The Luminescence of α- and β-LaNb$_3$O$_9$

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The luminescence of undoped and rare-earth-doped LaNb$_3$O$_9$ is reported. The two modifications (α and β) show striking differences. Whereas undoped β-LaNb$_3$O$_9$ does not luminesce at all (down to 4.2 K), α-LaNb$_3$O$_9$ emits efficiently with a quenching temperature of 250 K. Energy transfer from niobate to rare-earth dopants is observed for the α, but not for the β modification. The rare-earth dopant emission consists of sharp lines for the α modification, but is considerably broadened for the β modification. The luminescence properties are discussed in terms of the crystal structure. In addition results for α-NbPO$_5$ will be given. © 1985 Academic Press, Inc.

1. Introduction

Recently the crystal structure of α-LaNb$_3$O$_9$, has been reported by Torardi *et al.* (*1*). That of the β modification was known since long (*2*). The latter can be described as an orthorhombically distorted perovskite with La^{3+} vacancies and is the high-temperature modification. The α phase could only be prepared hydrothermally. Its structure contains double chains of distorted NbO$_6$ octahedra which share opposite corners along the chain and share edges across the chain. The double chains are interconnected by single chains of corner-sharing NbO$_6$ octahedra. The La^{3+} ions are located in tunnels formed by the niobate framework and are in eight-coordination.

The two structures being different, it seemed tempting to investigate the luminescence properties of both modifications, especially because quite some niobates were studied in our laboratories before (*3, 4*). In this paper we report on the results of an investigation of α- and β-LaNb$_3$O$_9$, undoped as well as doped with Sm^{3+}, Eu^{3+}, Dy^{3+}, Tb^{3+}, and Tm^{3+}. For reasons which will become clear below, we investigated also α-NbPO$_5$.

2. Experimental

Samples of α- and β-LaNb$_3$O$_9$, doped and undoped, were prepared as described before (*1*). Samples of α-NbPO$_5$ were prepared as described in Ref. (*5*).

They were checked by X-ray diffraction. The performance of the optical measurements has been given before (6).

3. Results and Discussion

3a. Undoped α- and β-LaNb$_3$O$_9$

Undoped β-LaNb$_3$O$_9$ does not luminesce, not even at 4.2 K. The diffuse reflection spectrum shows an absorption edge at about 370 nm (see Fig. 1). The absorption edge of the α-modification is situated at higher energy, viz. at 320 nm (Fig. 1). Note that these are room temperature values. Below 250 K α-LaNb$_3$O$_9$ shows a greenish luminescence under ultraviolet excitation. The spectra are given in Fig. 1. The emission band has a maximum at about 535 nm, and the corresponding excitation band has a maximum at 310 nm (4.2 K values). The Stokes shift of the emission is 14.000 cm^{-1}.

Between 4.2 and 250 K the luminescence intensity decreases in a peculiar way, viz. about linearly with temperature. The decay curves of the luminescence are exponential. The decay times are plotted as a function of temperature in Fig. 2. If this curve is analyzed with a three-level scheme, where level 0 (ground state) < level 1 < level 2 (7), we find $E_2 - E_1 = 32$ cm^{-1}, $P_{10} = 6.3 \times 10^3$ sec^{-1}, and $P_{20} = 1.7 \times 10^5$ sec^{-1}. Here E_i denotes the energy of level i and P_{ij} the radiative transition rate from level i to level j. The curve corresponding to these values is also given in Fig. 2.

These results show that the crystal structure is of large influence on the luminescent properties, because one of the two modifications of one and the same compound does luminesce, whereas the other does not. One of us has argued before that two conditions are favorable for the occurrence of luminescence in niobates, viz. condensation of niobate octahedra to larger complexes by face- or edge-sharing and high-energy position of the emitting state (3). In a qualitative sense our results agree with these conditions, because the absorption edge of the luminescent phase is at higher energies than that of the nonluminescent phase and because the luminescent phase contains niobate octahedra which share an edge, whereas the nonluminescent phase contains only corner-sharing niobate octahedra.

