Contributing bands to the optical absorption of reduced $LiNbO_3$: thermal and optical excitation

Contributing bands to the optical absorption of reduced LiNbO₃: thermal and optical excitation

A García-Cabañes, E Diéguez, J M Cabrera and F Agulló-López

Departamento de Física Aplicada C-IV, Universidad Autónoma, Madrid 28049, Spain

Abstract. The effect of thermal and optical excitation on the optical absorption band of reduced LiNbO₃ has been investigated for crystals with different Li/Nb ratios. Fe- and Cu-doped samples were also studied. Although the main effect of the excitation is to enhance the infrared part of the spectra at the cost of the ultraviolet-visible region, a number of new features appear depending on stoichiometry and doping. In all cases, the effect of thermal excitation is reversible. The spectra for all undoped samples, before as well as after the various treatments were fitted with four gaussian bands peaking at 1.6, 2.3, 3.1 and 3.9 eV, Additional bands have to be used to fit the spectra for doped crystals (2.5 eV for Fe-doping and 2.8 eV and 3.3 eV for Cu-doping). The possible origin of the bands is discussed in relation to other available information, but a definite assignment cannot be offered yet.

1. Introduction

As many other oxides, LiNbO₃ can easily be reduced by heating in neutral (N₂, Ar, . . .) or reducing (H₂, CO/CO₂ mixture, vacuum, . . .) atmospheres. Reducing or oxidising LiNbO₃ is of major interest in connection with photorefractive and other non linear optics applications. The reduction process induces a rather strong and broad optical absorption band extending from the UV absorption edge to the near IR. The origin of this band is presently a matter of controversy. Although in early and recent LiNbO₃ papers the broad absorption has been attributed to oxygen vacancy centres [1, 2], the lack of any EPR signal from F^+ centres, difficulties in understanding some properties of the absorption spectrum, and the singular behaviour of Nb^{+5} ions in the LiNbO₃ lattice stimulated some authors to propose Nb^{+4} (small polaron) [3] and Nb^{+4}–Nb^{+4} (bipolaron) [4] centres as responsible for this absorption. This interpretation is based on the model put forward by Smith *et al* [5] for the reduction process in which no oxygen vacancies are required for the oxygen loss. The F and F^+ centre model is mainly based on the early paper by Jorgensen and Barlett [6] on high temperature conductivity data.

The reduction model requiring oxygen vacancies has recently received a strong experimental support. Hodgson and Agulló-López [7] have reported the observation of the same absorption band as that induced by reduction, when producing oxygen displacement in the LiNbO₃ lattice by electron irradiation. On the other hand, in a recent theoretical paper DeLeo *et al* [8] have pointed out that oxygen vacancies in LiNbO₃ are not likely to trap electrons to form F centres, electrons being preferentially trapped at those niobium ions closest to the oxygen vacancies. This result would explain

Table 1. Stoichiometry and doping of used samples.

Label	[Li]/[Nb] melt	[Li]/[Nb] crystal(*)	Dopant mol %	Grown in
A	1.2	1.0	—	CPL
B	1.1	0.976	—	CPL
C	0.833	<0.92	—	CPL
D	congruent	—	0.1 Fe_2O_3	UAM
E	congruent	—	0.1 CuO	UAM
F	congruent	—	—	UAM

CPL: Research Laboratory for Crystal Physics, Hungarian Academy of Sciences.
UAM: Departamento de Física Aplicada, Universidad Autónoma de Madrid.
* see [13].

the failure to observe any EPR signal arising from electrons trapped in the potential well of the oxygen vacancy (the spectra would be likely similar to that reported for Nb^{+4} [9]).

In this paper we have undertaken a systematic analysis of the different features exhibited by the optical absorption of reduced $LiNbO_3$ in a variety of physical situations. These include new data on thermal and optical excitation of reduced crystals with different stoichiometries, as well as iron-doped samples. The new experiments extend those already performed on congruent samples [4] and so provide additional relevant information for the analysis of the spectra and characterisation of the involved defects centres. In comparison to the data on congruent samples, new features are now observed for the other stoichiometries and the doped crystals. However, in all cases the high energy side of the spectra are observed to decrease to the benefit of the low energy side, either by thermal heating or optical illumination.

