiNbO_3

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Received 13 July 1989

Abstract. High-energy electron irradiation of stoichiometric LiNbO_3 produces a broad absorption band similar in form and structure to that observed in electron-irradiated congruent samples and in samples thermochemically reduced. The band shows a definite energy threshold for production, consistent with oxygen displacement damage. The observations, adequately explained in terms of F and F^+ centres, imply that oxygen vacancies also play a role in reduced samples.

1. Introduction

LiNbO_3 is a relevant technological material for opto-electronic applications because of its electro-optic and photorefractive behaviour [1, 2]. The photorefractive effect is dependent on certain impurities and/or lattice defects acting as donors and acceptors for free carriers (electrons or holes). However, to date, despite an extensive research effort, our knowledge of the defects and processes involved is still very limited.

In materials not susceptible to radiolysis, high-energy electron irradiation will introduce primary defects through atomic displacement damage. Recent experiments using such a technique to irradiate congruent LiNbO_3 single-crystal samples have shown the existence of a well defined energy threshold for the production of a broad structured optical absorption band at about 500 nm [3]. The observed threshold is consistent with oxygen displacement and the induced absorption band was subsequently attributed to oxygen vacancy centres, either F or F^+ . These results from the electron irradiation experiments are highly relevant to our understanding of the defects introduced during thermochemical reduction, since the observed absorption bands are identical, in both form and structure for the two cases. This would therefore imply that oxygen vacancies also play an important role in reduced LiNbO_3 .

The problem is still however a matter of controversy due to the different views held as to the microscopic model for reduction. One model described in [4, 5] proposes the production of Nb_{Li} anti-sites but not oxygen vacancies during reduction, whereas in [6] a model involving oxygen vacancies is suggested. In order to throw more light on the situation, and to be able to differentiate between the two views, further experiments have been performed by electron irradiating stoichiometric LiNbO_3 at temperatures down to -50°C . It is well known that the physical behaviour of LiNbO_3 is markedly dependent on the Li-to-Nb ratio, and in particular the reduction-induced colouration is

far less efficient for the stoichiometric than for the Li-deficient congruent material [7]. Hence, although the primary displacement damage process during electron irradiation will remain essentially unchanged for the two cases, the subsequent stabilisation processes may well be different.

The results to be reported here again indicate the importance of oxygen vacancy production. The radiation-induced broad band is far less stable than in the congruent case, and the observed thermal annealing of the lattice damage is consistent with a situation involving oxygen vacancies and interstitials rather than large lattice rearrangement during irradiation. The absorption band structure, both here and in the congruent case [3], indicates that the presence of three or four bands is responsible for the overall observed broad band. This is in agreement with other results in which an indication of structure is observed [7–10].

The observations may be adequately explained in terms of F, F⁺ and Nb⁴⁺ centres. A consistent assignment for the two types of vacancy centre is made by means of comparison with Al₂O₃.

2. Experimental details

The experimental work has been performed in a sample chamber mounted in the beam line of a HVEC 2 MeV Van de Graaff accelerator. The set-up permits samples to be electron irradiated in a high vacuum (less than 3×10^{-6} mbar) at any temperature between about -150 and 950 °C. An on-line spectrophotometer system enables *in situ* optical absorption and emission spectra to be measured, either during or following irradiation. In this way, stoichiometric LiNbO₃ single crystals of approximately $5 \times 5 \times 1$ mm (kindly supplied by the Hungarian Academy of Sciences) have been irradiated at different beam energies and temperatures, and the induced optical absorption spectra measured. To determine the energy threshold for the radiation-induced optical absorption, samples have been electron irradiated at 20 °C with the beam at 45° to the 5×5 mm face from 0.25 to 0.45 MeV, and edge on between 0.8 and 1.6 MeV, as previously described [3]. Following the threshold determination, a single sample was then irradiated with 1.6 MeV electrons at 20 and -50 °C to study the growth of the induced absorption during irradiation. Following irradiation the sample was linearly heated to either 70 or 350 °C to study the thermal annealing of the radiation-induced absorption and then reirradiated to observe the effect of the annealing.