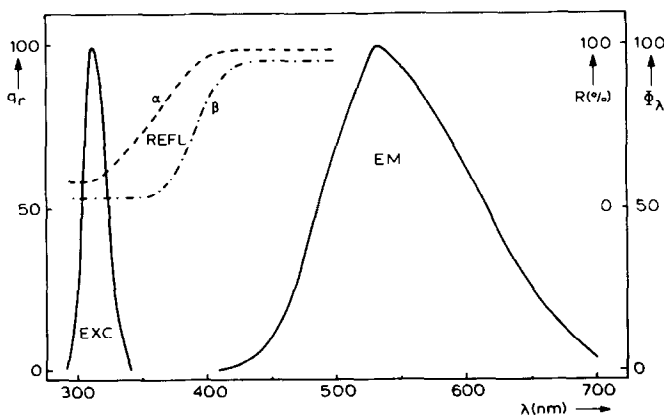Although these conditions have been confirmed by a vast amount of experimen-

FIG. 1. Emission and excitation spectra of the luminescence of α-LaNb$_3$O$_9$ at LHeT (solid lines). Diffuse reflection spectra of α-LaNb$_3$O$_9$ (dashed line) and β-LaNb$_3$O$_9$ (dashed-dotted line) at RT. q_r denotes the relative quantum output and Φ_λ the spectral radiant power per constant wavelength interval, both in arbitrary units. R gives the reflection.
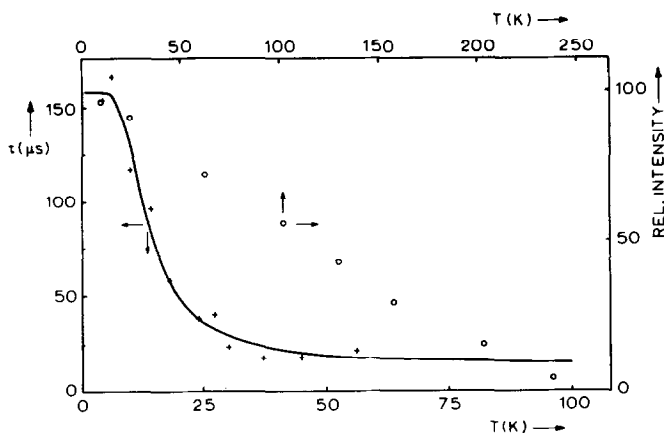
FIG. 2. Emission intensity (○) and decay time (+) of the emission band of α-LaNb$_3$O$_9$ as a function of temperature. The solid line gives the best fit to the experimental data (see text).

tal data, still another effect which can be of importance has recently been proposed (8). The niobate luminescence is usually described in terms of a configurational coordinate diagram, the large Stokes shift pointing to a considerable amount of lattice relaxation (self-trapped state) (3). However, in a few cases (TiO$_2$, CsVO$_3$), it has been found that another description should be used, because the exciton bandwidth is larger than the electron-lattice relaxation energy (9). This leads to nearly free states with free exciton emission if the compound is free enough of defects. In practice the excitation energy is easily captured by killer centers resulting in the absence of luminescence. Further, pronounced band formation increases the width of the bands, so that the absorption edge moves to lower energies.

Comparing the present results with those obtained for titanates (8), we propose to ascribe the absence of luminescence in β-LaNb$_3$O$_9$ to delocalization effects which overcome the electron-lattice relaxation. The bandwidth is given by $2B = 2\nu|J|$ (9). Here ν is the number of nearest neighbors and J the transfer energy. In the β phase ν = 6, in the α phase ν = 5. Moreover, the perovskite structure is well known for its

tendency to form relatively broad electronic bands. The Nb-O-Nb angles are more favorable for band formation in the β phase (160-180°, (2)) than in the α phase (130-155°, (1)). Consequently, J may be larger in the β than in the α phase. This model is also favored by the low-energy position of the absorption edge of β-LaNb$_3$O$_9$.

In terms of this description β-LaNb$_3$O$_9$ is in between WO$_3$ and SrTiO$_3$ (10). The Ti^{4+}, Nb^{5+}, W^{6+}, and O^{2-} ions form a ReO$_3$-like lattice in all three cases. SrTiO$_3$ is known to be a semiconductor, but intrinsic self-trapped exciton emission has been observed up to 35 K (8). For β-LaNb$_3$O$_9$ no emission was observed, so that we obviously have just passed the conditions under which the self-trapped excited state is still stable. For WO$_3$ the situation is the same, perhaps even more extreme. Thin-layer WO$_3$ has been reported to emit a very weak luminescence which can be assigned in terms of this model. It cannot be excluded that β-LaNb$_3$O$_9$ shows also luminescence if prepared under extreme severe conditions.

