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Luminescence and Crystal Structure of $LiNbGeO_5$

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The luminescence of $LiNbGeO_5$ is reported and discussed. The intrinsic emission band has a maximum at 390 nm. The Nb/Ge cation distribution is derived from the Raman spectrum and differs from an earlier report which gave an amount of disorder of 15%. © 1986 Academic Press, Inc.

1. Introduction

Recently a new compound $LiNbGeO_5$ has been reported by Belokoneva *et al.* (*1*). The crystal structure is similar to that of sillimanite (Al_2SiO_5). The Li^+ and Nb^{5+} ions are in octahedral coordination, the Ge^{4+} ions in tetrahedral coordination. The compound seems to be rather unique: Ge^{4+} cannot be replaced by Si^{4+} nor Nb^{5+} by Sb^{5+}. The niobate octahedron is distorted in a similar way as in α-$NbPO_5$ (*2*), i.e., there is one shorter and one longer Nb—O distance (1.78 and 2.32 Å, respectively).

The luminescence of niobates has been investigated since long in our group (*3*) and recently that of α-$NbPO_5$ was also reported (*4, 5*). It seemed interesting to investigate the luminescence of $LiNbGeO_5$ to study its relation to that of other niobates.

Another reason to study the spectroscopy of $LiNbGeO_5$ is the statement of Belokoneva *et al.* (*1*) that $LiNbGeO_5$ has some disorder resulting in a cation distribution $Li(Nb_{0.85}Ge_{0.15})^{VI}(Ge_{0.85}Nb_{0.15})^{IV}O_5$. The two different niobate groups should yield different emissions. Such a disorder should also be clearly observable in the Raman spectrum, which was also studied in this investigation. Our results show that the cation distribution in our sample is very near to $LiNb^{VI}Ge^{IV}O_5$.

2. Experimental

Powder samples were prepared as described in Ref. (*1*). They were checked by X-ray diffraction analysis using Cu$K\alpha$ radiation. The way in which the optical measurements were performed was described in Refs. (*4, 5*).

3. Results

The diffuse reflection spectrum of $LiNbGeO_5$ at 300 K shows the presence of a strong absorption band with a maximum at

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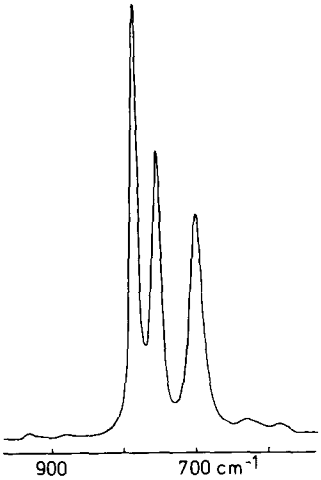

FIG. 1. Raman spectrum of $LiNbGeO_5$ in the region 500–1000 cm^{-1}.

250 nm. This band is ascribed to the niobate charge-transfer transition (*3*).

The Raman spectrum at 300 K is shown in Fig. 1. The figure covers the region 500–1000 cm^{-1}. Further we observed peaks at 450 cm^{-1} (m), 400 cm^{-1} (m), 330 cm^{-1} (m), 275 cm^{-1}, (s), 245 cm^{-1} (s), 210 cm^{-1} (m), 190 cm^{-1} (m), 170 cm^{-1} (m), 145 cm^{-1} (m), and 110 cm^{-1} (s). Here m indicates medium, and s strong intensity.

The compound $LiNbGeO_5$ does not luminescence at 300 K. Below 200 K, however, a blue emission appears under short-wavelength ultraviolet excitation. At 4.2 K its intensity is high. At about 130 K the emission intensity has dropped to 50% of the 4.2 K value.

Figure 2 shows the emission and excitations spectra of the luminescence of $LiNbGeO_5$ at 4.2 K. The main emission consists of a broad band with a maximum at about 390 nm. The corresponding excitation band peaks at 255 nm, so that the Stokes shift is about 13,000 cm^{-1}. Since this excitation band coincides with the absorption band in the reflection spectrum, this emission is ascribed to the intrinsic niobate group.

We observed also an additional emission band with a maximum at 450 nm. Its excitation band peaks at 280 nm. This excitation spectrum shows always the 255-nm band mentioned above, even if the emission wavelength monitored is not emitted by the intrinsic niobate group (e.g., 560 nm). This indicates energy transfer from the intrinsic group to the 450-nm emitting center. The latter is ascribed to an extrinsic niobate group. Such groups are often observed in the luminescence of niobates (*3*).

4. Discussion

The intrinsic niobate-group luminescence is very similar to that for niobates observed in general (*3*–*5*) and is, therefore, not discussed in detail here. The Stokes shift is relatively small, although its value is not unusual. Its value indicates a tendency for delocalization in the excited state (*4*, *5*).

