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LETTER TO THE EDITOR

Luminescence of the Ilmenite Phase of $LiNbO_3$

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The luminescence of the ilmenite phase of $LiNbO_3$ is reported and compared with that of the $LiNbO_3$-structured phase. The differences are discussed in terms of interaction between the niobate octahedra. © 1994 Academic Press, Inc.

1. INTRODUCTION

Lithium niobate, $LiNbO_3$, is a well-known electrooptic material. Its physical properties depend strongly on the stoichiometry of the samples. This has also been found for the luminescence properties (1–3). Stoichiometric samples show an emission band with a maximum at about 440 nm; Li-deficient samples show an emission band with a maximum at about 520 nm. The former has been ascribed to the intrinsic niobate group, the latter to niobate groups near defect sites.

Recently, the energetics of the ilmenite form of $LiNbO_3$ has been reported (4). This phase was prepared by ion exchanging the ilmenite form of $NaNbO_3$, which was synthesized hydrothermally.

The $LiNbO_3$ structure and the ilmenite structure are both superstructures of the corundum (α-Al_2O_3) structure, but the Li/Nb order is different. In ilmenite, there are alternating layers of exclusively Li^+ ions or Nb^{5+} ions perpendicular to the *c*-axis. Each niobate octahedron shares edges with three other niobate octahedra in the same plane. In the $LiNbO_3$ structure, these layers contain equal amounts of Li and Nb. Each niobate octahedron is connected to six others by corner sharing; these six approximately form an octahedron. The Nb–O–Nb angle is 125°.

This study compares the luminescence of the ilmenite and lithium niobate forms of $LiNbO_3$. The difference is substantial.

2. EXPERIMENTAL

The samples used were those prepared and characterized previously (4). One sample contained about 4, the other about 8 mole% Na (replacing lithium), due to the synthesis method.

The optical instrumentation has been described elsewhere (2, 5).

3. RESULTS

The samples of 8ilmenite-structured $LiNbO_3$ (further indicated $LiNbO_3$ (i)) at 4.2 K show a weak photoluminescence under ultraviolet excitation. The broad emission band shows a maximum at about 540 nm (see Fig. 1). The corresponding excitation band is broad and weak. Its maximum is estimated to be at 320 nm.

This value agrees well with the diffuse reflection spectrum which shows an optical absorption edge at 320 nm (see Fig. 2). Note that $LiNbO_3$ (i) has this edge at a much longer wavelength than $LiNbO_3$-structured $LiNbO_3$ (further indicated as $LiNbO_3$ (L)) (see Fig. 2).

The photoluminescence intensity decreases at higher temperature and disappears at 100 K. Table 1 summarizes the different luminescence properties of the two $LiNbO_3$ modifications.

4. DISCUSSION

The $LiNbO_3$ (i) phase shows niobate absorption at lower energy than the $LiNbO_3$ (L) phase. This follows from Fig. 2, independent of whether the $LiNbO_3$ (L) phase is stoichiometric or not. This suggests that the interaction between the niobate octahedra in $LiNbO_3$ (i) is staronger than in $LiNbO_3$ (L) (7).

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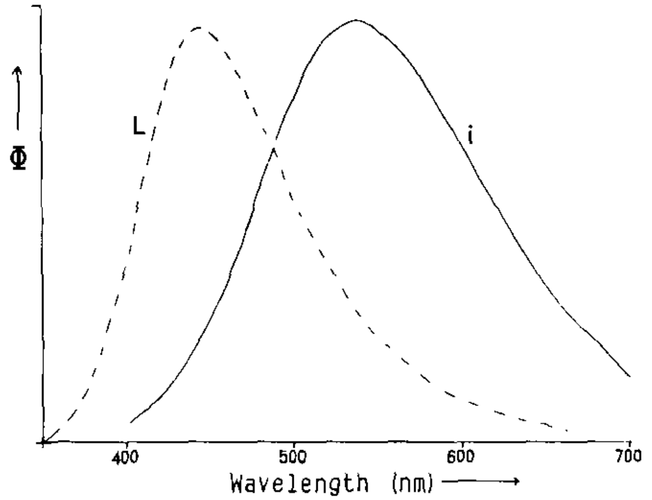

FIG. 1. Emission spectra of $LiNbO_3$ (i) (solid line) and $LiNbO_3$ (L) (broken line) at 4.2 K. Excitation is at the maximum of the excitation band.

Actually, this interaction vanishes in the $LiNbO_3$ (L) modification since the optical properties of the niobate octahedron in $LiNbO_3$ (L) and $LiTaO_3$ (L) are identical (5). Obviously, the Nb–O–Nb configuration with an angle of 125° and unequal Nb–O distances (8) is unfavorable for such an interaction.

In $LiNbO_3$ (i), such an interaction is possible via direct overlap of the *d* orbitals of the Nb^{5+} ions due to the edge sharing of the octahedra involved. In the case of ilmenites with transition metal ions with incompletely filled *d* shells (like $MnTiO_3$), such an interaction is responsible for the magnetic properties (9).

Therefore, the optical absorption edge of $LiNbO_3$ (i) decreases in energy in comparison with that of $LiNbO_3$ (L) due to energy band broadening of the conduction band, which consists mainly of the niobium 4*d* orbitals.