Let us now turn to α-LaNb$_3$O$_9$. It will be obvious from the arguments above that the occurrence of luminescence in the α modification is ascribed to a shift on the scale free-state vs self-trapped-state to the side of

the self-trapped state [cf. Ref. (8)]. We realize that the arguments are of a rough and qualitative nature only. However, the observation that luminescence is lost in a phase transition of an oxidic compound by an increasing amount of delocalization is new and appealing. We relate this effect to the change in crystal structure which will influence the band widths involved. Unfortunately the present samples are not suitable for electrical conductivity and photoconductivity measurements which would be of large interest. Let us now consider the luminescence (Figs. 1 and 2) in more detail.

The characteristics resemble those reported for self-trapped emission from niobates [3]. The Stokes shift is relatively small (14.000 cm^{-1} vs 16.000 cm^{-1}) and the absorption edge at rather low energy for a niobate. This may indicate that we are not far from a delocalized state. The decay times are typical (3), their relatively long values being due to the spin selection rule. However, the temperature dependence of the luminescence intensity is disturbing, especially since the decay times suggest that nonradiative processes can be neglected for not too high temperatures. Also it was carefully checked that the absorption remained constant during the measurements. Because of lack of further data we are only able to propose that absorption by a state

which does not lead to luminescence becomes more important at higher temperatures. This does not seem to be unreasonable. Since we are on the boundary of free and self-trapped states, the higher excited states may well be more delocalized and have a stronger temperature dependence than the lowest excited state.

The structure of α-LaNb$_3$O$_9$ contains single and double niobate chains. The former are also found in the structure of α-NbPO$_5$, the latter in the structure of CaTa$_2$O$_6$. For this reason we investigated α-NbPO$_5$. Emission and excitation spectra at LHeT are presented in Fig. 3. The emission maximum is at 490 nm, the excitation maximum at 260 nm. This emission is quenched at 150 K. The Stokes shift is large, viz. 18.000 cm^{-1}. Note that these spectral data are completely different from those for α-LaNb$_3$O$_9$, so that it can be excluded that the luminescent state in α-LaNb$_3$O$_9$ is mainly localized in the single chains.

In these linear chains (in α-NbPO$_5$ as well as in α-LaNb$_3$O$_9$) octahedra share corners along the chain direction, but the shared oxygen ions are not in between the two Nb^{5+} ions. They are shifted strongly into the direction of one of the two ions (in α-LaNb$_3$O$_9$, e.g., these distances are 1.77 and 2.18 Å (1)). The large Stokes shift of the emission of α-NbPO$_5$ suggests a considerable reorganization in the excited state. It
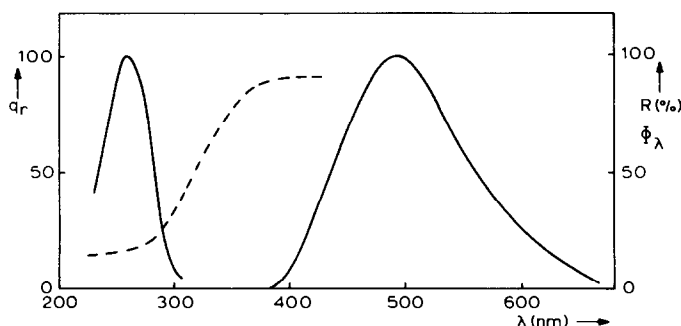

FIG. 3. Emission and excitation spectra of the luminescence of α-NbPO$_5$ at LHeT (solid lines). Diffuse reflection spectrum of α-NbPO$_5$ at RT (dashed line).

may well be that the shared oxygen ion moves to a more central position.

For α-NbPO$_5$ we observed also a weak additional emission, which is quite general for this type of compound (3). The emission and excitation maxima are located at 520 and ~300 nm, respectively. As usual, they are assigned to defect niobate groups.

The luminescence of CaTa$_2$O$_6$ (with the same double chains as α-LaNb$_3$O$_9$) has been mentioned in the literature, but no exact data are known (11, 12). If we correct the value of the absorption edge of CaTa$_2$O$_6$ (38.500 cm^{-1}) by the difference between those of Ta$_2$O$_5$ and Nb$_2$O$_5$ (7.500 cm^{-1}, Ref. (12)), we arrive at the same value as found for α-LaNb$_3$O$_9$. Also the emission would then shift to the same spectral region as that of α-LaNb$_3$O$_9$. Finally the quenching temperature of the CaTa$_2$O$_6$ emission is at about room temperature, i.e., only slightly higher than that of α-LaNb$_3$O$_9$. Although these facts are not convincing, they suggest that the emitting state of α-LaNb$_3$O$_9$ is considerably more localized in the double niobate chains than in the single niobate chains.

