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## Colouring and annealing behaviour of electron irradiated $\text{LiNbO}_3:\text{Fe}$

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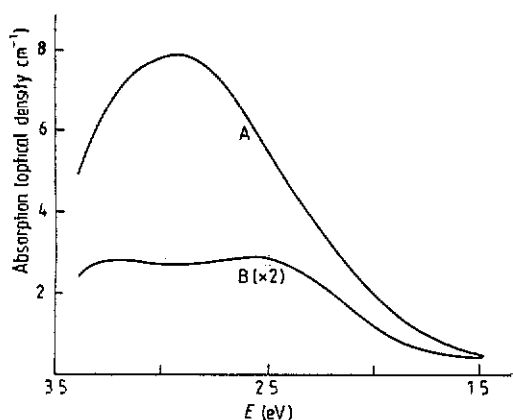
**Abstract.** Low dose electron irradiation of  $\text{LiNbO}_3:\text{Fe}$  induces an optical absorption band at 2.95 eV. The same effect is obtained by purely ionizing bremsstrahlung radiation. At variance with previous assignments, the band is associated with  $\text{Fe}^{2+}$ . It shows the same thermal annealing behaviour as that found for F-centres in irradiated stoichiometric  $\text{LiNbO}_3$ , confirming a hole recombination mechanism;  $\text{Fe}^{2+} + \text{h} \rightarrow \text{Fe}^{3+}$ . For high dose irradiation additional bands are observed, which are attributed to oxygen vacancy centres ( $\text{F}^-$ ) caused by displacement damage.

### 1. Introduction

The electro-optic and photo-refractive behaviour of  $\text{LiNbO}_3$  makes it of technological importance for opto electronic applications [1, 2]. The photo-refractive effect [3] is due to the presence of certain impurities and/or lattice defects that act as donors and acceptors for free carriers (electrons or holes). However, present knowledge of the defects and processes involved, which would permit one to optimize the photo-refractive behaviour, is still very limited [4].

As in many oxides, iron plays a particularly active role. In  $\text{LiNbO}_3:\text{Fe}$  it is known to be present as both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , the actual proportion being dependent on the thermochemical history (reduction or oxidation) of the material [5–8]. In the holographic process  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are generally assumed to exchange electrons and act respectively as donor and acceptor centres in the light and dark regions [8–11]. In contrast under uniform UV or x-ray irradiation [12–15], a net conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  occurs which must perforce involve impurity or defect centres other than Fe. However, to date, little is known about their nature.

The work presented here, in which  $\text{LiNbO}_3:\text{Fe}$  has been irradiated under different conditions of temperature, radiation type, and total radiation dose, provides information as to the character and thermal stability of these centres. The results are closely related to recent observations in electron irradiated stoichiometric  $\text{LiNbO}_3$  [16], and indicate that hole rather than electron trapping is involved. Furthermore, the results help to



**Figure 1.** Radiation induced absorption spectra in  $\text{LiNbO}_3:\text{Fe}$  relative to the un-irradiated spectrum. Curve A, irradiation at  $-50^\circ\text{C}$  to a dose of  $10^{14}$  electrons  $\text{cm}^{-2}$ ; curve B, irradiation at  $40^\circ\text{C}$  to  $10^{17}$  electrons  $\text{cm}^{-2}$ .

clarify a certain confusion as to the assignments of the band components observed in pure and iron doped  $\text{LiNbO}_3$ .

## 2. Experimental procedure

$\text{LiNbO}_3$  single crystals have been pulled from grade I Johnson–Matthey powder under pure oxygen at 1.1 atm, with a 0.1 mol% concentration of  $\text{Fe}_2\text{O}_3$  added to the melt. The experimental work has been performed in a sample chamber mounted in the beam line of a HVEC Van de Graaff accelerator. The set up permits samples to be irradiated in high vacuum (less than  $3 \times 10^{-6}$  mbar) either directly with electrons of up to 2 MeV, or indirectly with bremsstrahlung radiation produced by stopping the electron beam in a gold target. The sample may be maintained at any temperature between about  $-150$  and  $+950^\circ\text{C}$ , or linearly heated or cooled between these limits. An on-line spectrophotometer system enables 'in situ' optical absorption spectra to be measured either during or following irradiation. In this way samples of approximately  $5 \times 5 \times 1 \text{ mm}^3$  have been irradiated at  $-50$  and  $+40^\circ\text{C}$  by 0.25 and 1.60 MeV electrons, and with bremsstrahlung radiation. The low temperature irradiations were carried out with small beam currents  $\sim 2 \times 10^{-9} \text{ A cm}^{-2}$  up to total doses of approximately  $10^{14}$  electrons  $\text{cm}^{-2}$ , corresponding to an ionizing dose of  $\sim 1$  Mrad. The bremsstrahlung irradiations were carried out up to a total dose of  $5 \times 10^4$  rad. The  $40^\circ\text{C}$  irradiations were carried out at high beam currents up to total doses of  $\sim 10^{17}$  electrons.

