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## Luminescence of Cr<sup>3+</sup> in lithium niobate: influence of the chromium concentration and crystal composition

F Lhomme<sup>†</sup>||, P Bourson<sup>†</sup>, M D Fontana<sup>†</sup>, G Malovichko<sup>†‡¶</sup>, M Aillerie<sup>†</sup>  
and E Kokanyan<sup>§</sup>

<sup>†</sup> Laboratoire Matériaux Optiques à Propriétés Spécifiques, CLOES, University of Metz and Supelec, 2 rue Belin, 57078 Metz Cédex 3, France

<sup>‡</sup> Institute for Problems of Material Sciences, Kiev, Ukraine

<sup>§</sup> Institute of Physical Researches, Ashtarak 2, Armenia

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**Abstract.** The luminescence spectrum of Cr<sup>3+</sup> in LiNbO<sub>3</sub> has been investigated, especially in the R-line range from 7200 up to 7500 Å. For this, we have studied several chromium-doped LiNbO<sub>3</sub> crystals with various Li/Nb ratios and different doping concentrations. In addition to the lines which were previously reported, several new peaks were detected in our investigations. In fact, the structure, the shape and the relative intensity of each line are shown to be strongly dependent on the content of doping and on the intrinsic defects related to the non-stoichiometry of the crystal. Among all peaks, we focus our attention on four main lines, which can be separated into two groups, according to their behaviours. The contribution of the first group to the whole spectrum diminishes with increasing Li/Nb ratio so that it vanishes for the stoichiometric composition. The second group of lines, occurring at higher wavelengths, is reported for the first time and is shown to be closely related to the Li/Nb ratio, especially when approaching the stoichiometric composition. These lines exhibit a similar behaviour with increasing Li/Nb ratio or Cr concentration. An explanation of the possible origins of these four peaks is given.

### 1. Introduction

Lithium niobate (LN) is a good optoelectronic material owing to its electro-optical and non-linear optical properties. Various applications can be quoted: optical waveguides [1] and photorefractive devices [2] as well as self-frequency doubled and self-Q-switched solid state lasers [3].

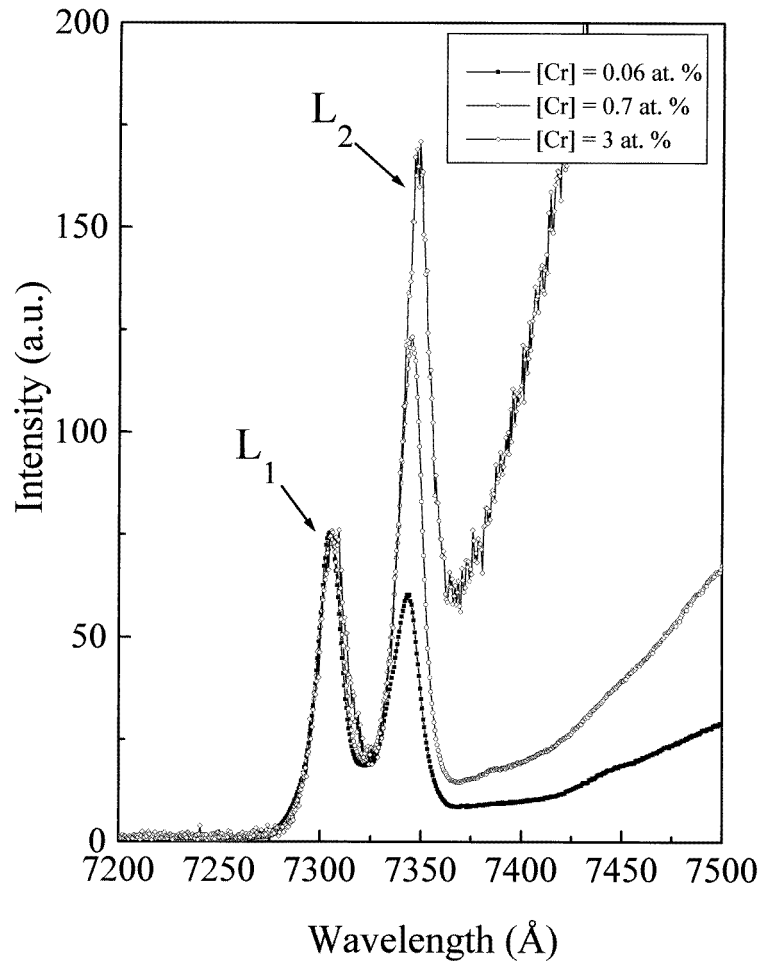
Investigations and applications of LN generally use single crystals, which are grown from a congruent composition (about 48.4 mol% Li<sub>2</sub>O in the melt and in the crystal) and thus contain a large number of intrinsic defects associated with the deviation from the stoichiometric composition (50 mol% Li<sub>2</sub>O in the crystal).

