

## **ANALYSIS OF OPTICAL PHONON VIBRATIONS IN RAMAN SPECTROSCOPY OF LITHIUM NIOBATE CRYSTAL**

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### **ABSTRACT**

The Raman spectrum of  $\text{LiNbO}_3$  has been measured for various scattering configurations in crystals with different compositions. The comparison between spectra recorded for congruent and the nearly stoichiometric crystals shows significant differences in the shape and the number of Raman peaks. The analysis of results may be used to describe a complete vibrational modes of the long-wavelength optical phonons in  $\text{LiNbO}_3$  crystals.

### **INTRODUCTION**

The lattice dynamics of  $\text{LiNbO}_3$  (LN) has been the object of numerous investigations using the Raman [1–3] spectroscopy. Despite this, the phonon characteristics were not clearly established and some disagreements have been reported between various authors [2, 3]. All these investigations were carried out on crystals with the congruent composition, in which the Li deficit is nearly 3% with respect to the stoichiometric composition. Since, the possibility of obtaining crystals with off-congruent compositions was shown using vapour transport equilibration techniques [4] or by introducing  $\text{K}_2\text{O}$  in the melt [5]. It was then proved that several properties of LN, such as the optical absorption edge and the refractive indices, are dependent on the concentration of the non-stoichiometry defects in the crystal [5, 6]. The possible variation of the Raman lines (shape and positions) with the composition or the Li/Nb concentration ratio in the crystal are a interesting focus of investigation. The Raman scattering technique is one of several methods which could be used to determine the composition from the measurement of the width of some particular lines [7].

The goal of this paper is to complete the assignment of optical phonons with the new measurements in off-congruent crystals. For this, it is decided to study the influence of the crystal composition on the whole Raman spectrum recorded in several geometrical configurations. The comparison of the Raman data obtained for the congruent and the nearly stoichiometric crystals reveals some differences which lead to propose a new assignment of the long-wavelength optical phonons.

A complete and clear assignment can thus provide some useful information to understand the nature of the phase transitions and the origin of some physical and optical properties of lithium niobate [2].

## EXPERIMENTAL

The pure  $\text{LiNbO}_3$  crystals have been grown by the Czochralski technique with various initial compositions of  $\text{Li}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  in the melt. One is a congruent pure crystal with the composition of  $x_c = [\text{Li}]/([\text{Li}]+[\text{Nb}]) = 48.5\%$ , and the other is a nearly stoichiometric crystal with composition used in this study is  $x_c = [\text{Li}]/([\text{Li}]+[\text{Nb}]) = 49.74\%$ .

At room temperature, the structure of LN crystal belongs to the  $R3c$  space group with two molecules per unit cell. Accordingly, 18 vibrational modes at zero wavevector are decomposed into  $4A_1+9E+5A_2$ . Whereas the  $A_2$  phonons are Raman inactive,  $A_1$  and  $E$  modes are both Raman and infrared active [8].  $A_1$  modes are polarized along the  $Z$  axis while the doubly degenerate  $E$  modes correspond to ionic motions along  $X$  or the  $Y$  axis. Hereafter we consider the co-ordinate  $XYZ$  system where  $X$  refers to the crystallographic axis  $a$ ,  $Z$  is along the ferroelectric  $c$  axis and  $Y$  is normal to  $X$  and  $Z$ .

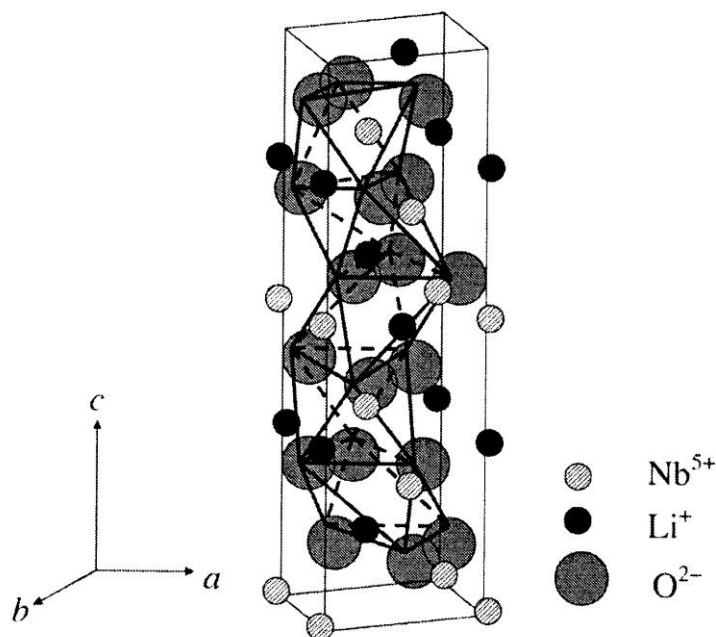


Figure 1 : Representation structure of  $\text{LiNbO}_3$  crystal

Raman scattering experiments have been performed in right-angle geometry using a Raman Pelkin Elmer Spectrometer of an Ar-ion laser with 350 mW output power.

