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Some Optical Properties of Aluminum and Gallium Niobate

G. BLASSE AND R. U. E. 'T LAM,

Physical Laboratory, State University, Princetonplein 5, 3508 TA Utrecht, The Netherlands

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The vibrational and electronic (diffuse reflection and luminescence) spectra of $AlNbO_4$ and $GaNbO_4$ are reported. They show features which deviate markedly from those observed for other niobates. In the vibrational spectra a very high frequency (≅950 cm^{-1}) band is observed. The reflection spectra show an extended long-wavelength tail. The emission and excitation spectra of the luminescence contain more than one band. The thermal quenching temperature of the luminescence is relatively low. These phenomena have been related to peculiarities of the crystal structure, viz., a relatively short Nb–O distance and the presence of extended defects as shown recently be electron microscopy. A centrosymmetrical space group is proposed on the basis of the vibrational spectra.

Introduction

Aluminum and gallium niobate ($AlNbO_4$ and $GaNbO_4$) are compounds with a simple composition but a relatively complicated crystal structure which deviates from those of other compounds $MNbO_4$. This structure has been determined by Pedersen (*1*) and Morosin and Rosenzweig (*2*). It is monoclinic with all cations in octahedral coordination. In Ref. (*1*) the space group was proposed to be centrosymmetric (*C*2/*m*); in Ref. (*2*) the noncentrosymmetric *C*2 was assumed to be correct. There are four formula units per unit cell.

The luminescence of $AlNbO_4$ at room temperature has been described superficially (*3*). The shape of its emission spectrum is not simple and justifies the assumption that more than one emitting center is present. Undoubtedly these will be niobate groups, the luminescence of which has been studied extensively (*3*, *4*). The crystal structure, however, contains only one crystallographic site for niobium.

Recently an electron optical study on $GaNbO_4$ has been reported (*5*). This investigation suggests a certain amount of disorder in the 2 × 2 block structure of $GaNbO_4$.

A pecularity of the crystal structure is the occurrence of a very short Nb–O distance, viz., 1.74 Å in $AlNbO_4$ (*1*) and 1.80 Å in $GaNbO_4$ (*2*). It has been shown that short distances may lead to deviating optical properties (*6*, *7*).

In view of these facts it seemed interesting to investigate the vibrational and electronic spectra of $AlNbO_4$ and $GaNbO_4$ and to compare the results with those for other niobates. This is the aim of the present paper.

Experimental

Samples were prepared by firing intimate mixtures of the starting materials ($Al(OH)_3$, Ga_2O_3, Nb_2O_5, Cr_2O_3, Dy_2O_3, TiO_2) in air. Final firing temperatures were about 1350°C.

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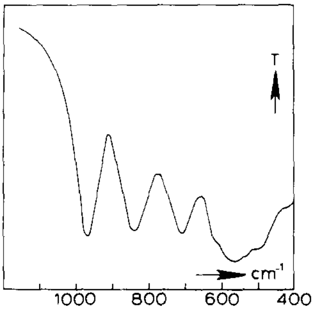

FIG. 1. Infrared spectrum of $AlNbO_4$ (300°K, KBr pellet).

Samples were checked by X-ray analysis using a Philips X-ray diffractometer.

Vibrational spectra were recorded at room temperature as described earlier (*6*). Electronic spectra were recorded at temperatures down to 77°K. The apparatus used has been described (*8*).

Results

$AlNbO_4$ and $GaNbO_4$ are white compounds. The infrared and Raman spectra of $AlNbO_4$ are given in Figs. 1 and 2. Those of $GaNbO_4$ are similar, but are situated at slightly different wavenumbers. In addition the bands are broader. A sample $0.98AlNbO_4 \cdot 0.02TiO_2$ also showed broader bands than $AlNbO_4$. Note the band at about 950 cm^{-1} in the spectra, which is an unusually high value in comparison with other niobates (*9*).

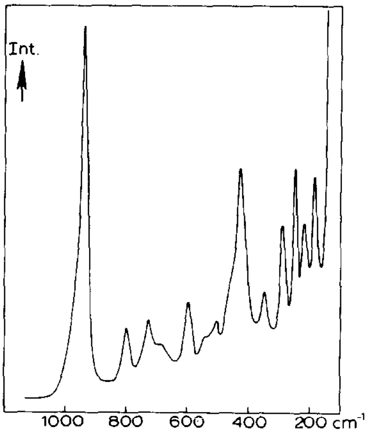

FIG. 2. Raman spectrum of $AlNbO_4$ at 300°K.