An appropriate doping is able to enhance interesting properties or to provide new ones. For instance, Qiu [4] proposed Cr<sup>3+</sup>-doped LN as a candidate for a room-temperature tunable solid state laser owing to its strong broad-band luminescence spanning the 770–1170 nm range.

With the help of electron paramagnetic resonance (EPR) a remarkable difference of Cr<sup>3+</sup> centres in LN crystals has been found [5, 6] with variation of compositions (or Li/Nb ratio) for a wide composition range (from below congruent up to stoichiometric composition).

|| E-mail address: lhomme@ese-metz.fr

¶ Present address: Fachbereich Physik, Universität Osnabrück, Postfach 4469, D-49069 Osnabrück, Germany.



**Figure 1.** Effect of Cr concentration on R-line luminescence spectra at 10 K in congruent LN crystals ( $X_c = 48.4\%$ ).

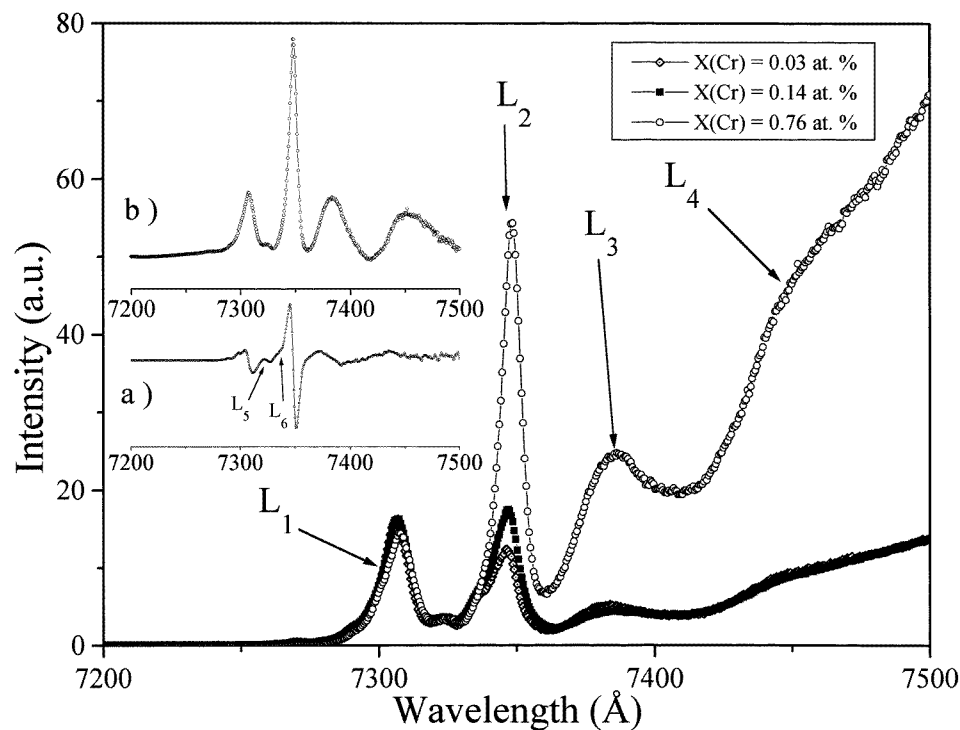
Recent obtaining of completely stoichiometric LN crystals with properties quite different from those in congruent crystals [7] led to a renewal of interest to this material.

The present paper is devoted to the study of the luminescence spectrum recorded in doped crystals with different crystal compositions and various amounts of  $\text{Cr}^{3+}$  and their changes owing to variation of either the crystal composition or the chromium concentration.

Indeed, most of the previous experimental investigations of the luminescence of Cr-doped LN were performed in congruent crystals [8–10]. In our study, we tried intentionally to separate the effect of the composition and impurity contents on  $\text{Cr}^{3+}$  luminescence spectra to investigate the independent influence of both defect subsystems. We discuss the possible origins of the main four lines in relation to the defect structure of LN.

## 2. Experimental results

The crystals used in our measurements were grown by the Czochralski method with various compositions and different levels of Cr doping in the melt. The composition can be evaluated



**Figure 2.** Effect of Cr concentration of R-line luminescence spectra in nearly stoichiometric samples ( $X_c = 49.5\%$ ). Inset (a) the derivative of the spectrum recorded in 0.76 at.% Cr-doped crystal. Inset (b) the same spectrum corrected by the subtraction of the broad band.

