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NOTE

The Luminescence of the High-Pressure Modification of Gallium Niobate ($GaNbO_4$)

The luminescence of the high-pressure wolframite modification of $GaNbO_4$ is reported. It differs from that of the atmospheric pressure phase. The infrared spectra are also different. The spectra present evidence for a slight amount of disorder in the wolframite modification of $GaNbO_4$.

1. Introduction

The crystal structure of $GaNbO_4$ at atmospheric pressure has been found to be of the $AlNbO_4$ type (*1*). It is monoclinic with all cations in octahedral coordination. Recently Tamura *et al.* (*2*) have reported a high-pressure modification of $GaNbO_4$ which is of the wolframite type.

The luminescence properties (and also the vibrational spectra) of $GaNbO_4$ at standard pressure have been reported by Blasse and 't Lam (*3*). They were shown to be determined, in large part, by the complexity of the crystal structure.

Materials with wolframite structure are well known for their luminescence. Outstanding examples are $MgWO_4$ and $CdWO_4$ (*4*). The wolframite structure can be considered as a superstructure of the α-PbO_2 structure. Other ordered variants also show efficient luminescence, e.g., $MgNb_2O_6$ and $CaNb_2O_6$ with columbite structure (1 : 2 superstructure in α-PbO_2) (*5*). It seemed interesting, therefore, to investigate the luminescence of the high-pressure modification of $GaNbO_4$ and to compare the results with those known for other wolframites. The luminescence properties of the high-pressure phase (hp) are different not only from those of the standard-pressure phase (sp) of $GaNbO_4$, but also from those of other compounds with wolframite structure.

2. Experimental

The preparation of the hp sample has been described in Ref. (*2*). Due to the preparative conditions, the sample is light gray. The performance of the optical measurements is the same as that described before (*6*).

3. Results

The sample of $GaNbO_4$ (hp) does not luminesce at room temperature. Below 100 K, however, a blue-green emission of medium efficiency occurs. Emission and excitation spectra at LHeT reveal an excitation band peaking at about 270 nm and a corresponding emission band with a maximum around 465 nm. Excitation into the tail of the excitation band yields an emission at somewhat longer wavelengths. It turns out that there is an additional, weak excitation band at about 295 nm. Excitation into this band gives an emission band peaking at about 485 nm. Because these additional bands overlap the main bands, a further study is difficult. However, it seems quite certain that (a) the longer-wavelength excitation band corresponds to a weak absorption band and (b) energy transfer from the main emission center to the additional emission center is, at least at LHeT, not very efficient. These results are summa-

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rized in Table I, where they are compared with some relevant literature data.

The infrared spectrum of $GaNbO_4$ (hp) in the Nb–O stretching frequency region is situated at much lower frequencies than that of $GaNbO_4$ (sp). Using an approximation similar to that applied in Ref. (*3*), we find for ν_1, 950 cm^{-1} (sp) and 770 cm^{-1} (hp); and for ν_3, 805, 680, and ~500 cm^{-1} (sp) and ~640, 570, and 480 cm^{-1} (hp). The values for the sp phase are very high and have been related to the lack of local charge compensation in the sp crystal structure (*3*). The values for the hp phase are much more in line with values observed for other niobates (*7*). Finally, we note that the infrared spectrum of the hp phase is very broad.

4. Discussion

As is to be expected, the luminescences of the sp and hp modifications are different. It is well known that the crystal structure is of large importance for the luminescence of centers like the niobate group (*10*). This has also been observed in the case of the sp and hp modifications of $LiZnVO_4$ (*6*), where the luminescent center (the vanadate group) is similar to the niobate group. The analogy between the luminescences of $GaNbO_4$ (hp) and $MgNb_2O_6$ is striking (see Table I), but not unexpected. Their crystal structures are very similar, both being ordered variants of the α-PbO_2 crystal structure which contain zigzag chains of niobate octahedra. The tungstate wolframites yield a similar picture, although the spectra are somewhat shifted to lower energy (Table I).

The quenching temperature of $GaNbO_4$ (hp), however, is much lower than expected for this type of crystal structure; $MgNb_2O_6$ (*5*), $MgWO_4$ (*4*), and $CdWO_4$ (*8*) all have their quenching temperature above room temperature. One factor of importance may be the gray color of the sample which will certainly influence the quenching temperature (and especially the efficiency) in a negative way. The same gray color was observed for the hp phase of $LiZnVO_4$, which nevertheless showed luminescence up to room temperature (*6*). As will be shown now, there may be an additional reason for the low quenching temperature.