It is a pity that the crystal structures of the α and β modification of LaNb$_3$O$_9$ are so complicated. This seems to exclude a more accurate analysis at the moment.

3b. The Luminescence of Sm^{3+}, Eu^{3+} and Dy^{3+} in LaNb$_3$O$_9$

The dopant concentration in all samples amounts to 6 mole%, i.e., the composition is La$_{0.94}$RE$_{0.06}$Nb$_3$O$_9$. Since the results for Sm^{3+}, Eu^{3+}, and Dy^{3+} are similar, they are dealt with together. Excitation into the rare-earth dopant results in efficient luminescence, in the α as well as in the β modification. Since the transitions involved can be considered as classic, they are not further discussed here. A striking difference between the spectra of the rare earths in the α and in the β modification is the following. In the α phase the spectra consist of sharp line emissions, whereas in the β phase the lines are broadened, so that they overlap, forming narrow bands. This is observed for all dopants and under the same optical conditions under which the sharp lines of the α phase are observed. Figure 4 illustrates this effect for the case of LaNb$_3$O$_9$–Sm^{3+}.

The explanation follows immediately from the crystal structures. In α-LaNb$_3$O$_9$ there is only one crystallographic site for the rare-earth ions (1), so that the crystal field at all ions is the same (apart from inhomogeneous broadening). In β-LaNb$_3$O$_9$, however, the La^{3+} sites are occupied by $\frac{2}{3}$La^{3+} in a random way (2). Consequently the crystal field at the rare-earth ion will vary strongly from site to site, so that the lines in the spectra are considerably broadened. This experiment shows in a very direct way the disordered arrangement of the La^{3+} ions in the crystal structure of β-LaNb$_3$O$_9$.

The simple emission spectrum of α-LaNb$_3$O$_9$-Eu^{3+} gives direct information on
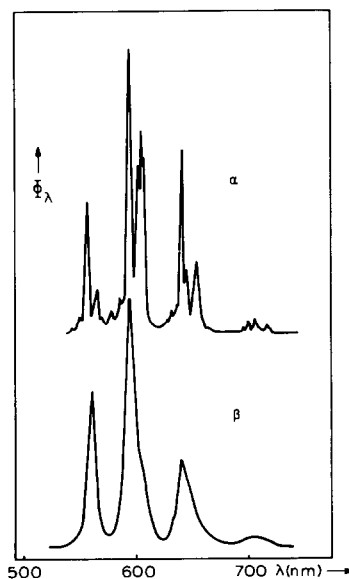
FIG. 4. Emission spectra of α- and β-La$_{0.94}$Sm$_{0.06}$Nb$_3$O$_9$ at RT. The excitation wavelength is 406 nm. Note the broad line in the case of the β modification.

the site symmetry of the La^{3+} ion in this modification. We observe 1 line in the $^5D_0$–$^7F_0$ transition, 3 in the $^5D_0$–$^7F_1$ and 4 in the $^5D_0$–$^7F_2$ transition. The actual site symmetry is C$_1$ (*1*), but Fig. 2 of Ref. (*1*) shows that C$_{2v}$ is a good approximation. This is confirmed by our results, since the number of lines for C$_1$ would be 1, 3, and 5 and for C$_{2v}$ they would be 1, 3, and 4, respectively.

Let us now turn to niobate excitation. In the case of the β modification, excitation into the niobate group does not yield any luminescence at all. Obviously the recombination rate of the charge carriers formed upon excitation is so fast, that capture by or transfer to the activators cannot compete with this rate. This is completely different in the α modification, where niobate excitation results in activator as well as niobate emission (below the quenching temperature of the niobate emission). The excitation spectrum of the rare-earth emission shows the 310-nm excitation band of the niobate lattice, indicating energy transfer from the niobate lattice to the emitting rare-earth ion. Such an excitation band is, of course, not observed in the rare-earth excitation spectrum in case of the β modification. Table I gives the ratio of the niobate and rare-earth emission intensities at 10 K upon niobate excitation. For Sm^{3+}, Eu^{3+}, and Dy^{3+} these values are about equal, the error in the tabulated figures being a few percent.