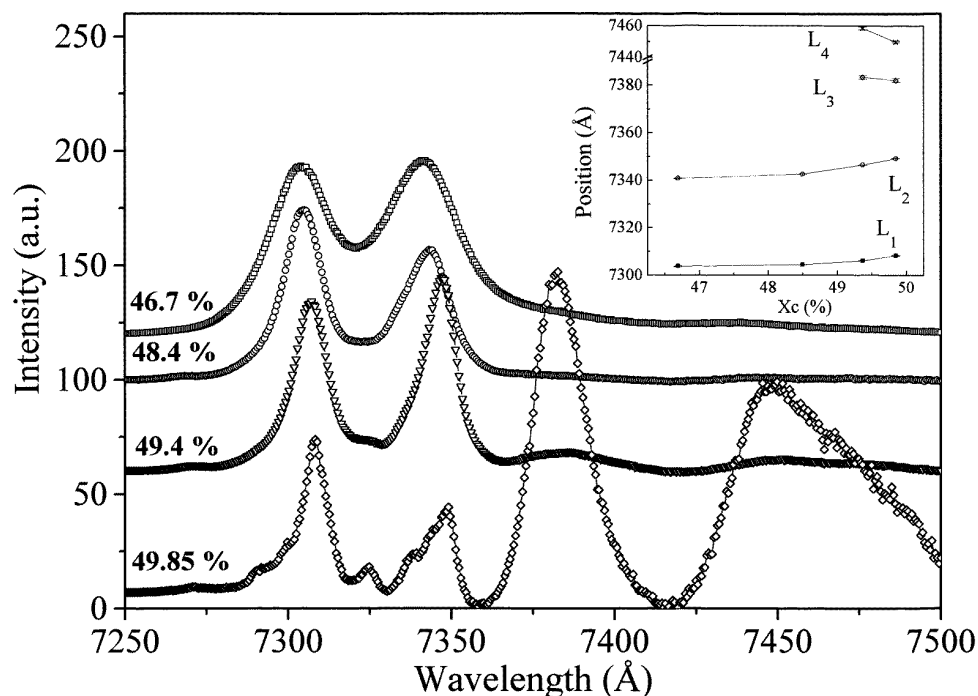
by various techniques [7]. Among them, we have chosen the measurement of the width of some Raman lines, which vary linearly with the ratio  $X_c = [\text{Li}]/([\text{Li}] + [\text{Nb}])$  in the crystal [11, 12].

Experiments were done with samples which were mounted in a cryostat and cooled down to 15 K. The 5145 Å  $\text{Ar}^+$  laser line was used to pump the absorption band for the  $\text{Cr}^{3+}$  fluorescence experiments. All measurements of emission were obtained using a Spex 1401 double-grating spectrometer and a cooled RCAC 31034 PMT. The light beam was propagating perpendicular to the  $c$ -axis and polarized parallel to this axis.

Figure 1 shows the luminescence spectrum characteristic of the Cr-doped congruent lithium niobate ( $X_c = 48.4\%$ ). At the shortest wavelengths are two sharp lines ( $L_1$  and  $L_2$ ), usually called R-lines and ascribed to the transition  ${}^2E \Rightarrow {}^4A_2$  [8] whereas the signal at high wavelength is the tail of a broad band, which is assigned to the transition  ${}^4T_4 \Rightarrow {}^4A_2$ .

These spectra, as for all spectra reported in this study, are normalized to the intensity of the line  $L_1$ . The shapes of the luminescence spectra vary with the Cr concentration (0.06, 0.7 and 3 at.%). Compared with previous data [8–10], our results allow us to point out additional features as follows. We note the increase of the intensity of the  $L_2$  line with increasing chromium concentration. Further the position of the peak maximum and the width for both lines exhibit an upward trend. These effects are stronger for the line  $L_2$ .

Figure 2 displays the R-lines in LN:Cr crystals with nearly stoichiometric composition ( $X_c = 49.5\%$ ) for 0.03, 0.14 and 0.76 at.% Cr concentration. The behaviour of the lines  $L_1$  and  $L_2$  appears to be similar to that observed in the congruent sample. Compared with