Following irradiation the samples were heated to either  $70$  or  $250^\circ\text{C}$  to study the thermal annealing of the radiation induced absorption, and then re-irradiated to observe the effect of the annealing.

## 3. Results

Low dose irradiation of  $\text{LiNbO}_3:\text{Fe}$  at  $-50^\circ\text{C}$  with 1.60 MeV electrons induces a broad absorption band peaked at about 2.95 eV, as shown in figure 1. During irradiation the

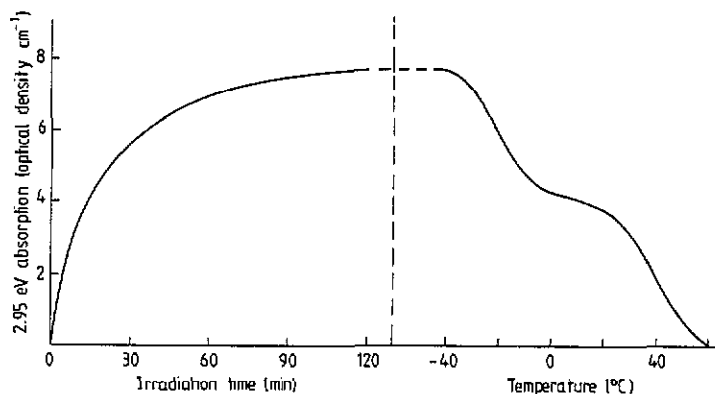


Figure 2. Radiation growth and thermal annealing for the 2.95 eV  $\text{Fe}^{2+}$  band.

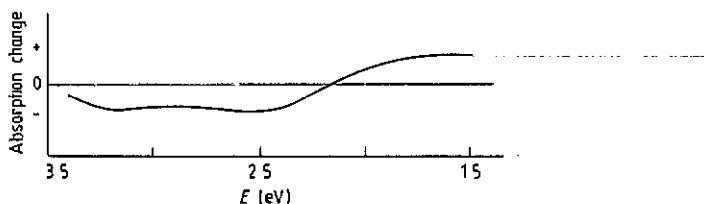
band grows rapidly, approaching saturation by about 1 Mrad, see figure 2. Irradiation at 0.25 MeV has almost the same effect, while the bremsstrahlung irradiations produce an identical but much smaller band.

The observed 2.95 eV band is not the same as that produced by electron irradiation of stoichiometric or congruent  $\text{LiNbO}_3$  where broad structured bands are observed at about 2.3 and 2.5 eV respectively [16, 17]. On heating to 70 °C following irradiation, the 2.95 eV band anneals out in two distinct stages as may be seen in figure 2. These two stages occur at the same temperatures as those observed for the 2.3 eV band annealing in stoichiometric  $\text{LiNbO}_3$  [16]. On re-irradiation and thermal annealing, exactly the same behaviour was observed. Following several irradiation and annealing cycles, evidence was found for a residual effect in the absorption spectrum that showed only partial annealing by 250 °C. To study this effect an irradiation was carried out to a higher total dose ( $\sim 10^{17}$  electrons) at 40 °C. Since it is unstable at this temperature, the 2.95 eV band was not observed. However, a different band was produced with a maximum at 2.5 eV and evidence of a further band at 3.2 eV, figure 1. This band structure is identical to that observed in both congruent and stoichiometric  $\text{LiNbO}_3$ , and shows the same reversible changes in the shape of the spectrum as the sample is heated and cooled, figure 3 [16, 17].

#### 4. Discussion

Low temperature electron irradiation of  $\text{LiNbO}_3:\text{Fe}$  induces a broad optical absorption band peaked at 2.95 eV (figure 1). The low total dose required ( $\sim 10^{14}$  electrons  $\text{cm}^{-2}$ ), strongly suggests a purely electronic process due to the ionizing effect of the radiation. This has been confirmed by irradiating with electrons below the oxygen displacement threshold [17], and with bremsstrahlung radiation. The induced absorption band is clearly different from that produced in pure (congruent or stoichiometric) crystals, where a broad structured band peaked at about 2.5 eV is observed [16, 17].