This ratio of the emission intensities follows also from a simple model. If the excited state is localized at the low temperature of the measurements (which is certainly correct) and if it is localized in the double niobate chains (see above), then we expect 78% niobate and 22% rare-earth emission. Here we assume that transfer occurs only between nearest neighbors and that its rate exceeds the radiative rate. Since the niobate groups in the double chain have 4 nearest neighbors La^{3+} sites (*1*), the probability that the niobate group has only La^{3+} neighbors (and will therefore emit) is 0.94^4 = 0.78. If the niobate group has one or more activator ions on the nearest neighbor sites, activator emission will occur in this model. It is clear that this simple model, which has been successfully applied elsewhere (*13*), is a suitable approximation of the niobate-activator transfer in the α modification.

3c. The Luminescence of Tb^{3+} in LaNb$_3$O$_9$

The results for Tb^{3+} activation are similar to those for Sm^{3+}, Eu^{3+}, or Dy^{3+} activation with two exceptions, viz. the total luminescence intensity of LaNb$_3$O$_9$–Tb^{3+} is considerably lower under all possible excitations and the relative amount of Tb^{3+} emission is higher (see Table I). The low overall efficiency shows that Tb^{3+} quenches the niobate emission in a complicated way. Similar observations have been made for other systems, the most well-known being YVO$_4$–Tb (*14*). This quenching has been explained by assuming a charge-transfer state Tb^{4+}–V^{4+} (Nb^{4+}) with large offset in the configuration coordinate model. Such a state will be at relatively low energy in case of Tb^{3+} with 4f^8 configuration. It is clear that under this condition the Tb^{3+}-niobate intensity ratio (Table I) is not easy to interpret.

The excitation spectra of the Tb^{3+} emission of α- and β-LaNb$_3$O$_9$–Tb^{3+} contain only a very weak and no niobate excitation

TABLE I

RATIO OF THE RARE-EARTH AND NIOBATE EMISSION OF α-La$_{0.94}$RE$_{0.06}$Nb$_3$O$_9$ AT LHeT FOR EXCITATION INTO THE NIOBATE GROUP

RE^{3+}	RE^{3+} emission (%)	Niobate emission (%)
Sm^{3+}	30	70
Eu^{3+}	24	76
Dy^{3+}	17	83
Tb^{3+}	40	60
Tm^{3+}	0	100

band, respectively. Therefore it is possible to find another broad band with a maximum at 250 nm for the β phase and at 265 nm for the α phase (see Fig. 5). Although these bands have low intensity, their existence is beyond doubt. Obviously these bands correspond to absorption in the Tb^{3+} center. One possibility to assign these transitions is the well-known $4f \rightarrow 5d$ transition on Tb^{3+}. However, in view of the arguments used above, these bands can also, tentatively, be ascribed to the charge-transfer transition involved ($Tb^{4+}-Nb^{4+}$).

3d. The Luminescence of Tm^{3+} in $LaNb_3O_9$

No luminescence was observed for the β modification, not even for direct Tm^{3+} excitation. The α modification yields at room temperature weak Tm^{3+} emission ($^1D_2-^3F_4$) upon Tm^{3+} excitation ($^3H_6-^1D_2$) (compare Fig. 6). At 4.2 K, excitation into the niobate lattice yields mainly niobate emission. No
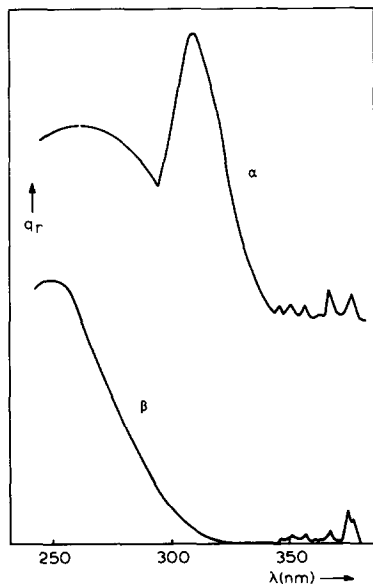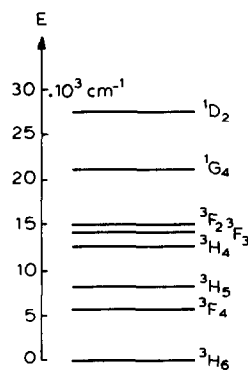
FIG. 6. Energy level scheme of Tm^{3+}.