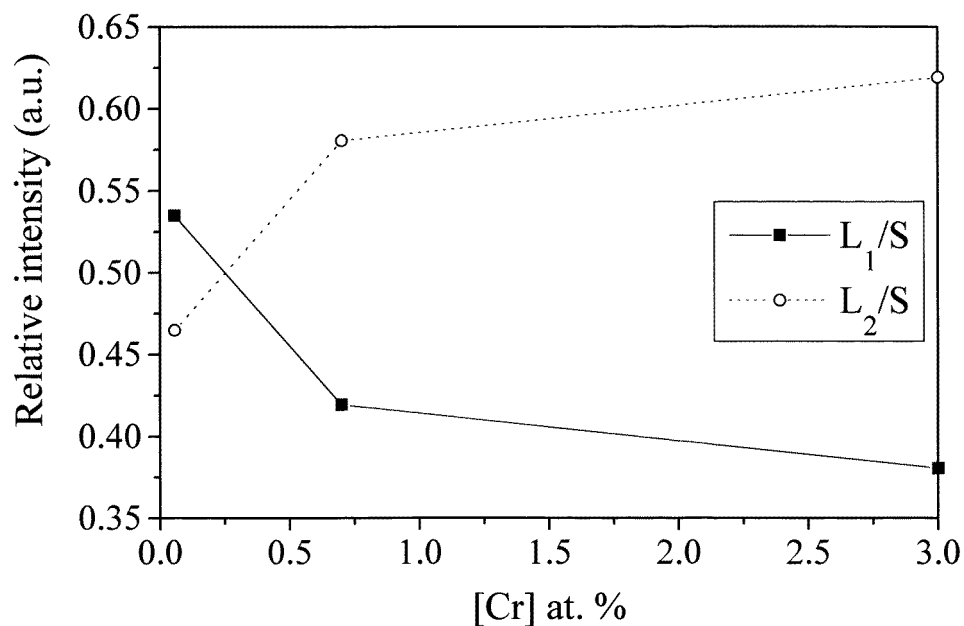


**Figure 3.** Corrected spectra of LN crystals with different compositions ( $X_c = 46.7\text{--}49.85\%$ ) but with the same  $[\text{Cr}] = 0.06$  at.% in the melt. Inset, composition dependence of the peak positions.

the spectra recorded in the congruent crystal, a new line and a shoulder occur at higher wavelength than the lines  $L_1$  and  $L_2$ . These new features can be more clearly detected if we consider the derivative of the spectrum shown in the inset (a) of figure 2. These lines denoted  $L_3$  and  $L_4$  are located at  $7384 \text{ \AA}$  and  $7454 \text{ \AA}$  respectively. In addition, lines  $L_5$  and  $L_6$  lying at  $7324 \text{ \AA}$  and  $7336 \text{ \AA}$  are observed between  $L_1$  and  $L_2$ .

The lines  $L_3$  and  $L_4$  are partly hidden by the low-frequency tail of the broad emission band. They are therefore more visible in the corrected spectra, as deduced by the subtraction of the broad band, likewise in [13]. An example of the corrected spectrum is reported in the inset (b) of figure 2, which clearly shows that the lines  $L_3$  and  $L_4$  are much broader than the lines  $L_1$  and  $L_2$ . The peak position of the four lines does not show any clear trend but their intensity clearly increases with rising Cr concentration.

Up to now, we have mainly paid attention to the study of behaviour of LN:Cr luminescence with Cr concentration. Now we turn on the dependence of emission spectra on the composition in crystals with the same chromium content. Figure 3 displays the corrected spectra for the crystals LN doped with 0.06 at.% Cr but having different compositions:  $X_c = 46.7, 48.4, 49.4$  and  $49.85\%$ . The spectrum exhibits four main peaks and five additional peaks which could be seen in the derived spectrum. For the lines  $L_1$  and  $L_2$ , the change of the composition from congruent to stoichiometric induces changes in some characteristics of the luminescence spectra. The maximum position of each peak moves towards higher wavelength (see the inset) whereas the width decreases with increasing  $X_c$ . Furthermore, the change of intensity of  $L_2$ , normalized to  $L_1$ , shown in figure 3 is not



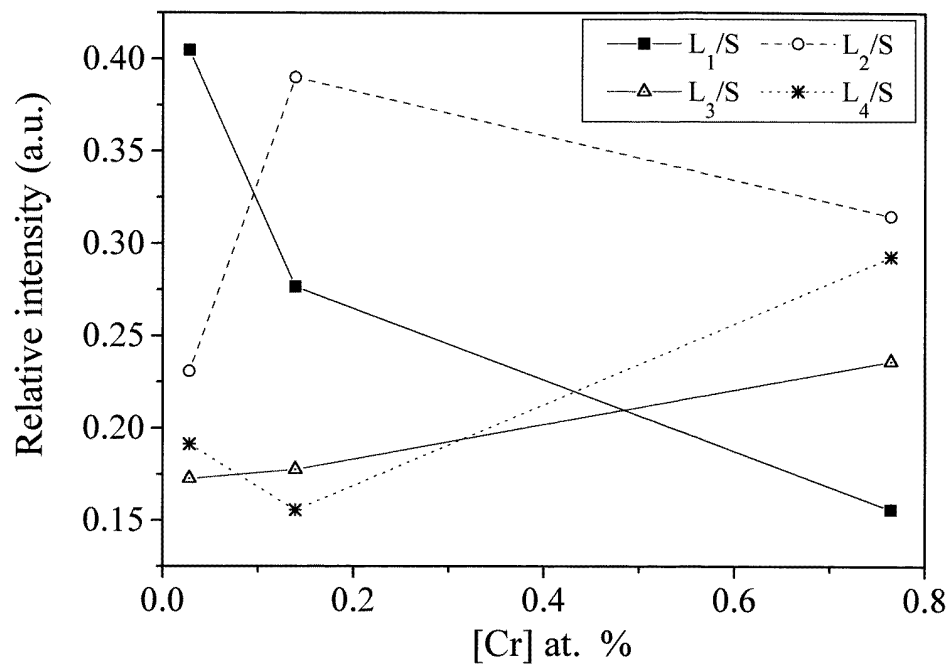
**Figure 4.** Cr dependence of the relative integrated intensities of the lines  $L_1$  and  $L_2$  for congruent samples ( $X_c = 48.4\%$ ).  $S$  is the sum over all peaks.