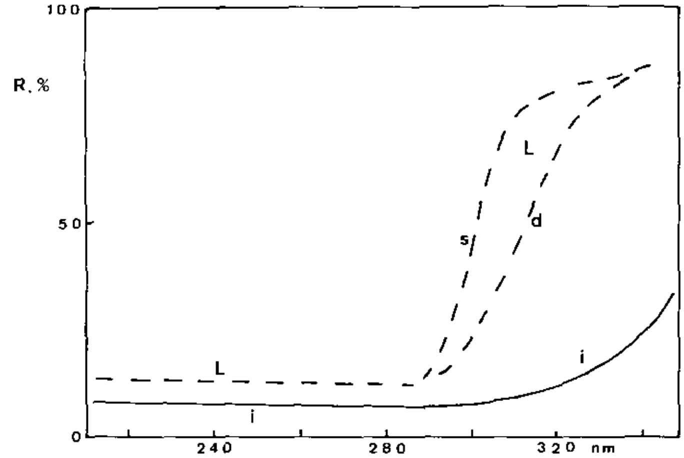

FIG. 2. Diffuse reflection spectra of $LiNbO_3$ (i) (solid line) and $LiNbO_3$ (L) (broken lines: s, stoichiometric; d, lithium deficient).

TABLE 1

Luminescence Properties of Compositions under Study

	$LiNbO_3$ (L)[a]	$LiNbO_3$ (i)[b]	$Mg_4Sb_2O_9$:Nb[c]
Optical absorption edge	290 nm	320 nm	—
Emission maximum	440 nm	540 nm	520 nm
Excitation maximum	260 nm	320 nm	285 nm
Stokes shift	16.000 cm^{-1}	13.000 cm^{-1}	16.000 cm^{-1}
Luminescence intensity at 4.2 K	High	Low	—
T_q[d]	300 K	100 K	270 K

Note. Optical data at 4.2 K.

[a] $LiNbO_3$-structured phase; data from Ref. (1).

[b] Ilmenite-structured phase; this work.

[c] Data from Ref. (6).

[d] Thermal quenching temperature.

Examples of this phenomenon have been reported by us before: $Sr_2Nb_2O_7$ with 330 nm (10, 11) and $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ with 360 nm (12).

As argued elsewhere, this band broadening reduces the value of the Stokes shift and the thermal quenching temperature of the luminescence (7, 10–12). Also, the luminescence efficiency can be expected to decrease. Table 1 shows that all this is observed when the luminescences of the $LiNbO_3$ (i) and the $LiNbO_3$ (L) modifications are compared. This confirms the present explanation of the difference between the optical properties of the two phases.

It is interesting to compare the results for $LiNbO_3$ (i) with those for $Mg_4Sb_2O_9$:Nb(6). The latter composition has also the ilmenite structure. The cation layers are alternately occupied by Mg^{2+} and a statistical mixture of (1/3 Mg^{2+} + 2/3 Sb^{5+}). In this ilmenite phase, the niobate octahedron has no interaction with other niobate groups because only 1% of the Sb^{5+} ions is replaced by Nb^{5+}. Although the niobate octahedra in $LiNbO_3$ (i) and in $Mg_4Sb_2O_9$ (i) have chemically different surroundings, the Stokes shift and the thermal quenching temperature of the niobate group in $Mg_4Sb_2O_9$ are similar to those in $LiNbO_3$ (L), and not to those in $LiNbO_3$ (i). This confirms that the low values found for $LiNbO_3$ (i) are a consequence of the interaction between the niobate octahedra.

In conclusion, the luminescence properties of $LiNbO_3$ (L) and $LiNbO_3$ (i) are different. This difference is due to interaction between the niobate octahedra in $LiNbO_3$ (i), which lowers and delocalizes the *d* orbitals of niobium.

REFERENCES

1. D. M. Krol, G. Blasse, and R. C. Powell, *J. Chem. Phys.* **73**, 163 (1980).
2. M. H. J. Emond, M. Wiegel, G. Blasse, and R. Feigelson, *Mater. Res. Bull.*, in press.

3. C. Fisher, M. Wöhlecke, T. Volk, and N. Rubinina, *Phys. Status Solidi A* **137,** 247 (1993).
4. A. Mehta, A. Navrotsky, N. Kumada, and N. Kiomura, *J. Solid State Chem.* **102,** 213 (1993).
5. M. Wiegel, M. H. J. Emond, E. Stobbe, and G. Blasse, in preparation.
6. G. Blasse, *J. Chem. Phys.* **48,** 3108 (1968).
7. G. Blasse, *Prog. Solid State Chem.* **18,** 79 (1988).
8. S. C. Abrahams, J. M. Reddy, J. L. Bernstein, W. C. Hamilton, and H. J. Levinstein, *J. Phys. Chem. Solids* **27,** 997, 1013, 1019 (1966).
9. J. B. Goodenough, "Magnetism and the Chemical Bond." Wiley, New York, 1963.
10. G. Blasse and L. H. Brixner, *Mater. Res. Bull.* **24,** 363 (1989).
11. M. Wiegel, M. Hamoumi, and G. Blasse, *Mater. Chem. Phys.*, **36,** 289 (1994).
12. M. Wiegel, G. Blasse, and M. Ouwerkerk, *Mater. Res. Bull.* **27,** 617 (1992).