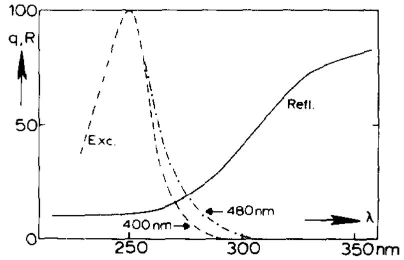

FIG. 3. Diffuse reflection spectrum (solid line) of $AlNbO_4$ at room temperature. Excitation spectra of the emission of $AlNbO_4$ at 77°K. q gives the relative quantum output. Dashed line: 400-nm emission monitored; dot–dash line: 480-nm emission monitored.

The diffuse reflection spectrum of $AlNbO_4$ in the ultraviolet is given in Fig. 3. The optical absorption edge is situated at about 40 000 cm^{-1}, corresponding to a charge–transfer transition in the niobate octahedron (*4*). There is a conspicuous long tail in this spectrum which extends down to about 350 nm. Its characteristics vary slightly from sample to sample.

Samples $AlNbO_4$ containing a small amount of Cr^{3+} had a green color. Their diffuse reflection spectrum contains three extra bands, viz., at 15 500 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{2g}$ on Cr^{3+}), at 22 000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{1g}(^4F)$ on Cr^{3+}), and, superimposed on the tail mentioned above, at about 28 000 cm^{-1} (intercation charge–transfer (*10*)). This yields $Dq = 1550$ cm^{-1} and $B = {\sim}650$ cm^{-1} for the crystal-field parameters. Spectra of this type have been discussed (*10*).

Under short-wavelength ultraviolet excitation $AlNbO_4$ and $GaNbO_4$ show a weak bluish luminescence at room temperature. This emission becomes rather intense at lower temperatures. In Fig. 4 the emission spectrum of $AlNbO_4$ has been given. It clearly contains two subbands whose intensity ratio depends on the excitation wavelength. Figure 3 contains the excitation spectra of the luminescence. Excitation into the optical band edge (250 nm) yields mainly the shorter-wavelength emission. Excitation into the long-wavelength tail of the excitation band yields

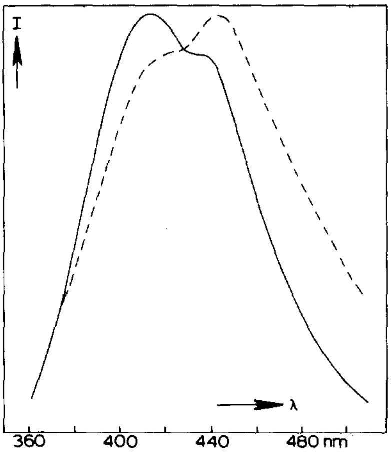

FIG. 4. Emission spectra of $AlNbO_4$ at 77°K. Solid line: 250-nm excitation; dashed line: 280-nm excitation.

considerably more of the longer-wavelength emission. From Fig. 3 it is also clear that excitation into the greater part of the tail in the reflection spectrum does not yield luminescence.

Similar luminescence properties are observed for $GaNbO_4$, but its luminescence intensity is somewhat lower. In addition the long-wavelength shoulder in the excitation spectrum of $AlNbO_4$ appears as a separate excitation band in the case of $GaNbO_4$. Its maximum is situated at about 275 nm. In the emission spectrum the longer-wavelength component, peaking at about 460 nm, is always the stronger one, independent of the wavelength of the exciting radiation. The shorter-wavelength component is visible as a shoulder only. Its relative intensity is higher under 250 nm than under 275 nm excitation. Because of the broadness of the bands concerned it is not possible to excite one or both of the emission subbands selectively.