In addition to the new spectra now measured, some other ones on the effect of doping and stoichiometry, including some previously published [10], have also been analysed. By handling all this extensive information, it has been possible to obtain a reliable set of bands that provide a good fit to all available spectra. Some of the proposed components have been already inferred from previous optical [2, 10] and XPS experiments [12]. The relative height of the various bands is sensitive to crystal stoichiometry and physical treatment, so yielding some hints on the possible nature of the responsible centres. Various reasonable alternatives are discussed, although the problem still remains open.

2. Experimental

Pure and doped $LiNbO_3$ crytals were pulled from congruent melt (Li/Nb = 0.945) in our laboratory using Johnson Matthey chemicals (Puratronic Grade I) as starting powders. Non-congruent crystals, kindly provided by K. Pólgar, were pulled at the Research Laboratory for Crystal Physics (Budapest). Crystal blocks were x-ray oriented, sawn and polished in a conventional way to obtain $1 \times 10 \times 10$ mm^3 sized plates with their c-axes parallel to the large faces. Actual stoichiometry of non congruent samples were determined by the absorption edge method [13]. Table 1 gives details of the different samples used throughout this work. Optical absorption spectra were taken with a Cary 17 spectrophotometer from 300 nm to 2000 nm.

The same set of reduction experiments and subsequent spectrum measurements were carried out for all the samples indicated in table 1. First, the samples were oxidised

by keeping them in oxygen atmosphere for 2 h at 950 °C. Then, they were reduced at increasingly higher temperatures from 400 °C up to 900 °C in 100 °C steps. Reduction was performed by maintaining the samples in a vacuum for 2 h at a given temperature. Heating and cooling rates ranged between 50 °C/h and 60 °C/h in all cases. To avoid any direct contact between the alumina crucible and the samples, which is known to produce chemical reaction at high temperature, platinum foil was used to separate them. Further details are given in § 3.1.

Changes induced by either optical or thermal bleaching in these spectra have also been analysed. Optical bleaching and subsequent measurement of the modified spectra have been carried out at 80 K. An Applied Photophysics Irradiator model UV-90 (xenon lamp plus monochromator) was used to illuminate the samples with an intensity of 1 mW/cm² and a bandwidth of about 16 nm. A small furnace, purposely designed to fit the spectrophotometer beam compartment, enabled heating the sample up to 250 °C in rough vacuum. Spectra of reduced LiNbO₃ samples have been taken and analysed in different experimental conditions, as described above.

3. Results

3.1. Reduction

In a previous paper [11], a strong inhibition of the reduction induced absorption, as well as differences in the shape of the band, were found for stoichiometric samples of LiNbO₃. Hint of inhomogeneities in the reduction process were also reported in that paper for this and other non-congruent compositions. Therefore, a detailed research of the reduction induced absorption in such a sample has been undertaken in the present paper. A parallelepipedic block of pure LiNbO₃ with the stoichiometric composition (A in table 1) with approximated dimensions of $9 \times 10 \times 12$ mm³ was reduced at 900 °C as described in the experimental section, and the absorption spectrum was measured under different circumstances which are now described.

About a half of the block was loosely wrapped up with platinum foil to avoid any contact with the alumina crucible during the reduction treatment. This procedure resulted in two crystal halves of different colour, i.e. different levels of reduction. As shown in figure 1 the 'uncovered' half (spectrum labelled 1) exhibits higher absorption than the 'covered' one (spectrum 2) on the 2.5–3.8 eV region. Since no contamination is expected to come from a vacuum atmosphere, this effect has to be attributed to differences occurring between the surroundings of the covered and uncovered regions in the partial pressure of those components out-diffusing from the sample surface (O₂ and Li₂O). For the highest reduction temperatures the uncovered region partially lost its optical finishing and had to be repolished (between 5 μm and 10 μm of surface material had to be removed).