monotonic. The intensity of both lines  $L_3$  and  $L_4$  increases with increasing  $X_c$ , especially close to stoichiometry.

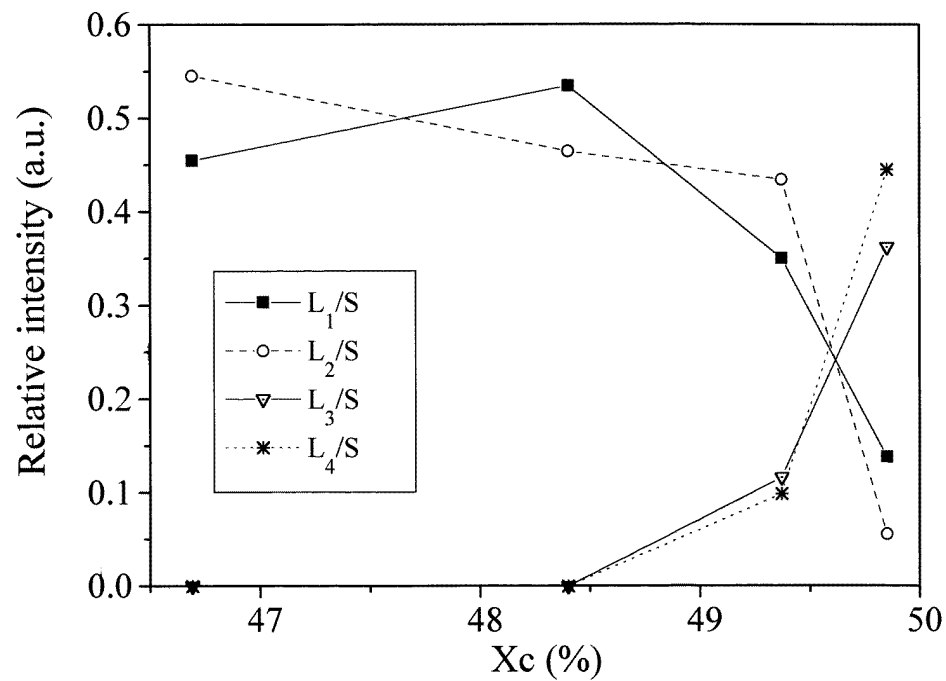
Now we discuss the behaviour of the peaks reported in the various spectra, especially in regard to the influence of both the composition and the Cr concentration. Although a total of nine peaks was detected, we pay attention to the characteristics of the four most intense peaks:  $L_1$  to  $L_4$ . First, owing to their difference in their width and position, we can distinguish the lines  $L_1$  and  $L_2$  on one hand and the lines  $L_3$  and  $L_4$  on the other hand. Second, we consider the dependence of the intensity of each peak on  $X_c$  or  $[\text{Cr}]$ . In fact, we study for each peak the ratio of the integrated intensity  $J$  to the sum of areas of all peaks. This normalization of the data allows the comparison of results between various crystals. Such a procedure is valid only if the peaks arise from the same luminescence transition for different centres.

Figure 4 displays the dependence of the integrated intensity on the chromium concentration in congruent samples. The integrated intensities of  $L_1$  and  $L_2$  show opposite trends:  $J(L_1)$  decreases for increasing Cr content whereas  $J(L_2)$  displays an upward trend.  $J(L_1)$  is larger than  $J(L_2)$  for the lowest concentration  $[\text{Cr}] = 0.06$  at% and a crossover occurs for larger  $[\text{Cr}]$ . We can therefore describe the effect of chromium in congruent samples from two concentration ranges for the substitution process. The first concentration range for a low Cr doping concerns a preferential substitution by the  $\text{Cr}^{3+}$  ion of the site the gives rise to the line  $L_1$ . The second range with a higher Cr doping gives a preferential substitution in the centre leading to the line  $L_2$ .