transfer of any importance to Tm^{3+} is observed. Under high resolution the niobate emission band shows some structure around 470 nm (see Fig. 7). At 461 and 469 nm negative dips are observed which must be due to radiative energy transfer from the niobate complex to Tm^{3+}. The latter reabsorbs via the $^3H_6-^1G_4$ transition. At 476 nm there is a positive peak on the niobate emission band. This is emission from $^1G_4$ to the ground state $^3H_6$. Upon excitation into the $^1G_4$ level this emission cannot be observed for practical reasons. Only $^1G_4-^3F_4$ emis-
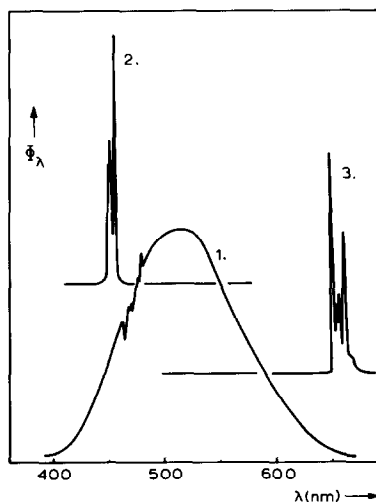
FIG. 5. Excitation spectra of the Tb^{3+} emission (λ_{em} = 544 nm) of α- and β-$La_{0.94}Tb_{0.06}Nb_3O_9$ at LHeT. The band at about 320 nm (α) corresponds to niobate excitation.

FIG. 7. Emission spectra of α-$La_{0.94}Tm_{0.06}Nb_3O_9$ at LHeT for excitation at 320 nm (1), at 357 nm (2), and at 460 nm (3).

sion at 650 nm and some longer wavelength emissions are then observed (Fig. 7).

It remains surprising that Tm^{3+} is not fed by nonradiative transfer as in the case of Sm^{3+}, Eu^{3+}, or Dy^{3+}. The present results can be understood by the assumption that the Tm^{3+} concentration is considerably lower than 6 mole%, the starting concentration. Since the $LaNb_3O_9$ crystal structures are only found for the very large rare-earth ions, viz. La^{3+}, Pr^{3+}, and Nd^{3+} (*1*), this assumption does not seem unreasonable. Obviously Tm^{3+} prefers the second phase which is inevitable (*1*).

In conclusion we have described and discussed the luminescence properties of a compound which occurs in two modifications which seem to lie on different sides of the boundary localized–delocalized. This results in strikingly different properties which, however, can be discussed only qualitatively.

3e. The Raman Spectra of α- and β-LaNb₃O₉

Finally we wish to report that also the Raman spectra of α- and β-LaNb₃O₉ are strikingly different (see Fig. 8). Note the broad lines in the case of β-LaNb₃O₉. This broadness is undoubtedly due to the same reason as the broadness of the rare-earth emission lines in β-LaNb₃O₉, viz. the disordered nature of the β phase. It is interesting to note that the Raman spectrum of the β phase in the Nb–O stretching region is similar to that of $NaNbO_3$, i.e., there is one dominating peak at ~600 cm^{-1} (*15*). This comparison is relevant, because the NbO_3 parts of β-LaNb₃O₉ and of $NaNbO_3$ are equal, i.e., a (distorted) ReO_3 structure.

Due to the complicated crystal structure of α-LaNb₃O₉ its Raman spectrum is hard to discuss. The peaks above 500 cm^{-1} are mainly Nb–O stretching in character. The upper one (~915 cm^{-1}) is at high energy. Most probably this one is related to the short Nb–O bond (1.77 Å). For $NaGdTiO_4$,
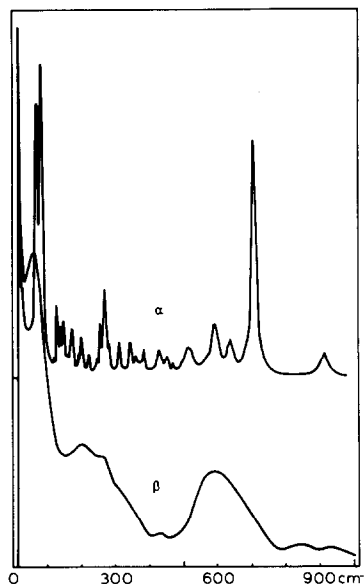

FIG. 8. Raman spectra of α- and β-LaNb₃O₉ at room temperature.

in which the Ti^{4+} ion has also been shifted off-center to one of the Ti^{4+} ions, a value of 900 cm^{-1} has been observed for the stretching frequency of the short Ti–O bond (*16*). For α-$NbPO_5$ the stretching frequency of the short Nb–O bond has been reported as 800 cm^{-1} in the Raman spectrum and 891 cm^{-1} in the infrared spectrum (*17*). Here, however, a certain amount of mixing with P–O vibrations with higher frequencies and the same symmetry may obscure the picture.

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