However, the additional absorption exhibited by the uncovered half with respect to the covered one arises from the outer sample layer (between 100 μm to 200 μm thick). This thickness was estimated by grinding-polishing each face until the absorption spectrum did not change with further grinding. The final spectrum was found to be the same as that of the covered half (spectrum 2 in figure 1). On the other hand, the absorption left after the last grinding-polishing process, was found homogeneously distributed inside the crystal block. This was proved by comparing the spectrum of the ground block with that of a slice sawn from the middle of the block: both spectra were found identical.
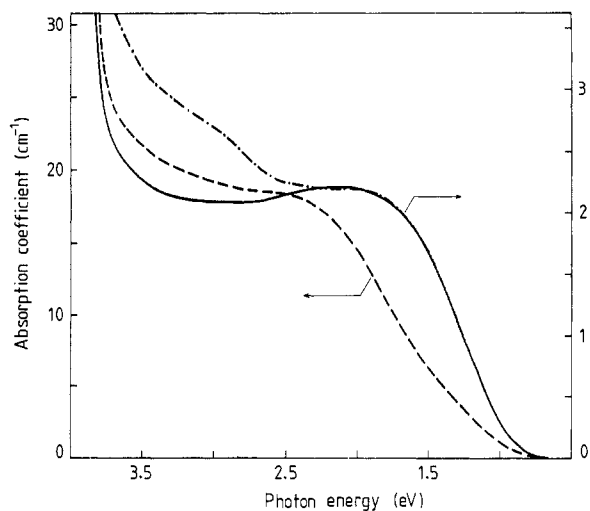
Figure 1. Reduction induced absorption of an 'uncovered' (see text) stoichiometric sample (1, chain curve), a 'covered' stoichiometric sample (2, full curve), and a congruent sample (3, broken curve). The reduction temperature was 880 °C and the spectra were taken at RT.

It has to be mentioned that on decreasing the [Li]/[Nb] ratio the layer effect appears weaker, and for congruent samples, including doped ones, is negligible. This means that for the congruent and lower [Li]/[Nb] ratios the absorption is homogeneous throughout the whole sample. The overall absorption strongly increases on decreasing the [Li]/[Nb] ratio, although the relative height of the 0.5–2.5 eV region is substantially smaller than for the Li richer cases, as shown by spectrum 3 in figure 1. Also the slope of the absorption curve in the 3.5–3.8 eV region is somehow in between that of the inner part and that of the outer part of the stoichiometric sample. On the other hand, as a general rule, reduction induces a small absorption edge shift towards the short wavelength side.

For iron and copper doped congruent samples the reduction induced absorption resembles that of pure crystals but the spectrum presents a much smaller contribution in the 0.5 eV–2 eV region (figure 2). Only for the highest reduction temperatures, the absorption in this region, although weaker, takes the shape typical of pure crystals indicating that the impurity reduction has saturated.

All these points will be further commented in the discussion section when identification of different components of the absorption permits to be more precise on which one is increasing or decreasing.

