

NOTE

The Nature of the Luminescence Transition of the Vanadate Group

The blue luminescence of the vanadate group in YVO_4 has been studied extensively (1, 2). In this note, we report some results of a study on the luminescence of the vanadates $LiMgVO_4$, $LiCdVO_4$, $NaCaVO_4$, $Mg_3(VO_4)_2$, $Zn_3(VO_4)_2$ and $LiZnVO_4$, all of which show a yellow emission under short as well as long wavelength uv excitation. $LiMgVO_4$, $LiCdVO_4$, and $NaCaVO_4$ have the Na_2CrO_4 structure (3). We investigated the low-temperature form of $Zn_3(VO_4)_2$ and the isostructural $Mg_3(VO_4)_2$, which have a spinel-like structure (4). Last, we examined two modifications of $LiZnVO_4$, viz. the ordinary phenacite phase and the high-pressure spinel modification (5). The high-pressure modification will be denoted by an asterisk.

Samples were prepared by firing an intimate mixture of the starting materials for about 24 hr at temperatures of 500–900°C. Starting materials were high-purity CdO (Koch Light), NH_4VO_3 (BDH), and Li_2CO_3 , Na_2CO_3 , $MgCO_3 \cdot Mg(OH)_2$, ZnO, $CaCO_3$ (all Merck p.a.). $LiZnVO_4^*$ was obtained using a piston cylinder (6) under the following conditions: pressure, 22.5 kb; temperature, 300°C; period, 4 hr. The sample was cooled under pressure to room temperature, so that the high-pressure modification was frozen in. The compounds were checked by X-ray analysis on a Philips X-ray diffractometer using $CuK\alpha$ radiation. The optical experiments were performed on a Perkin-Elmer spectrofluorimeter MPF-2A, equipped with a helium flow cryostat. The performance of the decay time measurements has been described elsewhere (7).

All vanadates under examination are white powders with the exception of $LiZnVO_4^*$, which was gray due to the high-pressure experiment. In Table I we present the experimental results. In the second and third column the maxima of the emission and excitation bands recorded at 5°K are summarized. All emission spectra consist of a broad band, the

half-width of which lies in the range 0.4–0.5 eV. Only in the case of $Zn_3(VO_4)_2$ did we observe a temperature-dependent shift of the emission maximum: 2.15 at 5°K and 2.35 at 300°K. The excitation spectra of the emissions consist of broad bands; these bands correspond to the optical absorption edge of the compounds. No shift was observed in going from 5 to 300°K. In the fourth column of Table I we present the quenching temperatures of the emissions as defined by Kröger (8). In the fifth and sixth columns we summarize the decay times of the different compounds as measured at 5 and 300°K, respectively. Furthermore, we observed that in accordance with the law of Perrin the decay times show the same temperature dependence as the luminescence intensity.

In view of the results on YVO_4 it is obvious to ascribe the yellow luminescence to transitions within the VO_4^{3-} group. In handling the 24 valence electrons of complexes consisting of closed-shell first-row transition metal ions (like the V^{5+} ion) coordinated tetrahedrally to four oxide ligands, Ballhausen and Liehr (9) have proposed a level scheme which is generally accepted today. The order of the levels relevant to the luminescence process is

$$3t_2 < t_1 < 2e < 4t_2.$$

The highest completely-filled MO is the nonbonding (oxygen-localized) t_1 giving rise to a 1A_1 ground state. The antibonding $2e$ level consists mainly of the $3d$ level of the metal ion. The first excited configuration $(t_1)^5(2e)$ (charge-transfer state) gives rise to four multiplets viz. 1T_1 , 1T_2 , 3T_1 , 3T_2 . In view of the long decay times and the coincidence of the temperature dependence of these decay times and the luminescence intensities, the emission must take place from one of the triplet states. Our experiments cannot decide between the two possibilities. This assignment is confirmed by the fact that in all samples the site symmetry

TABLE I

MAXIMA OF EMISSION AND EXCITATION BANDS, QUENCHING TEMPERATURES, AND DECAY TIMES OF COMPOUNDS STUDIED

Compound	5 K			τ (5 K) (μ sec)	τ (300 K) (μ sec)
	Max. em. (eV)	Max. exc. (eV)	T_q (K)		
NaCaVO ₄	2.45	4.15	105	>1000 ^a	Quenched
LiCdVO ₄	2.35	3.9	265	800	125
LiMgVO ₄	2.35	3.9	265	>1000 ^a	225
LiZnVO ₄	2.35	3.65	265	850	50
LiZnVO ₄ *	2.35	3.65	310	300	75
Mg ₃ (VO ₄) ₂	2.15	3.75	295	>1000 ^a	115
Zn ₃ (VO ₄) ₂	2.15	3.55	335	>1000 ^a	190

^a No more precise statement can be made, due to the fact that the measuring limit of the electronic device used is of the order of a millisecond.

of the V⁵⁺ ion is lower than T_d (see Table II), leading to a splitting of the T_1 and T_2 levels and thus making all transitions $A_1 \leftrightarrow T_1$, T_2 orbitally allowed. Using the ordering of Ballhausen (10) we assign the absorption band corresponding to the excitation band to the transition ${}^1A_1 \rightarrow {}^1T_1$ ($t_1 \rightarrow 2e$). The present results are easier to explain than those for YVO₄ where the Perrin rule is violated due to energy transfer (1). In our compounds, energy transfer between the vanadate groups does not

seem to occur. This can be related to the larger Stokes shift (YVO₄ = 1 eV, our compounds = 1.3 eV or more). As a consequence, the emission of YVO₄ is concentration-quenched at room temperature whereas many of our compounds emit efficiently at room temperature. The lower T_q of the sodium compound in comparison with the lithium compounds (all having the Na₂CrO₄ structure) agrees with rules given before (11).

TABLE II

CRYSTALLOGRAPHIC DATA OF COMPOUNDS STUDIED

Compound	Structure	Space group	Site symmetry V ⁵⁺
NaCaVO ₄	Na ₂ CrO ₄	D_{2h}^{17}	C_{2v}
LiCdVO ₄			
LiMgVO ₄			
LiZnVO ₄	Phenacite	C_{3i}^2	C_1
LiZnVO ₄ *	Spinel	O_h^7	T_d^a
Mg ₃ (VO ₄) ₂	α -Zn ₃ (VO ₄) ₂	D_{2h}^{18}	C_s
Zn ₃ (VO ₄) ₂			

^a Further lowered by the disordered arrangement of the Li⁺ and Zn²⁺ ions.

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References

1. C. HSU AND R. C. POWELL, *J. Luminescence* **10**, 273 (1975).
2. G. BLASSE, *Philips Res. Repts* **23**, 344 (1968).
3. M. TH. PAQUES LEDENT, *Chem. Phys. Letters* **35**, 375 (1975).
4. R. GOPAL AND C. CALVO, *Canad. J. Chem.* **49**, 3056 (1971).
5. G. BLASSE, *J. Inorg. Nucl. Chem.* **25**, 136 (1963).
6. W. JOHANNES, *N. Jb. Miner. Mh. H.* **7/8**, 337 (1973).
7. W. v. LOO AND D. J. WOLTERINK, *Phys. Letters* **47A**, 83 (1974).

8. F. A. KRÖGER, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam (1948).
9. C. J. BALLHAUSEN AND A. D. LIEHR, *J. Mol. Spectr.* **2**, 342 (1958).
10. C. J. BALLHAUSEN, *Theoret. Chim. Acta (Berl.)* **1**, 285 (1963).
11. G. BLASSE AND A. BRIL, *Philips Tech. Rev.* **31**, 304 (1970).

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