JOURNAL OF SOLID STATE CHEMISTRY **108**, 410–412 (1994)

BRIEF COMMUNICATION

Luminescence of Pyrochlores

M. Hamoumi, M. Wiegel, and G. Blasse

Debye Research Institute, Utrecht University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

Received February 26, 1993; accepted May 27, 1993

The luminescence of the pyrochlores $Y_2Ti_2O_7$, $Cd_2Nb_2O_7$, and $Pb_2Nb_2O_7$ is reported and discussed. Relations with the luminescence of comparable compounds is made. © 1994 Academic Press, Inc.

INTRODUCTION

The pyrochlore structure is an interesting one, and it is striking that not much research has been performed on the luminescence of compositions with this crystal structure. Wachtel's early observation (1) that the pyrochlore $Cd_2Nb_2O_7$ luminesces "very, very weakly" at 77 K is in fact not encouraging. Macke (2) reported that $Y_2Ti_2O_7$ hardly emits at 4.2 K. In another study the inversion symmetry of the rare earth ion site in $Gd_2Ti_2O_7$ was used to demonstrate the parity selection rule in the Eu^{3+} emission spectrum (3), but excitation in the titanate host lattice does not yield efficient Eu^{3+} luminescence (4). Recently, however, efficient luminescence was found in this laboratory for $Y_2Ti_2O_7$ below room temperature (5). This prompted us to reinvestigate other pyrochlores too. Results are presented in this paper.

2. EXPERIMENTAL

Samples were prepared by usual solid state techniques. The final firing temperature for $Cd_2Nb_2O_7$ was 1150°C and for $Pb_2Nb_2O_7$ was 1000°C. Firing was performed in air. Samples were checked by X-ray powder analysis and were single phase pyrochlores. The optical measurements were performed on a Spex Fluorolog-2 spectrofluorometer equipped with a liquid helium flow cryostat.

3. THE PYROCHLORE CRYSTAL STRUCTURE

There are two ways to describe the pyrochlore structure (6). The cubic unit cell contains eight formula units $A_2B_2X_6X'$. The pyrochlore structure can be derived from the fluorite structure by writing $A_2B_2X_7\Box$, where $\Box$ is an anion vacancy. It is also possible to consider this structure as a BX_3 framework of vertex-sharing BX_6 octahedra. This framework has large holes which contain the X' and A ions. The latter form an A_2X' sublattice of the cuprite-type which interpenetrates the BX_3 framework. The A ions are eight coordinated: six X ions form a puckered hexagon; two X' ions complete the coordination in such a way that the collinear $X'AX'$ system is perpendicular to the hexagon. The distance A–X' has been reported to be shorter than A–X. The X' ion does not belong to the B coordination.

4. RESULTS

4.1. $Cd_2Nb_2O_7$

Surprisingly enough our $Cd_2Nb_2O_7$ sample shows at 4.2 K an efficient yellow luminescence which persists up to room temperature. In view of the case of $Y_2Ti_2O_7$ which was first reported to emit very little (2), but was recently reported to emit efficiently (5), it seems as if the luminescence of pyrochlores is very sensitive to the preparative history, since $Cd_2Nb_2O_7$ was also originally reported to luminesce very little (1).

In Fig. 1 the emission and excitation spectra of the luminescence of $Cd_2Nb_2O_7$ at 4.2 and 290 K are presented. The emission at 290 K is at a considerably longer wavelength. This is not due to a spectral shift of the emission, but to the appearance of another emission band at higher temperatures. This was shown by measuring the emission band width as a function of temperature (Fig. 2). The pronounced maximum between 100 and 120 K shows that in this temperature region both emission bands occur. Table 1 summarizes some of the luminescence data obtained.

4.2. $Pb_2Nb_2O_7$

The pyrochlore $Pb_2Nb_2O_7$ has a yellow color with an optical absorption edge derived from the diffuse reflection spectrum at room temperature at 440 nm. At 4.2 K we observed a weak luminescence consisting of a broad emission band with a maximum at about 680 nm. The corre-

0022-4596/94 $6.00

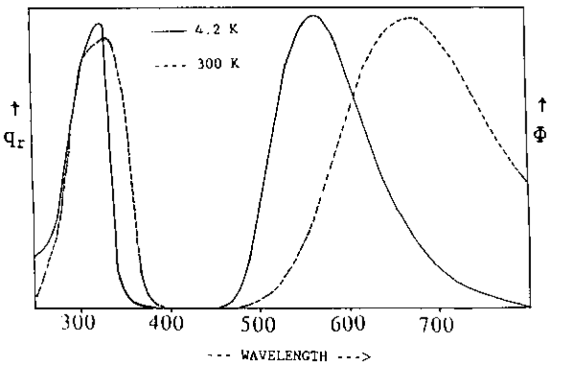

FIG. 1. Emission and excitation spectra of the luminescence of $Cd_2Nb_2O_7$ at 4.2 and 300 K.