3.2. Thermal excitation

Samples of reduced $LiNbO_3$ with the various stoichiometries were heated above room temperature up to 250 °C and the absorption spectra measured at the high temperature. For crystals B and C, the results appear qualitatively similar to those previously reported for congruent reduced [4] and electron irradiated [7] samples. The spectral region above 2 eV decreases to the benefit of a well defined band peaking at 1.6 eV (see figure 3). However, some differences are now noted between crystals B and C. For crystal B (higher Li content) the absolute magnitude of the changes is smaller, particularly the decrease of the absorption in the visible spectral region. The effect is much more marked for crystal A, where even some increase in the absorption at 2.1 eV–2.8 eV is observed. Some caution has to be, nevertheless, taken in view of the small absorption involved.
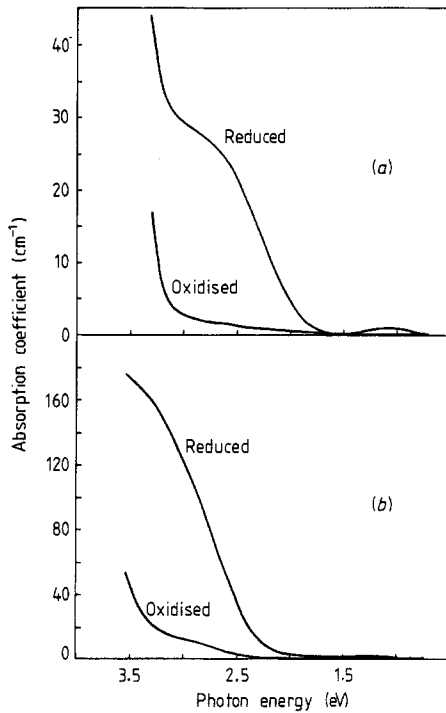
Figure 2. reduction induced spectra of (*a*) Fe::LiNbO$_3$ and (*b*) Cu:LiNbO$_3$ (crystals D and E in table 1). Spectra before reduction are also shown for comparison. Reduction temperature, 750 °C. Spectra taken at RT.
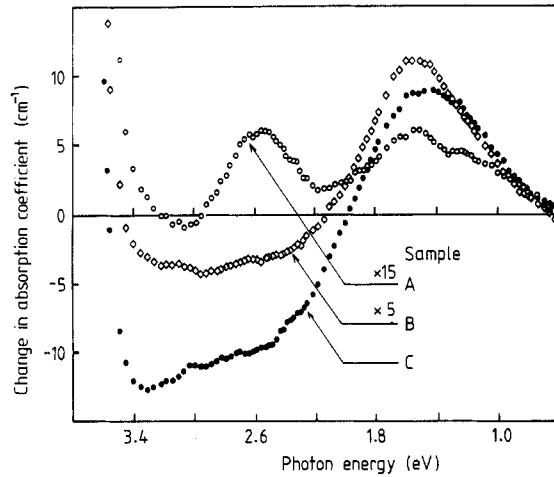

Figure 3. These spectra are obtained by substracting the reduction induced absorption taken at RT from that taken at 200 °C. Spectra have been labelled with the letter corresponding to the crystals indicated in table 1.
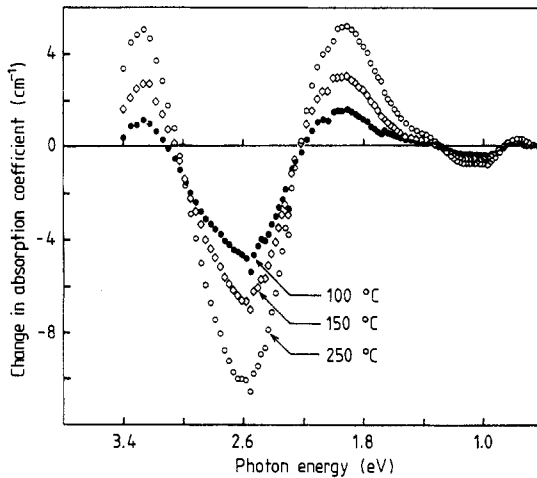

Figure 4. Incremental absorption coefficient of a reduced LiNbO$_3$:Fe sample (crystal D in table 1) at different measuring temperatures as indicated in the figure.

Data from the three stoichiometries are illustrated in figure 3, where the change in absorption coefficient is plotted as a function of the wavelength.

Similar experiments have been performed on Fe-doped LiNbO$_3$ and the results are shown in figure 4. A clear decrease is observed in the 2.5 eV region, where the peak
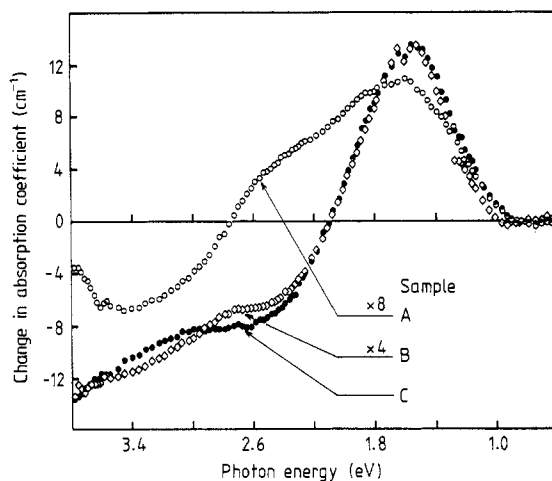
Figure 5. Incremental absorption coefficient induced by illumination ($\lambda = 405$ nm, $E = 3.06$ eV) in reduced samples with different stoichiometries. Illumination and measurement were carried out at 77 K. Each spectrum corresponds to the crystal indicated in table 1 with the same labelling letter.

associated to the Fe^{2+} charge transfer band occurs, as well as in the 1.1 eV band arising from a crystal field transition of this ion. This is accompanied by essentially symmetric increases at the wings of both bands. In fact the effect can be completely accounted by the thermally induced broadening of the band, as suggested by the observed constancy of the band areas during heating.