## RESULTS AND DISCUSSION

Both  $A_1$  and  $E$  modes have been measured with particular attention to the  $E$  phonons since some discrepancies were reported for this symmetry. Purely transverse  $E(\text{TO})$  modes can be detected in the  $X(\text{ZY})Z$  configuration whereas  $E(\text{TO})$  and  $E(\text{LO})$  phonons are simultaneously detected in the  $X(\text{YZ})Y$  or  $X(\text{ZX})Y$  geometry. According to the group theory, 9 and 18 Raman lines are respectively expected [9].

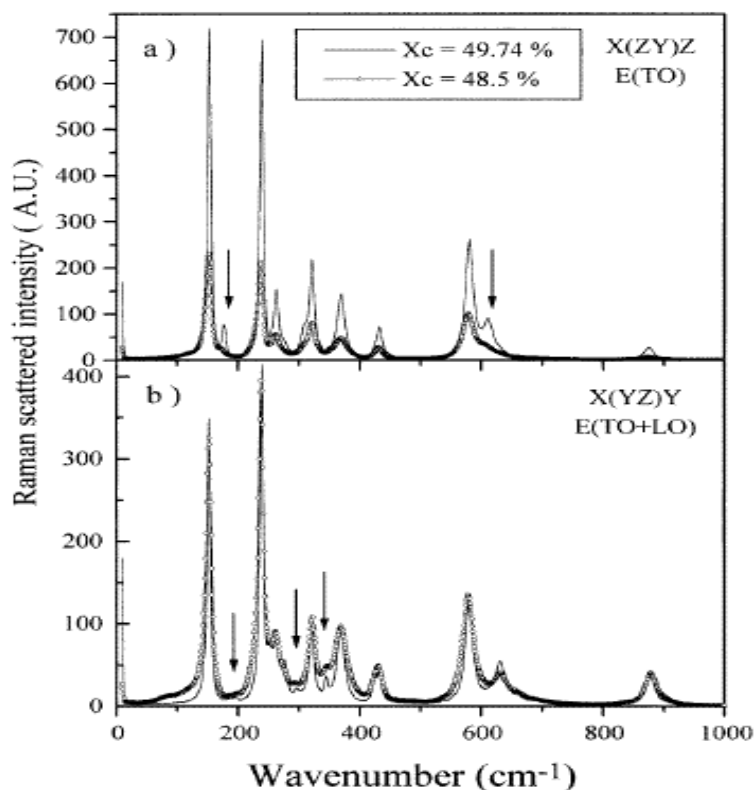


Figure 2 : Raman spectra recorded for the LN crystals with compositions  $x_c = 49.7\%$  and  $x_c = 48.5\%$ . The arrows point the frequency ranges where new lines clearly appear for the nearly stoichiometric crystal.

Figure 2 exhibits the Raman spectra recorded in the two geometries for both samples. First, it is noted that the lines are thinner, better resolved and more intense for the nearly stoichiometric sample compared with the congruent sample. Therefore, first-order phonons can be unambiguously attributed only to peaks which clearly appear in the spectrum for the stoichiometric sample. Thus, in the E(TO) spectrum, one peak is detected just below  $200\text{ cm}^{-1}$  and another one just above  $600\text{ cm}^{-1}$  for the stoichiometric crystal, instead of weak shoulders of intense peaks in the case of the spectrum recorded for the congruent sample. In the E(TO)+E(LO) spectrum (see Figure 2(b)), well defined lines occur around  $200$ ,  $300$  and  $350\text{ cm}^{-1}$  for the nearly stoichiometric crystal. These lines are hidden by an intense and continuous background in the corresponding spectrum recorded for the congruent sample. Moreover, this last spectrum exhibits bands at low frequency (below  $100\text{ cm}^{-1}$ ) and above  $660\text{ cm}^{-1}$  which are absent in the spectrum for the nearly stoichiometric sample. The new lines appearing in the E(TO) spectrum for the stoichiometric sample are more clearly seen in Figure 3. Thus, peaks at  $177$  and at  $610\text{ cm}^{-1}$  are unambiguously assigned and attributed to E(TO<sub>2</sub>) and E(TO<sub>9</sub>) phonons. It is also clear that no line exists beyond  $650\text{ cm}^{-1}$  in the E(TO) spectrum contrary to what was previously reported [1, 3].