3. Results

An irradiation-induced optical absorption spectrum together with the threshold measurement results are shown in figure 1. The absorption corresponding to an irradiated congruent sample is also given for comparison. The radiation-induced broad optical absorption band peaked at about 540 nm is very similar to that observed in the congruent case and furthermore shows exactly the same energy threshold for production, i.e. 0.30 MeV [3]. However, the induced band is highly unstable and anneals out by about 70 °C. The detailed behaviour is complex, as may be seen in figure 2. On irradiating at 20 °C with electrons above the threshold energy, the 540 nm band grows slowly with increasing irradiation time. On heating to 70 °C following irradiation, the band anneals out in one single stage (labelled 2), leaving a small residual structured absorption with

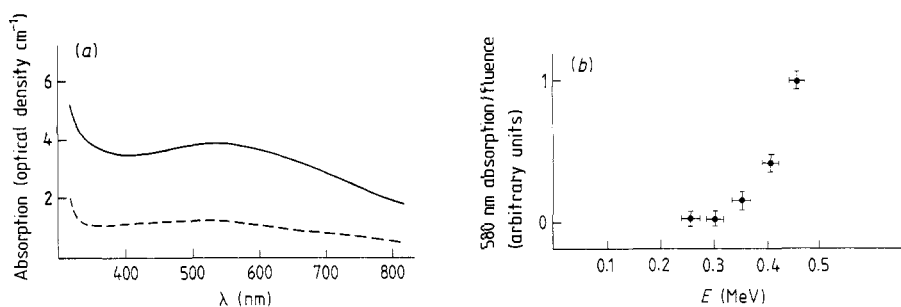


Figure 1. (a) Absorption spectra induced in stoichiometric (—) and congruent (---) LiNbO_3 on irradiation with 1.8 MeV electrons, to a fluence of 10^{18} at 20 °C. (b) Induced absorption at 580 nm as a function of electron beam energy, for a fluence of 2×10^{17} at each energy.

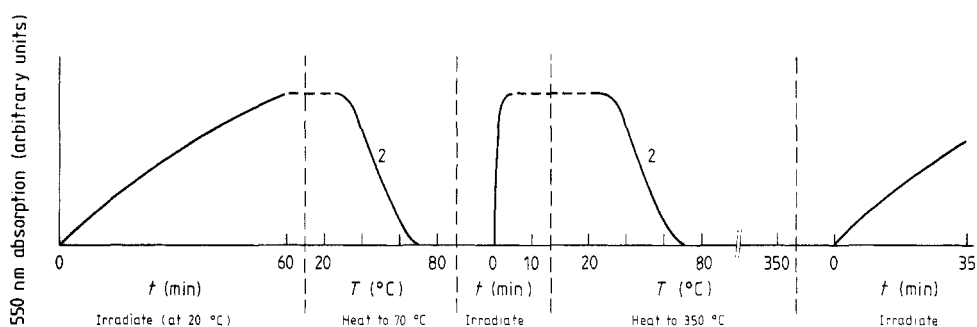


Figure 2. Irradiation and annealing behaviour of the 540 nm band for irradiation at 20 °C.

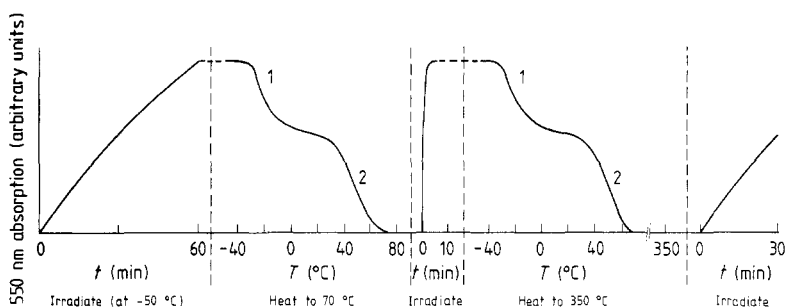


Figure 3. Irradiation and annealing behaviour of the 540 nm band for irradiation at -50 °C.

evidence of components at about 400, 500 and 750 nm (see figure 5(d) later). If the sample is then reirradiated at 20 °C, the original broad band at 540 nm immediately recovers the intensity prior to annealing. However, on subsequent heating to 350 °C, full annealing is achieved with no residual absorption, and this time on reirradiation at 20 °C the 540 nm band again grows slowly with increasing time from the initial zero height.