3.3. Optical illumination

Samples of reduced pure and Fe-doped $LiNbO_3$ were illuminated at 80 K with light of either 380 nm (3.26 eV), 405 nm (3.06 eV) and 480 nm (2.58 eV). The results for pure crystals with the various stoichiometries are illustrated in figure 5 corresponding to 405 nm illumination. They somehow resemble those described above for the thermal excitation experiments. The absorption in the 1.6 eV region markedly grows at the expense of the decrease in the absorption at photon energies above about 2 eV. The situation appears somewhat different for crystal A, where some increase in absorption is also observed at the 2.0–2.7 eV region. All these results are not apparently dependent on the excitation light wavelength.

For Fe-doped $LiNbO_3$ results are shown in figure 6. Here, an increase is again observed in the near IR absorption but the growing band is much broader at the high-energy side and centred around 1.8 eV. This may suggest that some other band is increasing together with that one at 1.6 eV observed for pure samples (see the discussion section). This is also consistent with the smaller decrease in the absorption above 2 eV, where the Fe^{2+} band is assumed to occur. It is to be remarked that the light-induced increase in the near IR absorption is about 3–4 times smaller than that found for pure (congruent) samples. On the other hand, for the Fe-doped samples the effect is clearly enhanced on going to lower excitation wavelength, as shown in figure 6.

4. Analysis of the spectra

By a detailed analysis and comparison of all measured spectra it can be realised that the broad absorption band appearing in any of them, is actually made up of a number of
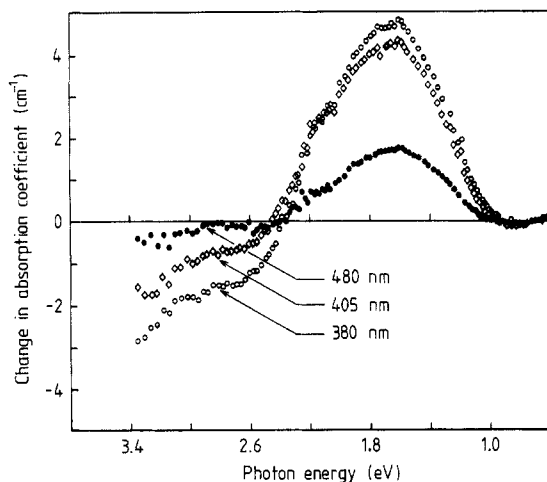
Figure 6. Light induced incremental absorption in LiNbO$_3$:Fe (sample D) with different excitation energies as indicated in the figure. $T = 77$ K.

components as previously proposed [2, 11]. In some particular spectra these components can be observed with a small enough degree of overlapping, so that reasonably well defined peaks and halfwidths can be obtained. This procedure has been found useful for dealing with the difficulty of the experimental definition of the various componets in the otherwise broad and little structured spectrum. It will be assumed that in nominally pure crystals, regardless of their [Li]/[Nb] ratios, the same component bands are present, although their relative heights can substantially change. In doped samples, new impurity bands have to be added to those present in pure crystals. The shape of all the components was assumed to be approximately gaussian.