Let us now turn to the extrinsic luminescence. From the data available it is possible to estimate the critical distance (R_c) for energy transfer from the intrinsic to the extrinsic niobate group if the interaction is of the electric dipole–dipole type. We use the expression

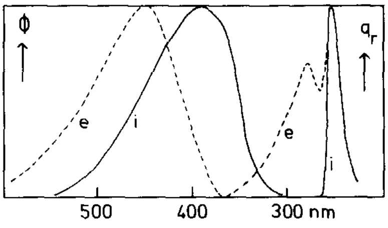

FIG. 2. Luminescence spectra of $LiNbGeO_5$ at 7 K. Curves i relate to the intrinsic niobate group, curves e to the extrinsic niobate group. Emission spectra, left-hand site; excitation spectra, right-hand side. Excitation wavelengths 245 nm (i) and 280 nm (e); emission wavelength monitored 360 nm (i) and 560 nm (e). q_r gives the relative quantum output and Φ the spectral radiant power per constant wavelength interval, both in arbitrary units.

$$R_c^6 = 0.6 \times 10^{28} \times (4.8 \times 10^{-16} \times f) \times E^{-4} \times SO$$

derived in Ref. (*6*). Here f denotes the oscillator strength of the absorption transition on the extrinsic niobate group, which is taken as 0.1 (*6*), E is the energy of maximum spectral overlap, and SO denotes the spectral overlap between the intrinsic emission band and the extrinsic absorption (excitation) band. From the spectra we find $SO = 0.01$ eV^{-1}. This yields for R_c 15 Å which justifies the assumption of electric dipole–dipole interaction. This means that an excited, intrinsic niobate group will transfer its energy to any extrinsic niobate group within a sphere with volume $\frac{4}{3}\pi R_c^3 \simeq$ 13,500 Å^3. From the crystallographic data we find that there is about 100 Å^3 available per niobate group in the crystal structure. Since excitation into the intrinsic niobate group yields mainly intrinsic emission, i.e., the transfer is by far not complete, the concentration of the extrinsic niobate groups must be considerably less than 1%.

These results make the cation distribution in $LiNbGeO_5$ as proposed in Ref. (*1*) not very likely. Let us now turn to the Raman spectrum. It is well known that Raman spectroscopy is a suitable tool to study order–disorder phenomena in solids (*5, 7, 8*).

The higher-frequency region shows three strong peaks, viz. at 785, 755, and 700 cm^{-1} (see Fig. 1). Let us first compare with some model compounds. For the niobate group we consider α-$NbPO_5$. Its vibrational spectra were reported and discussed in Ref. (*9*). A strong Raman line at 800 cm^{-1} was assigned to the short Nb—O bond. Weak Raman lines at 612 and 467 cm^{-1} were assigned to the four normal Nb—O bonds. This suggests that the 785- and/or 755-cm^{-1} peaks may be due to the short Nb—O bond in $LiNbGeO_5$.

The GeO_4 group in $LiNbGeO_5$ is not connected to other GeO_4 tetrahedra. Therefore we compare with orthogermanates. Tarte *et al.* (*10, 11*) have reported the GeO_4 stretch in normal spinels Me_2GeO_4 at 690 cm^{-1} and in zircons $MeGeO_4$ at 700–710 cm^{-1}. This suggests that the 700-cm^{-1} peak in the Raman spectrum of $LiNbGeO_5$ is mainly due to the GeO_4 tetrahedron.

This assignment can be even made more complete by considering only the GeO_4 stretching frequency and the short Nb—O bond frequency, i.e., we consider Li(NbO)GeO_4. The space group of $LiNbGeO_5$ is Pbnm (D_{2h}^{16}, Ref. (*1*)) with Nb and Ge on C_s site symmetry. The ν_1 mode of the GeO_4 tetrahedron has symmetry A' in C_s. The same holds for ν(Nb—O short). Since the unit cell contains four units, factor group analysis yields that there should be two Raman-active GeO_4 vibrations and two Nb—O (short) vibrations. The latter are clearly the 785- and 755-cm^{-1} peaks, the former the broad 700-cm^{-1} peak. In case of the germanate groups the factor group splitting is obviously so small that it can only be observed as a line broadening. The weak peaks around 600 cm^{-1} are then assigned to the normal Nb—O bond stretching vibrations.

What is of importance here, is that the Raman spectrum fits exactly the expectations for a cation distribution $LiNb^{VI}Ge^{IV}O_5$. A distribution with 15% disorder is clearly not observed. Since such a distribution was derived from crystallographic data on single crystals, it cannot be excluded that the crystals are disordered, but the powders are not.

The luminescence measurements indicate a small amount (<1%) of disorder. The Raman spectrum shows weak features at about 875 and 930 cm^{-1}. These may well be due to Nb^{VI}—O—Nb^{IV} bonds (*12*) which are possible, due to a slight amount of disorder.

In conclusion $LiNbGeO_5$ is an ordered compound. The intrinsic luminescence is quenched below room temperature. Energy transfer occurs to extrinsic niobate groups, the concentration of which is well below 1 at.%.

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