When the irradiation temperature is lowered to -50 °C, the behaviour of the band is very similar to that described for the 20 °C irradiation. However, in this case (figure 3) the annealing shows two stages, labelled 1 and 2, stage 2 being identical with that observed for the 20 °C irradiation (figure 2). Figures 4(a), 4(b) and 4(c) shows the band induced by irradiation at -50 °C, that remaining following annealing of stage 1 and the

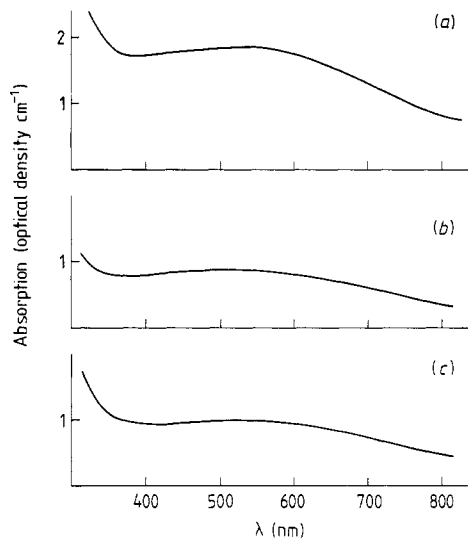


Figure 4. Absorption spectra at $-50\text{ }^{\circ}\text{C}$ for the bands annealed in stages 1 and 2 (a) following irradiation at $-50\text{ }^{\circ}\text{C}$, i.e. contains stages 1 and 2; (b) following annealing to $10\text{ }^{\circ}\text{C}$, i.e. contains only stage 2; (c) difference between (a) and (b), i.e. equivalent to stage 1.

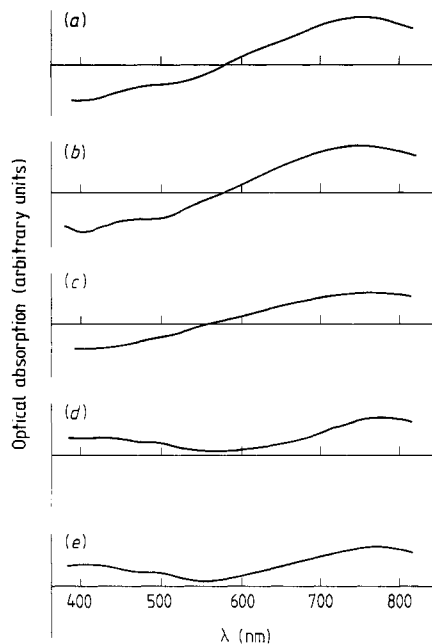


Figure 5. (a) Radiation-induced band transfer, stoichiometric sample. (b) Thermally induced band transfer, congruent sample. (c) Thermally induced band transfer, stoichiometric sample. (d) Residual absorption following annealing to $70\text{ }^{\circ}\text{C}$. (e) Difference between congruent and stoichiometric absorption bands.

difference between these two spectra, respectively. It is clear that the same broad band at 540 nm is involved in the two annealing stages.

During irradiation the broad 540 nm band changes shape, the 750 nm side of the spectrum is enhanced while the region of $400\text{--}500\text{ nm}$ is suppressed (figure 5(a)). This radiation-induced transfer process is identical with that observed when an electron-irradiated congruent sample is heated (figure 5(b)) [3] and has also been observed in thermochemically reduced samples [10]. Identical behaviour is observed on heating the residual absorption left over following the stage 2 annealing to $70\text{ }^{\circ}\text{C}$, (figure 5(c)).