Figure 7 shows the absorption spectra of two reduced LiNbO$_3$ pure samples. Figure 7(a) corresponds to crystal C of table 1 reduced at 700 °C and taken at RT (the oxidised spectrum has been subtracted in order to emphasise the reduction induced changes). Figure 7(b) corresponds to crystal A in table 1 reduced at 900 °C, illuminated with 405 nm bleaching light and taken at 80 K. Unfortunately no oxidised spectrum was taken at low temperature which could be subtracted in this case, the tail of the absorption edge being then included in this spectrum. In figure 7(a) two components bands can be inferred peaking at about 2.3 eV and 3.9 eV, whereas in figure 7(b) two peaks are inferred at about 1.6 eV and 3.1 eV. In order to make easier the band visualisation, the gaussian components obtained from the fitting are also shown in this figure. These gaussians bands will be referred to by the values of their energy peak positions. From spectra such as those shown in figures 1, 3 and 5, as well as from all others not included here to avoid redundance, the same four bands are also inferred. By using these four bands, all 22 spectra of reduced pure samples (including the bleached ones) have been nicely fitted; only the relative band heights (four parameters) have been changed, whereas peak positions and halfwidths have been kept constant. It is worth noting that for all these spectra the ratio between the heights of the 3.9 eV and 3.1 eV components is approximately constant (~1.3). The best values obtained on optimising all the 22 fittings are given in table 2.

In spite of the fact that there are four parameters to be varied, spectra of reduced doped (iron and copper) crystals could not be fitted with the four components appearing in pure crystals, and new bands had to be introduced. In the Fe : LiNbO$_3$ sample a new band peaked at 2.5 eV (see table 2) is present, together with those appearing in pure
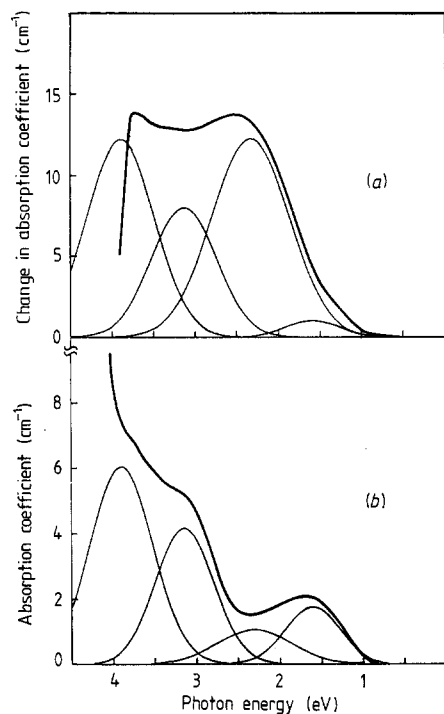
Figure 7. Two examples of gaussian decomposition. (*a*) Crystal C (see table 1) reduced at 700 °C and measured at RT where the bands peaking at 3.9 eV and 2.3 eV are emphasised; the spectrum before reduction has been substrated, the shift of the absorption edge to the high energy side being apparent. (*b*) Spectrum from crystal A, reduced at 900 °C and bleached at 77 K with 3.06 eV light, where the bands peaking at 3.1 eV and 1.6 eV are emphasised; no substraction of the oxidised spectrum has been performed in this case.

Table 2. Peaks and halfwidths of the proposed gaussian components.

Gaussian bands Peak (eV)	Halfwidth (eV)	Samples A	B	C	D	E	F
3.89	0.48	×	×	×	×	—	×
3.13	0.46	×	×	×	×	—	×
3.33	0.49⎱						
2.76	0.27⎰	—	—	—	—	×	—
2.52	0.37	—	—	—	×	—	—
2.33	0.54	×	×	×	(1)	(2)	×
1.59	0.39	×	×	×	(1)	(2)	×
1.15	0.16⎱						
0.94	0.11⎰	—	—	—	×	—	—

(1) Only after optical bleaching.
(2) Only after high temperatures reduction treatments (>800 °C).

crystals at 3.9 eV and 3.1 eV. Since the components at 2.3 eV and 1.6 eV are not present in these samples, some kind of electron trapping competition has to be present during the reduction process between Fe^{3+} ions and the centres responsible for these bands. However, upon optical bleaching a small contribution from both bands appear, whereas the others decrease by a similar amount. In the $Cu:LiNbO_3$ sample the well known charge transfer band from Cu^+ is observed (see table 2), without any presence of those occurring in pure crystals. It has then to be concluded that the $Cu^{2+} - Cu^+$ conversion strongly inhibits the reduction process operating in pure samples. Only for high reduction

Table 3. Sign of the light induced changes on the gaussian components of table 2 ($\downarrow$ decrease, $\uparrow$ increase).