The Cr^{3+}-containing $AlNbO_4$ sample did not show luminescence. Substitution of Al^{3+} by Dy^{3+} (up to 1%) did not change the luminescence characteristics. No Dy^{3+} emission was observed. The sample $0.98AlNbO_4 \cdot 0.02TiO_2$ showed luminescence characteristics which resemble those of $GaNbO_4$ more than those of $AlNbO_4$. The longer-wavelength emission and excitation bands are situated at somewhat longer wavelengths than in the case of $GaNbO_4$, viz., 485 and 290 nm, respectively.

The luminescence intensity of the samples under 250-nm excitation decreases strongly between 200 and 300°K, but is not completely quenched. Weak luminescence usually persists up to about 400°K.

Decay time measurements were performed on $AlNbO_4$ under short-wavelength pulse excitation. At 4°K the intensity–time curves show exponential behavior after about 70 μsec. The nonexponential part vanishes with increasing temperature. From the exponential part of the curve we find a decay time of about 200 μsec. Above 200°K this value decreases down to 50 μsec at room temperature.

Discussion

a. Vibrational Spectra

The crystallographic papers (*1*, *2*) give some attention to the question whether the space group of the crystal structure under discussion is centrosymmetric (*C*2/*m*) or not (*C*2). The vibrational spectra chould contain information which makes a decision possible. Let us first consider those of $AlNbO_4$ (Figs. 1 and 2). The fact that the infrared band at 840 cm^{-1} is definitely lacking in the Raman spectrum seems to indicate that *C*2/*m* is the correct choice. This is based upon the fact that in *C*2 all vibrations should appear in the infrared as well as in the Raman spectrum, whereas in *C*2/*m* the exclusion principle is active.

In view of the fact that the NbO_6 octahedron in this crystal structure has four shorter (e.g., in $AlNbO_4$: 1.74, 1.85, and 1.91 Å (2×)) and two longer Nb–O distances (2.30 and 2.38 Å) (*1*), we applied an approximate treatment of the higher-frequency part of the vibrational spectra which was fruitful earlier (*11*). We consider the niobate group as a distorted tetrahedron, neglecting the two longer Nb–O distances. The primitive unit cell contains four of these groups with site sym-

TABLE I

Analysis of Vibrational Spectra in Terms of a NbO_4 Tetrahedron[a]

T_d symmetry		C_1 symmetry	Four tetrahedra in $C2/m$		Assignment $AlNbO_4$		Assignment $GaNbO_4$	
			R	ir	R	ir	R	ir
ν_1	A_1(R)	A	$A_g + B_g +$	$A_u + B_u$	940 + sh	965	995 + 920	950(br)
					800	840 + sh	835 + 775	805(br)
ν_3	T_2(R, ir)	$3A$	$3A_g + 3B_g +$	$3A_u + 3B_u$	730 + 690	710	705 + 640(br)	680(br)
					600	620 + 570	555	~500(v br)
ν_2	E(R)	$2A$	$2A_g + 2B_g +$	$2A_u + 2B_u$	430			
ν_4	T_2(R, ir)	$3A$	$3A_g + 3B_g +$	$3A_u + 3B_u$				

[a] R: Raman active; ir: infrared active; br: broad; sh: shoulder; frequencies in cm^{-1}.

metry C_1. As a consequence the tetrahedral normal modes are split as shown in Table I. The site symmetry splitting is clearly visible in the spectra. In some cases the factor group splitting is also observable, although it is considerably less. An assignment has been given in Table I. The strong Raman line at about 430 cm^{-1} is probably mainly due to the ν_2 mode of the niobate tetrahedron, in view of its high intensity. Rough averages for the symmetrical (ν_1) and asymmetrical (ν_3) Nb–O stretching frequencies are 950 and 700 cm^{-1}, respectively. These are very high values in comparison with other niobates (*9*). A comparison of $YNbO_4$ with a comparable niobate group as far as relative distances are concerned is interesting. Here the averaged ν_1 and ν_3 frequencies are 816 and 650 cm^{-1}, respectively (*12*). In the present compounds the frequencies of the Nb–O stretching vibrations are very high; the ν_1 value is even exceptionally high.

A few years ago an exceptionally high frequency for the symmetrical Ti–O stretching vibration was reported in compounds $NaLnTiO_4$ (*6*). This was ascribed to the fact that one of the O^{2-} ions surrounding the Ti^{4+} ion did not receive the required electrostatic bond strength (*13*), viz., $1\frac{2}{3}$ instead of 2. As a consequence this Ti–O bond has a very high bond strength, resulting in a high frequency.