Compounds like tungstates and niobates, upon careful examination, often show an additional emission and excitation band at an energy somewhat lower than the main emission and excitation band (see e.g., Ref. (*10*)). The additional spectra are due to luminescent centers near defects in the crystal structure, for example, an oxygen

TABLE I

SURVEY OF LUMINESCENCE PROPERTIES OF $GaNbO_4$ (SP AND HP) AND SOME RELATED COMPOUNDS

Compound	Crystal structure	Maximum emission band[a] (nm)	Maximum excitation band[a] (nm)	Temperature	Reference
$GaNbO_4$ (sp)	$AlNbO_4$	(420+)460	250(+270)	LNT	(*3*)
$GaNbO_4$ (hp)	Wolframite	465(+485)	270(+295)	LHeT	This work
$MgNb_2O_6$	Columbite	≃460	≃270	300 K	(*5*)
$MgWO_4$	Wolframite	≃495	≃300	300 K	(*4*)
$CdWO_4$	Wolframite	490(+570)	300(+355)	LHeT	(*8*)
$LiNb_3O_8$	$LiNb_3O_8$	485	295	LHeT	(*9*)

[a] Additional bands in parentheses.

vacancy in the case of $CdWO_4$ (*8*) or complete defect regions as in the case of $GaNbO_4$ (sp) (*3*). In the latter compound the "additional" emission band even dominates the "main" emission band. These centers have usually lower quenching temperatures than the undisturbed centers. If energy transfer from the undisturbed centers to the defect centers occurs, a low-temperature quenching of the luminescence is observed, as was the case for $GaNbO_4$ (sp).

Our sample of $GaNbO_4$ (hp) shows also an additional emission and excitation band. It is striking that these bands coincide with the corresponding bands of $LiNb_3O_8$ (see Table I). The crystal structure of $LiNb_3O_8$ can be considered as an ordered variant of $GaNbO_4$ by replacing $2Ga^{3+}$ by $Li^+ + Nb^{5+}$ in an ordered way. It has been shown that the luminescence spectra of $LiNb_3O_8$ are due to the niobate group replacing the gallate group. The luminescence of this group has a low quenching temperature, which has been discussed in Ref. (*9*). It is obvious to assume that the hp phase of $GaNbO_4$ is not completely ordered so that a certain, low concentration of niobate groups on gallate group sites is present. These groups are then responsible for the additional spectra. The quenching temperature of the luminescence of $GaNbO_4$ (hp) may be determined by energy transfer at a certain temperature from the ordered to the disordered niobate groups yielding a low quenching temperature, as observed for $LiNb_3O_8$. The broad features of the infrared spectra sustain a slight amount of disorder in the $GaNbO_4$ (hp) modification.

This agrees with a general observation that a charge difference of 2 is not always high enough to obtain completely ordered superstructures. Whereas $MgWO_4$ seems to be an ordered variant, $GaNbO_4$ (hp) is a slightly disordered and $ZrTiO_4$ (*11*) a disordered variant of the α-PbO_2 crystal structure.

References

1. B. Morosin and A. Rosenzweig, *Acta Crystallogr.* **18,** 874 (1965).

2. S. Tamura, M. Wakakuwa, and K. Hirota, *J. Mater. Sci.* **15,** 2128 (1980).

3. G. Blasse and R. U. E. 't Lam, *J. Solid State Chem.* **25,** 77 (1978).

4. F. A. Kröger, "Some aspects of the Luminescence of Solids," Elsevier, Amsterdam/New York (1948).

5. A. Wachtel, *J. Electrochem. Soc.* **111,** 534 (1964).

6. H. Ronde and G. Blasse, *J. Inorg. Nucl. Chem.* **40,** 215 (1978).

7. G. Blasse and G. P. M. van den Heuvel, *Z. Phys. Chem. N.F.* **84,** 114 (1973).

8. M. J. J. Lammers, G. Blasse, and D. S. Robbertson, *Phys. Status Solidi A,* **63** (1981), in press.

9. G. Blasse, *Phys. Status Solidi A,* **20,** K99 (1973).

10. G. Blasse, *Struct. Bonding* **42,** 1 (1980).

11. G. Blasse, *Z. Anorg. Allg. Chem.* **345,** 222 (1966).

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