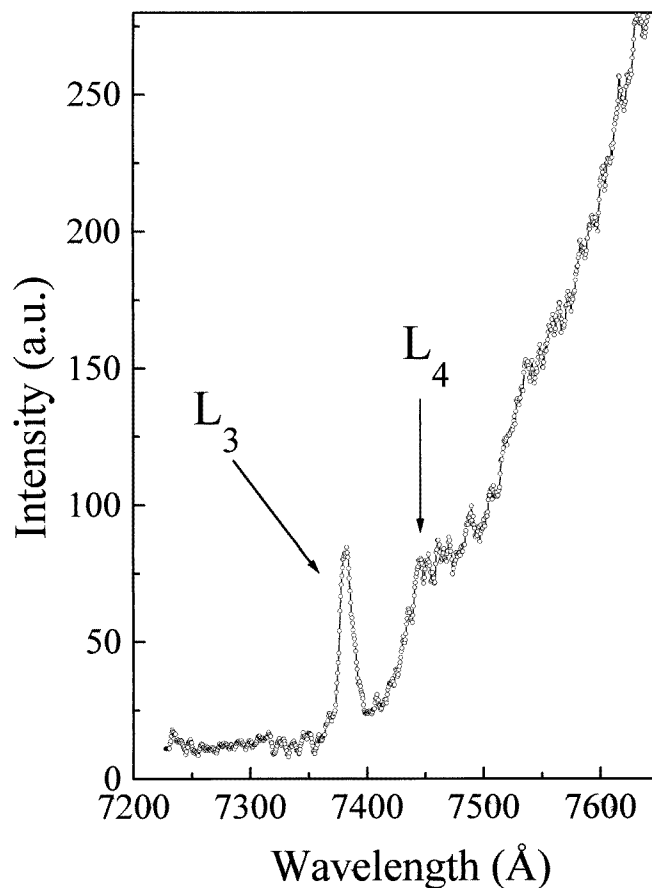
Figure 5 exhibits the dependence on the Cr concentration of the lines  $L_1$  to  $L_4$  in the crystals with the composition  $X_c = 49.5\%$ . The lines  $L_1$  and  $L_2$  exhibit a crossover similar to the situation in the congruent crystals. Moreover, it appears that the total integrated



**Figure 5.** Cr dependence of the relative integrated intensities of the lines L<sub>1</sub>-L<sub>4</sub> for nearly stoichiometric crystal ( $X_c = 49.5\%$ ).  $S$  is the sum over all peaks.



**Figure 6.** Composition dependence of the relative integrated intensities of the lines L<sub>1</sub>-L<sub>4</sub> for the crystals with [Cr] = 0.06 at.%.  $S$  is the sum over all peaks.



**Figure 7.** Emission spectrum of a stoichiometric sample ( $X_c = 50 \pm 0.01\%$ ) doped with  $[\text{Cr}] = 0.03$  at.% in the melt.

intensity of the lines  $L_1$  and  $L_2$  is partly transferred to the lines  $L_3$  and  $L_4$  when  $[\text{Cr}]$  increases.

Figure 6 displays the effect of the composition in the crystal with  $[\text{Cr}] = 0.06$  at.%. The intensities  $J(L_1)$  and  $J(L_2)$  compared to each other do not show a monotonic trend. With increasing  $X_c$ , the contribution of both  $L_1$  and  $L_2$  to the total integrated intensity diminishes to the benefit of  $L_3$  and  $L_4$ . This behaviour is enhanced for the crystals with compositions close to stoichiometry ( $X_c = 50\%$ ). It is remarkable to note that this feature is quite similar on increasing both the Cr concentration and the composition  $X_c$  (see figures 5 and 6).

According to the behaviour of the integrated intensities shown in figure 6, one can expect that, in the stoichiometric crystal, the lines  $L_3$  and  $L_4$  should be largely dominant in the emission spectrum. This was really observed for the crystal with a controlled stoichiometric composition ( $X_c = 50 \pm 0.01\%$ ) and doped with 0.03 at.% of chromium. The luminescence spectrum recorded for this crystal is shown in figure 7. The lines  $L_1$  and  $L_2$  completely vanish so that only the lines  $L_3$  and  $L_4$  are detected. This spectrum confirms the behaviour displayed by the lines  $L_1$  to  $L_4$  in figure 6. The peaks  $L_1$  and  $L_2$  are predominant for low  $X_c$  whereas the intensities of the lines  $L_3$  and  $L_4$  are large for samples with high composition



so that the opposite behaviours of  $L_1$ – $L_2$  and  $L_3$ – $L_4$  can be directly related to the defect structure of LN.