Optical [12, 13] and Mössbauer [14, 15] spectroscopy of  $\text{LiNbO}_3:\text{Fe}$  have shown that ionizing radiation induces the reaction  $\text{Fe}^{3+} + h\nu \rightarrow \text{Fe}^{2+} + \text{hole}$ . One should, therefore, attribute the observed 2.95 eV band to either  $\text{Fe}^{2+}$  or a hole centre. The thermal annealing of the band (figure 2) shows the same two distinct stages as those



**Figure 3.** Effect of heating or cooling on the absorption spectrum induced by high dose irradiation (figure 1, curve B). On heating, the 2.5 and 3.2 eV bands decrease while a band at  $\sim 1.6$  eV increases. The reverse occurs on cooling.

observed for the F-band annealing in stoichiometric  $\text{LiNbO}_3$ , where it was proposed that hole release from distinct traps was responsible for the two-stage annealing [16]. This implies that one should assign the 2.95 eV band to  $\text{Fe}^{2+}$ , and the observed annealing to  $\text{Fe}^{2+} + \text{h} \rightarrow \text{Fe}^{3+}$ .

This assignment is in disagreement with previous results that have associated the  $\text{Fe}^{2+}$ , produced in thermochemical reduction experiments, with a band at 2.5 eV [5, 8]. However, reduction treatments are likely to generate a substantial concentration of oxygen vacancy centres absorbing at approximately 2.5 and 3.2 eV, leading to an erroneous assignment. In effect the detailed EPR and optical data reported in [8] are not inconsistent with the assignment proposed here. Moreover, it provides a satisfactory explanation for the peak of the photorefractive sensitivity observed at approximately 3.1 eV in  $\text{LiNbO}_3:\text{Fe}$  [18].

At higher irradiation doses ( $\geq 10^{17}$  electrons  $\text{cm}^{-2}$ ) with electrons above the oxygen displacement threshold, the shape of the absorption spectrum progressively approaches that for pure samples due to the growth of bands at 2.5 and 3.2 eV corresponding to oxygen vacancy centres (figure 1). That they are the same bands as those observed in the pure material is confirmed by their behaviour under heating or cooling (figure 3 and [16, 17]). As a consequence, the  $\text{Fe}^{2+}$  band at 2.95 eV can only be observed clearly at low enough doses to avoid significant vacancy centre production. This facility, of being able to selectively induce purely electronic charge exchange processes or add vacancy centres using particle irradiation techniques, is clearly not available in reduction experiments.

## 5. Conclusions

Low and high dose electron irradiations of  $\text{LiNbO}_3:\text{Fe}$  indicate that, at variance with previous assignments, the  $\text{Fe}^{2+}$  band occurs at 2.95 eV, while F-type vacancy centres ( $\text{F}^+$ ) absorb at 2.5 and 3.2 eV. The results are consistent with a hole transfer and trapping process being responsible for the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  conversion.

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## References

- [1] Gunter P and Huignard J P ed 1988 *Photorefractive Materials and their Applications* vol 1 (Berlin: Springer)
- [2] Holman R L and Smyth D M ed 1985 *Processing of Guided Wave Optoelectronic Materials* (Chicago: SPIE)
- [3] Gunter P 1982 *Phys. Rep.* **93** 201-98
- [4] Agulló-López F and Cabrera J M 1989 *Properties of LiNbO<sub>3</sub>* (Data review) INSPEC, London
- [5] Clark M, G, Di Salvo F J, Glass A M and Peterson G E 1973 *J. Chem. Phys.* **59** 6209-19
- [6] Keune W, Date S K, Dezsi I and Gonzer U 1975 *J. Appl. Phys.* **46** 3914-24
- [7] Ketchum J L, Sweeney K L, Halliburton L E and Armington A F 1983 *Phys. Lett.* **94** 450-3
- [8] García-Cabañes A, Arizmendi L, Cabrera J M and Agulló-López F 1987 *Cryst. Latt. Defects Amorph. Mater.* **15** 131-5
- [9] Phillips W, Amodet J J and Staebler D L 1972 *RCA Rev.* **33** 94-109
- [10] Kratzig E and Kurz H 1977 *Opt. Acta* **24** 475-8
- [11] Orlovski R and Kratzig E 1978 *Solid State Commun.* **27** 1351-4
- [12] Bollman W 1980 *Krist. und Tech.* **15** k13-6
- [13] Glass A M, Peterson G E and Negran T J 1972 *Symp. on Laser Materials (Boulder, CO, 1972)* NBS special publication 372 (Washington, DC: US GPO)
- [14] Lauer J, Pfannes H D and Keune W 1979 *J. Physique Coll.* **40** C2 561-3
- [15] Engelmann H and Gonser U 1980 *Ferroelectrics* **23** 97-9
- [16] Hodgson E R and Agulló-López F 1989 *J. Phys.: Condens. Matter* **1** 10015-20
- [17] Hodgson E R and Agulló-López F 1987 *Solid State Commun.* **64** 965-8
- [18] Baquedano J, Canascosa M, Arizmendi L and Cabrera J M 1987 *J. Opt. Soc. Am. B* **4** 309-12