Bands (eV)	Samples			
	A	B	C	D
3.89	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
3.13	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
2.52	—	—	—	$\downarrow$
2.33	$\uparrow$	$\downarrow$	$\downarrow$	$\uparrow$
1.59	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
1.10	—	—	—	$\downarrow$

levels ($T > 800$ °C) when all Cu^{2+} ions have been reduced to Cu$^+$ (as monitored by the 1 eV Cu^{2+} band), small contributions from the 2.3 eV and 1.6 eV bands appear. This indicates the starting of the reduction mechanism operating in pure samples at lower temperatures. A total of 24 spectra from doped samples were thus fitted by adding the impurity absorption bands shown in table 2.

5. Discussion

From the analysis of the 46 spectra of reduced pure and doped LiNbO$_3$ samples presented above several conclusions can be drawn. As previously proposed [2, 10], it has been now confirmed that the broad band induced by reduction is not a simple one but made up of four component bands in pure samples, plus other impurity bands in doped crystals (see table 2). With these component bands it is, then, possible to account for the spectral changes induced by optical excitation (figures 5 and 6). The various bands grow or decrease as summarised in table 3 for pure crystals with the various stoichiometries as well as the Fe-doped samples. In all cases the 1.6 eV band increases with illumination. Some spectra exhibit enhanced intensity of certain components, facilitating peak and halfwidth determinations. The confidence in the decomposition is provided by the good fittings obtained in all of such a large variety of spectra by using only the bands indicated in table 2.

The problem still remains of assigning those bands to particular defects. After the paper by Hodgson and Agulló-López [7] it seems well established the connection between the absorption induced by reduction and the presence of oxygen vacancies in LiNbO$_3$ reduced samples. A band decomposition of a spectrum obtained in their work has been achieved with the same bands shown in table 2 for pure crystals. It is also to be noted that the same absorption and band decomposition has been obtained by proton bombardment in an experiment carried out with the Van der Graff accelerator of the Sussex Univerisity [14].

Therefore one would propose that some of the 3.8 eV, 3.1 eV and 2.3 eV bands appearing in the reduced pure samples is related to oxygen vacancy centres, i.e. F$^+$ or F centres. According to recent theoretical calculations [8] they can be respectively considered as a single or a bound pair of Nb^{4+} ions trapped at an oxygen vacancy site. Since two kinds of Nb (Nb$_{Nb}$ and Nb$_{Li}$) exist in the Li-defficient crystals, several defect configurations, possible having different spectra, could be formed. On the other hand,

the possibility that one of the bands is associated to the free bipolaron considered by Schirmer [4] cannot be ruled out.

In fact, the absence of any reported EPR signal that could be related to F^+ centres points out to F centres and/or free bipolarons as more plausible candidates for the UV and visible bands. Some additional considerations can now be made with regard to these spectral components. Since stoichiometric samples are supposed to contain a much lower concentration of Nb_{Li} and they show considerably weaker 3.1 eV and 3.9 eV bands (except for the thin layer where a strong lithium loss is expected), it is reasonable to associate these bands to centres (e.,g. F centres) involving Nb_{Li}. This is consistent with the much greater height of those bands in the thin layer, where more antisite disorder is expected. It should also be mentioned that the UPS measurements, Chab and Kubatova [12] have observed a band peaked at 3.9 eV in reduced crystals, although no assignment has been made. On the other hand, the 2.3 eV band may be related to normal F centres involving regular Nb_{Nb}. The 1.6 eV band, in accordance with the data on thermal and optical excitation reported in this and a previous paper, should be attributed to a Nb^{4+} (small polaron).

The data on optical and thermal excitation of the reduced samples are rather complex and only a few comments can be now made. Essentially, the 1.6 eV band grows at the expense of the UV-VIS bands, in accordance with that band being associated to Nb^{+4} small polarons, as previously assumed. Excitation apparently ionises the bound electron centres responsible for the 2.3 eV, 3.1 eV and 3.9 eV bands. Other features, such as the growth of the 2.3 eV band during illumination of stoichiometric or Fe-doped samples is not understood.

Acknowledgments

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