### 3. Discussion

In order to tentatively explain our results and interpret the origin of the different peaks it is necessary to review the previous papers on the emission spectra on LN:Cr. It is to be noted that the lines  $L_1$  and  $L_2$  were mainly detected in the previous studies. One of the first investigations was conducted by Glass [8] who stressed the defect structure of LN. He concluded that  $\text{Cr}^{3+}$  impurities occupy Nb sites but not Li sites and rejected the possibility of Cr substitution for structural vacancy. Later Jia *et al* [9] proposed that these lines could belong to a chromium on an Li site ( $\text{Cr}_{Li}$ ) and to a chromium on an Nb site ( $\text{Cr}_{Nb}$ ). As the oxygen octahedron around Li is more distorted than that around the Nb on, they assigned the most intense line (here denoted  $L_1$ ) located at 7306 Å mainly to  $\text{Cr}_{Li}$  and the second line peaked at 7344 Å (here denoted  $L_2$ ) to  $\text{Cr}_{Nb}$ . From the calculation of field strength carried out by Glass within a point ion model, Nicholls *et al* [14] asserted that the fact that the  $\text{Cr}_{Nb}$  peak is lying at shorter wavelength than the  $\text{Cr}_{Li}$  line was in contradiction with the assignment of Jia *et al*. More recently, Michel-Calendini [15] calculated the energies of  $\text{Cr}^{3+}$  in the  $\text{Li}^+$  and  $\text{Nb}^{5+}$  sites using a molecular orbital model and found that the emission of  $\text{Cr}_{Li}$  arises at shorter wavelength than the emission of  $\text{Cr}_{Nb}$ . To explain their results, Fisher *et al* [13] assumed that in stoichiometric crystals the isolated  $\text{Cr}_{Li}$  centres, responsible for the line  $L_2$ , disappear and only the lines of  $\text{Cr}_{Li}$ – $\text{Cr}_{Nb}$  dimers are observed in both absorption and emission spectra. Based on detailed analysis of optical and radio-spectroscopic data, Macfarlane *et al* [16] concluded that the main centre that dominates in both EPR and optical absorption spectra originates from  $\text{Cr}^{3+}$  in the undistorted  $\text{Li}^+$  site, but the group of R-lines observed in the luminescence spectra is related to  $\text{Li}^+$  sites that are perturbed by nearby Nb vacancies or antisites.

Regarding our data, we can reconsider the nature of the lines  $L_1$  and  $L_2$ . As they are dominant in the spectra recorded in crystals with composition far from stoichiometry, they are related to the presence of intrinsic defects. However, as their behaviours with the change of Cr concentration are not the same, they probably arise from different centres. This assumption differs from the description proposed by Jia *et al* [9], in which the lines  $L_1$  and  $L_2$  are closely related to each other and due to dimers.

The observation of the additional lines  $L_3$  and  $L_4$  in LN:Cr was not previously mentioned in the literature. In fact, in a crystal codoped with Cr and Mg, Camarillo *et al* [10] have detected a new peak at higher wavelength than the line  $L_2$  and close to our line. The assignment to a  $\text{Cr}^{3+}$  centre perturbed by  $\text{Mg}^{2+}$  ions, assumed by the authors, cannot be obviously retained in our case. The behaviours of the lines  $L_3$  and  $L_4$  are quite similar in intensity, width and position with increasing composition and Cr concentration. We could therefore attribute their correlated origins to the formation of dimers  $\text{Cr}_{Li}^{3+}$ – $\text{Cr}_{Nb}^{3+}$  because corresponding lines have been observed in a crystal doped with 0.2 at.% by EPR spectroscopy [6]. From atomistic-simulation study [17] it was concluded that the formation of such self-compensated impurity complexes is energetically very favourable for the  $\text{LiNbO}_3$  lattice. So this interpretation should not be discarded.

Various models were proposed in the literature to describe the structure of intrinsic defects, responsible for deviation from the stoichiometry in LN crystals and they could be also useful to explain the possible structure of extrinsic defects. Three sites in LN lattice are in principle available for the substitution by the dopant  $\text{Cr}^{3+}$ . They are the centres of

the oxygen octahedra which are normally occupied by the sequence of Li, Nb, empty site along the  $c$ -axis. Among these three sites, the structural vacancy was generally not invoked as a possible site substitution by Cr [8, 9].

Three simple models were proposed to describe the defect structures in LN. Fay *et al* [18] suggested a model assuming that oxygen and lithium vacancies are the main non-stoichiometric defects in LN with a corresponding formula as:



But this model should lead to a lower density of the crystal than derived from the density measurement [19]. Two other models were then proposed assuming the location of niobium in Li site, the so-called niobium antisites. These models differ in the description of the mechanism of the charge compensation. For Lerner *et al* [20], the charge compensation is due to lithium vacancies and corresponds to the formula:



whereas for Abrahams and Marsh [21], the charge compensation of  $Nb_{Li}$  is achieved by a niobium vacancy, leading to the following formula:



Since the lines  $L_1$  and  $L_2$  disappear in the completely stoichiometric sample, we consider that they are related to Cr ions having intrinsic defects as charge compensators in their nearest surroundings. Thus, in the frame of the two last models,  $L_1$  and  $L_2$  could be linked to niobium antisites ( $Nb_{Li}$ ) and cationic vacancies ( $V_{Nb}$  or  $V_{Li}$ ). the lines  $L_3$  and  $L_4$  could arise from the proper effect of Cr ions as extrinsic defects in the structure.