In $AlNbO_4$ (and $GaNbO_4$) we have a comparable situation. The O^{2-}(4) anion is surrounded (about linearly) by one Nb^{5+} ion and one Al^{3+} ion. If these ions are considered to be in six-coordination the electrostatic bond strength on this anion is clearly too low. This explains why the Nb—O(4) distance is so short (1.74 Å) and will also contribute considerably to the high value of the Nb–O stretching frequency.

If the crystal structure of $AlNbO_4$ is described as a packing of octahedra (as is usually done (*1*, *2*, *14*)), the bond strength of the anions is not satisfied. As a consequence the octahedra are distorted in such a way that some distances become longer and others shorter. This lifts the lack of local charge compensation. Another consequence is the fact that the vibrational spectra can be described starting from a niobate tetrahedron.

The vibrational spectra of $GaNbO_4$ are of poorer quality. Some data have been included in Table I. These spectra also indicate the centrosymmetric space group. Further, the factor group splittings in the Raman spectrum are larger than those for $AlNbO_4$. In the infrared spectra they are not observable, owing to the broadness of the bands. These larger splittings probably indicate that our simple model based upon niobate tetrahedra is less valid for $GaNbO_4$ than for $AlNbO_4$. In fact the difference between the averages of the four shorter and the two longer Nb–O distances is larger in $AlNbO_4$ than in $GaNbO_4$ (0.49 and 0.36 Å, respectively).

b. Electronic Spectra

The optical absorption edge at about 250 nm is undoubtedly due to an allowed charge–transfer transition in the niobate group. The longer-wavelength tail in the diffuse reflection spectra (Fig. 3) is suspicious. We did not succeed in decreasing the intensity of this tail drastically, either by longer firing times or by adding some surplus of $Al(OH)_3$. We therefore assume that this tail belongs at least partly to the niobates $MNbO_4$ themselves. It will be discussed further below.

Excitation into the 250-nm absorption band yields a blue luminescence. If the shorter-wavelength component of the emission (peaking at about 420 nm) is assumed to be the emission from the regular niobate group, the Stokes shift is 16 000 cm^{-1}, in good agreement with results for other niobates (*3*, *4*, *15*). The large Stokes shift suggests that the niobate excitation energy is not mobile (*16*). This follows also from the fact that no Dy^{3+} emission is observed, if the lattice contains some Dy^{3+}.

Since this niobate emission peaks into the $^4A_{2g} \rightarrow {}^4T_{1g}(^4F)$ absorption band of Cr^{3+} in $AlNbO_4$, it is not surprising that the Cr^{3+} ion is a killer of the niobate luminescence owing to efficient single-step energy transfer from the excited niobate group to the Cr^{3+} ion. Because of the low value of Dq a possible Cr^{3+} luminescence will be situated in the infrared (*10*). At the moment this optical region is not accessible to us.

Since the crystal structure contains only one crystallographic site for niobium, only one emission band is expected, in contradiction with experiment (Fig. 4). In addition to the band at about ~420 nm there is also a longer-wavelength component which is excitable in the long-wavelength tail of the excitation band peaking at 250 nm. In the case of $GaNbO_4$ and $AlNbO_4$–TiO_2 these longer-wavelength components become increasingly important. An explanation for this phenomenon can be the presence of a certain number of defects in the lattice. We will return to this point later.

From a relation given previously (*4*) the quenching temperature of the niobate luminescence is expected to be 450°K if the excitation band is situated at 250 nm. A sharp decrease of luminescence intensity occurs, however, between 200 and 300°K. Such a quenching temperature corresponds better with the position of the longer-wavelength excitation tail or band. In view of the general validity of this relation between the quenching temperature and the position of the excitation band the present deviation is remarkable.