The  $X(ZY)Z$  spectrum (see Figure 2(a)) exhibits all nine well resolved lines which correspond to all E(TO) phonons which are expected by the crystal symmetry. Their frequencies and dampings are reported in Table 1. E(LO) lines are also properly assigned by the comparison between the  $X(ZY)Z$  and  $X(YZ)Y$  spectra and reported in Table 1.

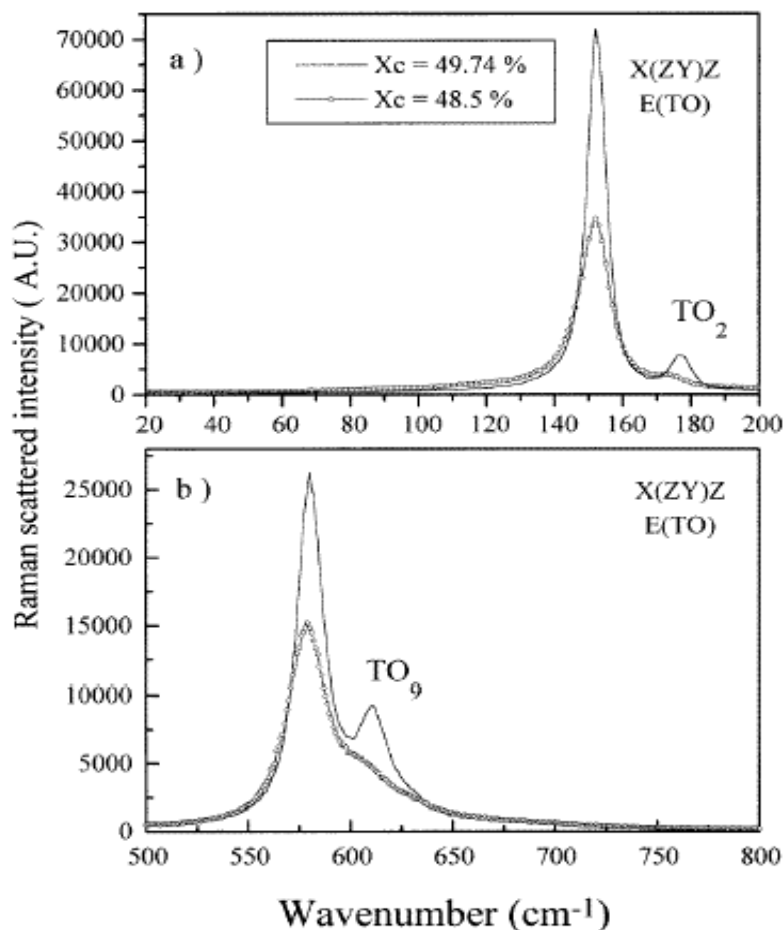


Figure 3 : Comparison of the Raman spectra recorded for LN crystals with two different compositions to point out the existence of new E(TO) lines.

Figure 4 exhibits the spectrum recorded in the  $X(ZZ)Y$  configuration corresponding to the detection of pure  $A_1(\text{TO})$  phonons. As expected by group theory, four peaks were detected around 252, 276, 333 and 633  $\text{cm}^{-1}$ . These positions are very close to those previously reported [2, 3]. However, additional bands with weak scattered intensities labelled a and b were observed around 700 and 100  $\text{cm}^{-1}$ . Their intensities are relatively enhanced when we proceed from the stoichiometric to the congruent crystal. In fact, it can be shown that these bands probably arise from two-phonon density of states [10].

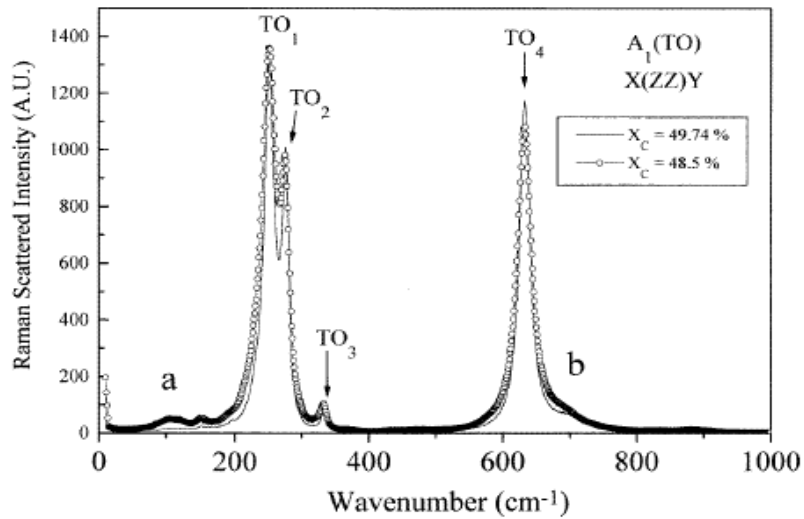


Figure 4 :  $A_1(\text{TO})$  Raman spectra recorded in LN crystals with two compositions.

