

Vibrational spectra of the ilmenite modifications of LiNbO_3 and NaNbO_3

E. J. BARAN, I. L. BOTTO

Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calles 47 y 115, 1900-La Plata, Argentina

F. MUTO, N. KUMADA, N. KINOMURA

Institute of Inorganic Synthesis, Yamanashi University, Miyamae-cho 7, Kofu, 400 Japan

Lithium niobate, LiNbO_3 , is a very important material for optical and other applications. It has been widely used in applications such as electric waveguides, memory elements, acoustic wave transducers, optical amplitude modulators, second harmonic generators, etc. [1]. Its structural type is one of the four most common "typical structures" for double oxides of ABO_3 stoichiometry [2, 3] and it can be considered as a disordered ilmenite lattice [3]. Recently, it has also been possible to prepare a metastable LiNbO_3 phase with the ideal ilmenite structure [4].

In order to extend our knowledge of the physico-chemical properties of this new material we have investigated its infrared and Raman spectra and compared them with those of some other structurally related double oxides as well as with that of normal LiNbO_3 . The spectra of the precursor-phase, NaNbO_3 , which can also be obtained as a metastable ilmenite-like phase [5] are also recorded and discussed.

NaNbO_3 was obtained, as described elsewhere [5], by hydrothermal synthesis, and the corresponding lithium compound by an ion-exchange procedure working with a LiCl/KCl eutectic mixture at 360 to 380°C [4]. The infrared spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr-pellet technique. The Raman spectra were recorded with a SPEX-Ramalog double monochromator spectrometer and using the 647.1 nm line of a krypton ion laser for excitation.

The infrared spectrum of LiNbO_3 is shown in Fig. 1. Although it closely resembles that of other ilmenite materials investigated earlier, such as the $\text{M}^{\text{II}}\text{TiO}_3$ and $\text{M}^{\text{II}}\text{SnO}_3$ oxides [6, 7] and NaSbO_3 [8], it is not as well and clearly resolved as in many of these phases. This is attributable, in part, to the fact that the material is not attainable in a well crystallized form. But, on the other hand, the spectrum of NaNbO_3 is almost identical to that in Fig. 1, despite the fact that it exhibits a higher degree of crystallinity than LiNbO_3 .

The Raman spectra of both materials are also very similar in their general features, but in this case, the NaNbO_3 spectrum, shown in Fig. 2, presents a better definition and resolution than that of LiNbO_3 . A comparison of these spectra with those of other ilmenite phases [9, 10], immediately shows that the Raman spectra are not as characteristic as the infrared ones.

A factor group analysis of the ilmenite lattice shows that the irreducible representation of the optical modes in the crystal is $\Gamma_{\text{opt}} = 5A_g + 5E_g + 4A_u + 4E_u$ [6]. As the structure presents an inversion centre, the exclusion rule holds, and therefore g phonons are only Raman active whereas u phonons present only infrared activity. These results imply that a maximum of eight and ten bands can be expected in the infrared and Raman spectra, respectively.

The measured band positions for both materials are shown in Table I. It can be seen that both infrared spectra show seven of the eight expected bands, whereas in the Raman effect one or two lines are also missing. It is possible that some of the lines are very near-lying doublets, as suggested by the spectrum of Fig. 2.

The main vibrational bands of both LiNbO_3 and NaNbO_3 lie at slightly higher wavenumbers than in the MTiO_3 and MSnO_3 systems [6, 7] but in a similar range as in NaSbO_3 [8]. This suggests that the charge of the B cation is probably the predominant factor on the band position in ABO_3 ilmenites. As it was discussed in cases investigated previously [7, 8, 10] the observed vibrations must be of a complex origin, and both, the movements of the " NbO_6 "- and " $\text{M}^{\text{II}}\text{O}_6$ "-polyhedra contributed in a greater or lesser extent to all of them.