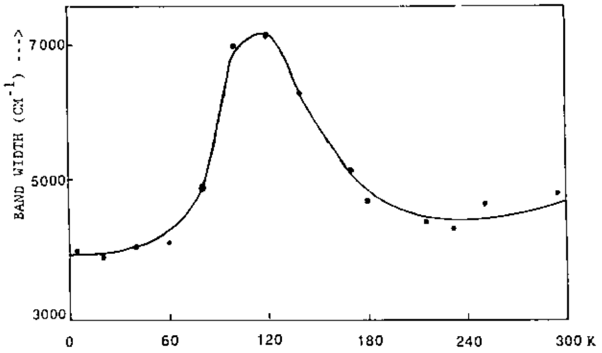

FIG. 2. The emission band width of $Cd_2Nb_2O_7$ as a function of temperature.

sponding excitation spectrum at this temperature has a maximum at 370 nm.

4.3. $Y_2Ti_2O_7$ and Related Compositions

Table 1 summarizes several other data. Our recent results on the pyrochlore $Y_2Ti_2O_7$ are given. For reasons of comparison we cite also data on niobates $M_2Nb_2O_7$ (M = Sr and M = $Alkali_{0.5}La_{0.5}$) (7). These compounds do not have the pyrochlore structure, but a layer structure. Further, literature data on $CdNb_2O_6$ and $CaNb_2O_6$ are presented (both with columbite structure).

5. DISCUSSION

5.1. Individual Compounds

First we consider the pyrochlore $Cd_2Nb_2O_7$ and its efficient yellow luminescence. It is tempting to assign the optical transitions to the niobate group as is done for practically all luminescent niobates (8). However, the situation is clearly more complicated in view of the following facts:

—The spectra of the isomorphous $Y_2Ti_2O_7$ lie at higher energy than those of $Cd_2Nb_2O_7$, whereas usually the titanate spectra are at about the same energy as the niobate spectra or even lower (7, 8).

—Unfortunately a niobate pyrochlore with only noble-gas ions does not exist; however, $Ca_2Nb_2O_7$ and $Sr_2Nb_2O_7$, both with a crystal structure with vertex-sharing octahedra, have their spectra at higher energy (Table 1, Ref. (7)) and show a low quenching temperature of their luminescence. On the other hand, the comparable compounds $ALaNb_2O_7$ (A = alkali ion) have spectra comparable to those of $Cd_2Nb_2O_7$, but the former have also a much lower quenching temperature of their luminescence.

TABLE 1
Some Luminescence Properties of Compounds under Discussion

Compound	Excitation maximum (nm)	Emission maximum (nm)	Stokes shift (10^3 cm^{-1})	T_q(K)[a]	Ref.
$Cd_2Nb_2O_7$	330	565	13	>300	[b]
	345[c]	670[c]	14.5[c]	>300	[b]
$Pb_2Nb_2O_7$	370	680	12	[d]	[b]
$Y_2Ti_2O_7$	310	485	12		(5)
$Sr_2Nb_2O_7$	295	475	13	65	(7)
$ALaNb_2O_7$[e]	~340	~600	~14	~120	(7)
$K_3Li_2Nb_5O_{15}$	350	550	11.5	~200[d]	(9)
Y_2TiO_5	260	425	16		(5)
$CdNb_2O_6$	270	460	15	>300	(1)
$CaNb_2O_6$	255	460	17	>300	(1)

Note. All values at 4.2 K, unless otherwise stated.
[a] Quenching temperature of the luminescence.
[b] This work.
[c] Values at room temperature.
[d] Very low emission intensity.
[e] A = alkali metal.

The same is true for $K_3Li_2Nb_5O_{15}$ with a three-dimensional corner-sharing of niobate octahedra (Table 1, Ref. (9)).

—Cadmium compounds which are luminescent at room temperature do exist: Cd_2PO_4F and $Cd_3(PO_4)_2$ (10). In CaO the Cd^{2+} ion is even a very efficient luminescent center (11).

—The difference between the luminescences of isomorphous $CaNb_2O_6$ and $CdNb_2O_6$ is small (Table 1, ref. (1)): the cadmium compound absorbs at somewhat lower energy and has a slightly lower quenching temperature.