From the discussion of the luminescence properties of $AlNbO_4$ and $GaNbO_4$ above, it becomes clear that they deviate from those reported for other niobates. To explain these deviations it is necessary to assume concentrations of native defects which are much larger than those normally observed. One possibility is that the order between the M^{3+} and Nb^{5+} ions on the cation sites is incomplete. Another possibility follows from the recent electronmicroscopical work by Hutchison and Anderson (*5*). They observed dark regions in the lattice images of $GaNbO_4$. After beam heating, dark contrasts extend along the (200) and $(20\bar{1})$ planes. Their lengths vary from 6 to 50 Å. The perfect $GaNbO_4$

structure can be indexed as a 2 × 2 block structure. It is assumed that the dark regions are due to a jump of a pair of adjacent cations from one cation level ($y = 0$) to the next ($y = \frac{1}{2}$), so that two 2 × 2 blocks are fused to form a 5 × 2 layer. This process can propagate so that columns of the 5 × 2 structure are formed.

The optical properties can now be explained as follows. The optical absorption edge at 250 nm is due to intrinsic niobate groups in $AlNbO_4$ and $GaNbO_4$. The tail is due to niobate groups belonging to various defect regions in the lattice. The more extended the local defect region, the longer the corresponding wavelength. Excitation into the 250-nm absorption band yields the intrinsic niobate emission at about 420 nm. Certain defect regions, perhaps the 5 × 2 layer formed by the initial cation jump, can be excited in the tail of the 250-nm excitation band, yielding 450-nm emission (Fig. 4). Still other regions with optical absorption at longer wavelengths do not luminesce at all as required by the relation given in Ref. (*10*). Because of the broadness of the excitation bands it is not possible to excite the various luminescent centers selectively, but even at low temperatures a slight amount of energy transfer cannot be ruled out. This follows from the presence of a considerable amount of the long-wavelength emission component under excitation into the intrinsic niobate groups (250 nm) and from the decay-time measurements (see below). We assume that at higher temperatures energy transfer from the intrinsic niobate group to the defect regions becomes more effective (compare, e.g., Ref. (*17*)), resulting in pronounced temperature quenching between 200 and 300°K. In view of the spectral overlap (compare Figs. 3 and 4) such a transfer seems not unreasonable and explains at the same time the low value of the quenching temperature.

A comparison between the luminescence spectra of $AlNbO_4$ and $GaNbO_4$ shows that in $GaNbO_4$ the concentration of defect regions is obviously higher. This is in agreement with the results of Hutchinson and Anderson (*5*), who showed that gallium evaporates as Ga_2O during their experiment. In our case gallium may evaporate during the preparation, in which a relatively high temperature is applied. This possibility can of course be ruled out in the case of $AlNbO_4$, because of the low vapor pressure of Al_2O_3, even at high temperatures.

In order to check this model we prepared a sample of $AlNbO_4$ doped with 2% TiO_2. Such a solid solution with Ti^{4+} ions (isoelectronic with Nb^{5+}) on Al^{3+} and Nb^{5+} sites will, itself, contain a large amount of disorder. In fact the luminescence properties of this solid solution deviate from the ideal situation even more than those of $GaNbO_4$. The somewhat longer wavelength position of the additional excitation and emission band in this case must be due to the titanate group, whose energy levels will not have exactly the same position as those of the niobate group.

In line with this explanation the broadness of the bands in the vibrational spectra increase in the sequence $AlNbO_4$, $GaNbO_4$, $AlNbO_4$–TiO_2. In conclusion we ascribe the deviating luminescence properties of compounds with $AlNbO_4$ structure to large deviations from the ideal crystal structure. Their presence has been observed by electronmicroscopy.

We are finally left with the decay-time measurements. The nonexponential decay directly after the excitation pulse seems to indicate energy transfer (*18*) which may occur from the short-wavelength emitting niobate groups to the long-wavelength emitting niobate groups. Probably the exponential part corresponds mainly to a radiative transition in the emitting niobate groups. The decay time observed is long (200 μsec). Macke (*19*) observed also a long decay time (130 μsec) for the niobate group in $Mg_4Nb_2O_9$. Since the site symmetry of the niobate group in the present compounds is low (C_1), it is difficult to imagine a symmetry-selection rule. Comparison with work on the luminescence of the vanadate tetrahedron ($\tau = \sim 1000$ μsec (*20*, *21*)) and the molybdate tetrahedron ($\tau = 250$ μsec (*22*)) seems to suggest a spin-selection rule. If this is correct, it is remarkable that such a selection rule has been observed neither for pure octahedral complexes of this type nor for $YNbO_4$ (*22*, *23*). This point warrants further investigation.

Acknowledgments

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