4. Discussion

As in the case of results on congruent samples already published [3], the results presented in figure 1 indicate that displacement damage is involved in the production of the defects responsible for the radiation-induced broad absorption band in stoichiometric LiNbO_3 crystals. The fact that this band, although annealing out by $70\text{ }^{\circ}\text{C}$, can be restored by a very short reirradiation, is indicative of the existence of some basic lattice damage, which itself only anneals out by about $350\text{ }^{\circ}\text{C}$ (see figure 2). The very short irradiation time required to restore the absorption is consistent with a purely electronic process being responsible for the colouring or bleaching of the induced lattice defect. This has been confirmed by performing the reirradiation below the threshold energy, where one still observes rapid restoration of the band. Since the observed threshold energy is consistent

with oxygen displacement [3], it is reasonable to suggest that the lattice damage is related to oxygen vacancies and their corresponding interstitials trapped within the lattice. The perfect thermal reversibility of the process on annealing to above 350°C together with the low irradiation temperature are more consistent with a vacancy interstitial situation rather than large lattice rearrangement during irradiation. The complete annealing observed above 350°C will then be due to the thermal release of trapped oxygen interstitials and their recombination with vacancies. In consequence, one should associate the induced absorption with F-type centres. This is in agreement not only with the threshold measurements but also with general results for other oxides such as MgO , Al_2O_3 and MgAl_2O_4 in which electron irradiation primarily produces F-type centres [11]. F-type centres have in fact already been proposed to account for the absorption in electron-irradiated [3] and reduced [8, 12] LiNbO_3 crystals.

Comparison of spectra following different irradiation and annealing treatments (figures 5(a)–5(d)) as well as the difference found for the irradiation-induced absorption in samples of different stoichiometries (figure 5(e)) indicate that the broad absorption band is complex, consistent with an underlying band at about 540 nm together with superimposed bands at approximately 400, 500 and 750 nm. Systematic work on LiNbO_3 samples of different stoichiometries and purities, both reduced and irradiated, has produced clear evidence for bands at 3.9 eV (320 nm), 3.1 eV (400 nm), 2.3 eV (540 nm) and 1.6 eV (750 nm) [7–9]. This structure is in agreement with the results reported here.

For the main band at 540 nm the most reasonable possibility is that it corresponds to an F centre and hence, being diamagnetic, explains the absence of any EPR signal. In this case the annealing data in figures 2 and 3 can be interpreted in terms of recombination of trapped holes with F centres leading to F^+ centres, the two-stage annealing being due to hole traps of different thermal stabilities. These F^+ centres must account in part for the residual absorption observed following annealing to 70°C . However, in order to explain the observed rapid recovery of the band on reirradiation, one must consider the non-conventional structure for the F^+ centre proposed in [13]. This model, in which two deeply trapped electrons are stabilised by a nearby hole, has been used successfully to describe the F and F^+ centres in Al_2O_3 whose structure is similar to that of LiNbO_3 , and in which F^+ -to-F conversion is observed [14].

The band at 750 nm is well documented and associated with Nb^{4+} small polarons [15]. The assignment for the other components is less clear. However, the 750 nm band is in some way closely related to the two bands at 400 and 500 nm in the sense that they can be reversibly converted into each other by either thermal or optical excitation (figures 5(a)–5(c) and [3, 8, 10]). It is reasonable to suggest that the bands correspond to different configurations of the F^+ centre, with the electron associated either with the vacancy (400 and 500 nm bands) or with the neighbouring Nb ion (750 nm band). Such a non-localised F^+ centre would not be expected to give rise to a strong characteristic EPR signal. The fact that these bands are more prominent in congruent samples (figure 5(e) and [7]) could in some way be related to Li_{Nb} anti-sites [16] which enhance their production.

5. Conclusions

The electron irradiation experiments on both stoichiometric and congruent LiNbO_3 crystal samples indicate that the broad structured optical absorption observed for both irradiated and reduced samples is closely related to oxygen vacancies. The band structure

may be adequately explained in terms of F-type centres. It is important to note, however, that conventional colour centre models lead to inconsistencies and that one must employ the description given in [13] for the F⁺ centre. This is indeed reasonable given the similarity between LiNbO₃ and Al₂O₃.

Acknowledgments

We wish to thank Mr E Sánchez-Cabezudo for his help with these experiments, and also the Hungarian Academy of Sciences to which we are indebted for the stoichiometric crystal samples. One of us (FA-L) acknowledges partial support of a CAYCIT Grant (MAT 88-0431).

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