The high luminescent efficiency of $Cd_2Nb_2O_7$ at room temperature is rather exceptional for a niobate with an absorption edge at relatively low energy (1, 7, 8) and suggests that the excited state is rather localized. This is not the case for other vertex-sharing niobate lattices (7). Therefore, we propose that the optical transitions of $Cd_2Nb_2O_7$ are not only related to the niobate sublattice, but also to the Cd_2O' sublattice. It may well be that transfer of electronic charge from the O′ ion to the cadmium 5*s*, 5*p* orbitals, as suggested before (12), plays also a role. The hole on the O′ ion could well be strongly localized.

The pyrochlore $Cd_2Nb_2O_7$ undergoes several phase transitions. In Ref. (13), for example, phase transitions are reported at 80 and 185 K, the latter being the ferroelectric Curie temperature. We assume that the change in, especially, the emission spectrum as a function of temperature (Figs. 1 and 2) is related to these phase transitions.

The compound $Pb_2Nb_2O_7$ shows the optical transitions under discussion at even lower energy. The compound is yellow with an optical absorption edge at about 440 nm. The emission is at very long wavelengths. Broad band emission in the red spectral range is never very efficient due to fast nonradiative transitions (14). The optical transitions are certainly not pure niobate transitions in view of the arguments given above. A mixed transition with a considerable $Pb^{2+} \rightarrow Nb^{5+}$ character seems obvious. This is very similar to assignments for $PbMoO_4$ and $PbWO_4$ (8, 15).

5.2. *A Comparison*

The delocalization in the pyrochlore $Y_2Ti_2O_7$ relative to Y_2TiO_5 has been discussed previously based on the longer-wavelength absorption edge of the pyrochlore and the more efficient energy transfer to Eu^{3+} in the pyrochlore. The even longer-wavelength edge of $Cd_2Nb_2O_7$ cannot be interpreted as a further delocalization, since not only the quenching temperature is high but also the compositions of the valence and conduction bands are probably different (see above).

In this connection the columbites $CaNb_2O_6$ and $CdNb_2O_6$ are interesting. In $CaNb_2O_6$ there is complete localization of the excited state, but in $CdNb_2O_6$ there is a small amount of delocalization as viewed from the energy transfer efficiency to Eu^{3+} (16). Obviously this amount of delocalization does not increase much when moving to $Cd_2Nb_2O_7$. The peculiar crystal structure may play a role here: there are two interpenetrating sublattices; the excited state consists of a hole in the Cd_2O system and an electron in the NbO_3 system. Obviously one of these is self-trapped in its sublattice. In this way it is also understandable that the structural distortions of the phase transitions have a pronounced influence on the luminescence properties.

In $Pb_2Nb_2O_7$ the situation may be comparable, but with a smaller band gap due to the different energy band composition. This will result in a large increase of the nonradiative transition rate to the ground state, so that it is hard to judge whether the excited state is localized or not.

In conclusion, the luminescence of pyrochlores deserves more attention than has been paid to up until now. However, energy band structure calculations are necessary to interpret the results.

REFERENCES

1. A. Wachtel, *J. Electrochem. Soc.* **111,** 534 (1964).
2. A. J. H. Macke, *J. Solid State Chem.* **18,** 337 (1976).
3. G. Blasse, A. Bril, and W. C. Nieuwpoort, *J. Phys. Chem. Solids* **27,** 1587 (1966).
4. G. Blasse, *J. Chem. Phys.* **45,** 2356 (1966).
5. J. Alarcon and G. Blasse, *Phys. Status Solidi A* **135,** 627 (1993).
6. A. F. Wells, "Structural Inorganic Chemistry," 4th ed. Clarendon Press, Oxford, 1975.
7. M. Wiegel, M. Hamoumi, and G. Blasse, *Mater. Chem. Phys.*, in press.
8. G. Blasse, *Struct. Bonding* **42,** 1 (1980).
9. M. Wiegel, G. Blasse, and M. Ouwerkerk, *Mater. Res. Bull.* **27** 617 (1992).
10. W. L. Wanmaker, J. G. Verriet, and J. W. ter Vrugt, *Philips Res. Rep.* **27,** 350 (1972).
11. H. Lange, *Tech. Wiss. Abh. München Osram Ges.* **10,** 87 (1969).
12. G. Blasse, *Chem. Phys. Lett.* **175,** 237 (1990).
13. D. G. Demurov and Yu.N. Venevtsev, *Sov. Phys. Sol. State* **12,** 1968 (1971).
14. G. Blasse, *in* "Advances in Nonradiative Processes in Solids" (B. Di Bartolo, Ed.), p. 287. Plenum, New York, 1991.
15. W. van Loo, *Phys. Status Solidi A* **27,** 565 (1975) and **28,** 227 (1975).
16. G. Blasse and M. G. J. van Leur, *Mater. Res. Bull.* **20,** 1037 (1985).