The bands a and b are also seen in the E spectra specially for the congruent sample (see Figure 2(b)). This means that their intensity is enhanced in both E and  $A_1$  spectra with increasing number of non-stoichiometric intrinsic defects. Therefore, they are probably due to a breaking of the Raman selection rules due to the presence of intrinsic defects in the congruent crystal, leading to the detection of broad density of states bands. These bands have often been erroneously attributed in the literature to normal first-order phonon scattering [2].

The results obtained are compared to that reported in the literature. The differences and the new attributions are pointed out. It focuses the attention on the E phonons, which are the main object of disagreements in the literature. As shown in Table 1, significant discrepancies are found when our results are compared with previous Raman data.

First Raman measurements were reported by Schaufele and Weber [1]. Instead of nine expected lines only seven lines were assigned to the E(TO) phonons. More complete studies were performed by Kaminow and Johnston [2] and Claus *et al* [3]. Some discrepancies have been already noted between these two results [3]. The main difference arises from the attribution of the low-frequency band around  $90 \text{ cm}^{-1}$ , which was detected in both investigations. It have clearly shown above that this band disappears (see figure 2) when the crystal composition is close to stoichiometry. This proves that this band has no intrinsic origin and has to be unambiguously discarded in the assignment.

Table 1: E(TO) and E(LO) phonon characteristics obtained in our Raman investigation. frequencies and dampings (in brackets) are deduced from the fit of the Raman lines to damped oscillators. These results are compared with the previous Raman data reported by Kaminow and Johnston [2] and Claus et al [3]. New phonons which are first evidenced in the nearly stoichiometric crystal are pointed out by boxes, while the stars indicate the peaks which were erroneously attributed to the first-order phonons in previous investigations.

Kaminow and Johnston		Claus <i>et al</i>		Our work	
E(TO)	E(LO)	E(TO)	E(LO)	E(TO)	E(LO)
92*	117*				
152	198	155	198	152.8	186.5
				177.3	194.9
238	243	238	243	238.3	240.4
262	298	265	295	264.2	299.0
322	345	325	371*	321.9	345.0
			371	369.5	424.2
436	448	431	454	432.4	456.0
582	621	582	668*	580.0	625
630*	881	668*	739*		
		743*	880	609.8	878

Compared with the study of Claus *et al* [3], it is exclude a first-order origin of the broad bands lying above 650  $\text{cm}^{-1}$  in our new assignment. These bands were observed in various previous investigations which were performed for congruent samples. It is clearly shown in Figures 2 and 3 that the intensities of these bands decrease with a lowering of the intrinsic defect concentration.

Instead of these bands, it can be considered that the well resolved lines around 177 and 610  $\text{cm}^{-1}$  can be clearly attributed to first-order E(TO) phonons.

In this paper, it have have compared Raman results obtained in pure lithium niobate for two different compositions. Our data obtained in the congruent crystal are quite similar to those previously reported [2, 3]. The new assignment of the lattice modes in  $\text{LiNbO}_3$  reported here was rendered possible thanks to the recent availabilities of more perfect samples. The difference between Raman spectra recorded in congruent and nearly stoichiometric crystals only concerns the less intense peaks. In the stoichiometric sample well resolved lines appear instead of wide bands detected in the congruent sample. These bands therefore arise from the activation by intrinsic defects of the phonons belonging to the whole Brillouin zone. Other broad bands appearing in the congruent sample only, and previously assigned in the literature as first order phonon

lines, are here attributed to two-phonon density of states. On the other hand, some new lines occur only in the nearly stoichiometric crystal, so it is obtained a new and complete description of the long-wavelength optical phonons.

## CONCLUSION

The Raman spectrum of various scattering configurations has been measured for LiNbO<sub>3</sub> crystals with different compositions. The long-wavelength of Raman spectra recorded for congruent and the nearly stoichiometric crystals shows significant differences in the shape and the number of Raman peaks. Some new lines occur only in the nearly stoichiometric crystal, so it is obtained a new and complete vibrational modes description of the long-wavelength optical phonons in LiNbO<sub>3</sub> crystals.

## ACKNOWLEDGMENT

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