#### 4. Summary

From the luminescence experiments performed on various LN:Cr crystals with different compositions and Cr concentrations, we were able to show the distinct effects of the chromium concentration and sample composition. Four main peaks called  $L_1$  to  $L_4$  have been pointed out in our spectra instead of two lines ( $L_1$  and  $L_2$ ) in the previous studies. Up to nine peaks have been resolved in the R-line range of our luminescence spectra. In order to understand the origin of these peaks, the behaviour of their characteristics (position, width, integrated intensity) were analysed under variation of Li/Nb ratio and/or doping concentration.

We can distinguish the main groups  $L_1$ – $L_2$  and  $L_3$ – $L_4$ . The effect of Cr doping on the lines  $L_1$  and  $L_2$  can be described by two substitution ranges. The first range for low Cr doping gives rise to the preferential creation of the  $L_1$  centre whereas the second range for a higher Cr doping corresponds rather to the creation mainly of the  $L_2$  chromium centre. In a nearly stoichiometric composition, the lines  $L_3$  and  $L_4$  occur and their contribution to the whole spectra, compared with that arising from the lines  $L_1$  and  $L_2$ , increases with rising Cr concentration.

The increase of the Li content in the crystal leads to the growth of relative intensity of lines  $L_3$  and  $L_4$ , similar to the influence of Cr concentration. The absence of  $L_1$  and  $L_2$  lines in a stoichiometric sample confirms the supposition that they are related to the complex centres due to Cr and intrinsic defects.

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## References

- [1] Armenise M N, Canali C, De Sario M and Zanoni E 1993 *Mater. Chem. Phys.* **9** 267
- [2] Krätzig E and Schirmer O F 1988 *Photorefractive Materials and their Applications I* (Berlin: Springer)
- [3] He Q, De Michelli M P, Ostrowsky D B, Lallier E, Pocholle J P, Papuchon M, Armani F, Delecourt D, Grezes-Beset G and Pelletier E 1992 *Opt. Commun.* **89** 54
- [4] Qiu Y 1993 *J. Phys.: Condens. Matter* **5** 2041
- [5] Malovichko G I, Grachev V G, Kokanyan E P and Gabrielyan V T 1986 *Sov. Phys.–Solid State* **28** 1453
- [6] Grachev V, Malovichko G and Schirmer O 1996 *Ferroelectrics* **185** 5
- [7] Malovichko G, Grachev V, Kokanyan E P, Schirmer O F, Betzler K, Gather B, Jermann F, Klauer S, Schlarb U and Wöhlecke M 1993 *Appl. Phys. A* **56** 103
- [8] Glass A M 1969 *J. Phys. Chem.* **50** 10908
- [9] Jia W, Liu H, Knutson R and Yen W N 1990 *Phys. Rev. B* **41** 10906
- [10] Camarillo E, Garcia-Solé J, Cusso F, Aguillo-Lopez F and Sanz-Garcia J A 1991 *Chem. Phys. Lett.* **185** 505
- [11] Schlarb U, Klauer S, Wesselmann M, Betzler K and Wöhlecke M 1993 *Appl. Phys. A* **56** 311
- [12] Ridah A, Bourson P, Fontana M D and Malovichko G 1996 *J. Phys.: Condens. Matter* **9** 9687–93
- [13] Fisher C, Kapphan S, Feng X-Q and Cheng N 1995 *Radiat. Eff. Defects Solids* **133** 199
- [14] Nicholls J F H, Han T P J, Henderson B and Jaqué F 1993 *Chem. Phys. Lett.* **202** 560
- [15] Michel-Calandini F 1994 *Radiat. Eff. Defects Solids* **134** 175
- [16] Macfarlane P I, Holliday K, Nicholls J F H and Henderson B 1995 *J. Phys.: Condens. Matter* **7** 9643
- [17] Donnerberg H, Tomlinson S M, Catlow C R A and Schirmer O F 1989 *Phys. Rev. B* **40** 201
- [18] Fay H, Alford W J and Dess H M 1968 *Appl. Phys. Lett.* **89** 12
- [19] Kovacs L and Polgar K 1986 *Cryst. Res. Technol.* **21** 6
- [20] Lerner P, Legras C and Duman P J 1968 *J. Crystal Growth* **3/4** 231
- [21] Abrahams S C and Marsh P 1986 *Acta Crystallogr. B* **2** 61