The comparison with the spectra of the stable LiNbO_3 and NaNbO_3 modifications is especially interesting. Only infrared data are known for both phases [11]. These spectra are markedly different from those reported in the present letter, mainly in the

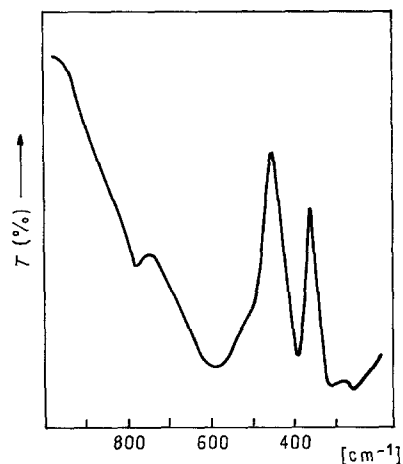


Figure 1 Infrared spectrum of the ilmenite form of LiNbO_3 .

TABLE I Vibrational spectra of the ilmenite modifications of LiNbO_3 and NaNbO_3 (cm^{-1})

LiNbO_3	NaNbO_3
<i>Infrared</i>	
783 w	790 w
630 sh	630 sh
595 vs	590 vs
~ 500 sh	505 sh
398 s	387 s
318 s, br	295 s, br
245 vw	255 vw
<i>Raman</i>	
735 vs	733 vs
677 vw	673 vw
470 m	487 s
	476 sh
381 w	
291 m	287 s
275 m	257 m
214 m	212 s
	202 s
173 w	165 m

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

spectral range below 500 cm^{-1} . The principal absorptions in the higher wavenumber region are also centred, in both compounds, at $\sim 700\text{ cm}^{-1}$, i.e. they lie appreciably higher than in the ilmenite materials.

In conclusion, the present study has shown that the LiNbO_3 and NaNbO_3 with ilmenite structure show the infrared spectral pattern characteristic of such material. On the other hand, these spectra differ appreciably from those previously reported for the stable modifications, therefore allowing an easy and rapid identification of the two different polymorphic forms of these materials.

Acknowledgements

E.J.B. and I.L.B. were supported by CONICET, Argentina (Programa QUINOR) and CIC-Provincia de Buenos Aires. N.K. thanks the Grant-in-aid of

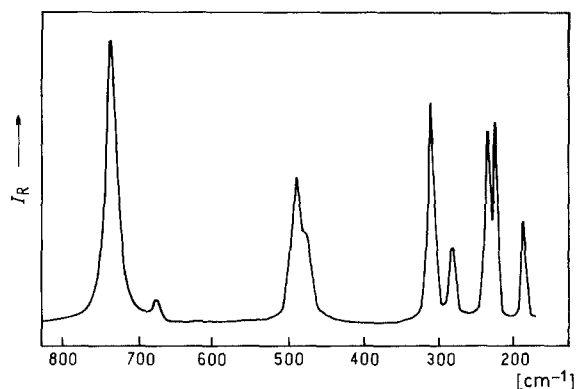


Figure 2 Raman spectrum of the ilmenite form of NaNbO_3 .

the Ministry of Education, Science and Culture (60750740) for financial support. The authors also thank Mr R. Garcia for the measurement of the Raman spectra.

References

1. R. S. WEISS and T. K. GAYLORD, *Appl. Phys.* **A37** (1985) 191.
2. J. B. GOODENOUGH and J. A. KAFALAS, *J. Solid State Chem.* **6** (1973) 493.
3. I. L. BOTTO and E. J. BARAN, *N. Jahrb. Miner. Abhandl.* **142** (1981) 320.
4. N. KUMADA, N. OZAWA, F. MUTO and N. KINOMURA, *J. Solid State Chem.* **57** (1985) 267.
5. N. KINOMURA, N. KUMATA and F. MUTO, *Mater. Res. Bull.* **19** (1984) 299.
6. E. J. BARAN and I. L. BOTTO, *Z. Anorg. Allg. Chem.* **444** (1978) 282.
7. I. L. BOTTO and E. J. BARAN, *ibid.* **465** (1980) 186.
8. E. J. BARAN and I. L. BOTTO, *An. Asoc. Quim. Argent.* **69** (1981) 283.
9. *Idem*, *Z. Anorg. Allg. Chem.* **448** (1979) 188.
10. N. L. ROSS and P. McMILLEN, *Am. Mineral.* **69** (1984) 719.
11. C. ROCCHICCIOLI-DELTCHEFF, *Spectrochim. Acta* **29A** (1973) 93.

Received 6 December
and accepted 9 December 1985