

THE LUMINESCENCE OF BARIUM TITANIUM PHOSPHATE, $\text{BaTi}(\text{PO}_4)_2$

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The luminescence of $\text{BaTi}(\text{PO}_4)_2$ is described. The yellow emission is due to titanate octahedra. This compound is one of the exceptional cases where the octahedral titanate luminescence can be described by a simple model.

1. Introduction

The luminescence of tetrahedral and octahedral groups consisting of a central, highly-charged, noble gas ion with empty d orbitals and surrounding oxygen ions has been studied for many years. Examples are the tungstate group in CaWO_4 [1] and Ba_2CaWO_6 [2], the niobate group in CaNb_2O_6 [3] and the vanadate group in YVO_4 [4]. In these systems one strong emission band has been observed which can be excited in the optical band gap. Compounds containing octahedral titanate groups have always been exceptional because they show several optical transitions depending on the excitation wavelength and because they show pronounced concentration quenching of their luminescence [1,6]. It is the purpose of this note to report on the luminescence of $\text{BaTi}(\text{PO}_4)_2$. This compound shows octahedral titanate luminescence, but it does not have the exceptional properties mentioned above. It is possible to propose the reason for this normal behaviour.

$\text{BaTi}(\text{PO}_4)_2$ has the monoclinic yavapaiite structure [6,7]. The Ti^{4+} ions are octahedrally coordinated by oxygen. The six oxygen ions belong to six different PO_4^{3-} groups, so that the titanate octahedra are isolated from each other. The shortest Ti—Ti distance is 5.18 Å. There is one titanate group per primitive cell.

2. Experimental

Samples were prepared as described in refs. [6,7]. They were checked by X-ray analysis. We restrict our report to results obtained for $\text{BaTi}(\text{PO}_4)_2$ and the isomorphous $\text{BaZr}_{0.95}\text{Ti}_{0.05}(\text{PO}_4)_2$. Luminescence measurements were performed as described before [8].

3. Results

Barium titanium phosphate, $\text{BaTi}(\text{PO}_4)_2$, shows a yellow photoluminescence at temperatures below 100 K. Fig. 1 shows the emission spectrum and the excitation spectrum of the luminescence at liquid nitrogen temperature. The former consists of one

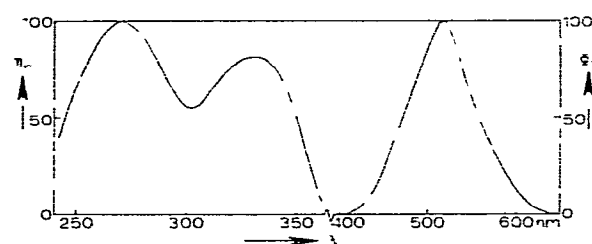


Fig. 1. Relative excitation spectrum of the yellow emission of $\text{BaTi}(\text{PO}_4)_2$ at 77 K (left-hand side, η_r : relative quantum output) and spectral energy distribution of the emission of $\text{BaTi}(\text{PO}_4)_2$ at 77 K (right-hand side; 320 nm excitation: Φ_λ : spectral radiant power per unit wavelength interval in arbitrary units). Note change in wavelength scale.

broad band, the latter of two broad bands. The Stokes shift of the emission amounts to some $11\,000\text{ cm}^{-1}$, the energy difference between the two excitation bands some $7\,000\text{ cm}^{-1}$. The emission spectrum does not depend on the excitation wavelength.

For the diluted system $\text{BaZr}_{0.95}\text{Ti}_{0.05}(\text{PO}_4)_2$ we observed essentially the same results. The emission band peaks at 510 nm . This emission shows only one excitation band which peaks at 315 nm .

4. Discussion

In his extended study on the luminescence of titanates Macke [5] was forced to assume the presence of different titanate centres to explain his results. As far as we know $\text{BaTi}(\text{PO}_4)_2$ is one of the few examples of compounds with octahedral titanate groups where such an approach is unnecessary. The presence of one emission band with its own excitation spectrum in the diluted as well as in the concentrated system shows clearly that the intrinsic titanate groups are responsible for the luminescence. An obvious difference, viz. the presence of two excitation bands in the case of the concentrated system, but one in the case of the diluted system, is only an apparent one. This is due to the fact that the host lattice absorption of $\text{BaZr}(\text{PO}_4)_2$ overlaps the spectral region where the second excitation band is to be expected, as was checked by measurement of the diffuse reflection spectra. Energy transfer from the host lattice to the Ti^{4+} activator does obviously not appear.

The presence of two excitation bands in the excitation spectrum of the luminescence of $\text{BaTi}(\text{PO}_4)_2$ is ascribed to the non-cubic crystal field splitting of the d level of titanium. The site symmetry of the Ti^{4+} ion in the yavapaiite structure is C_{2h} . The way in which the six nearest P^{5+} ions surround the titanate group is roughly tetragonal. We ascribe the observed splitting to this roughly-tetragonal crystal field.

We note further that the value of the Stokes shift is well in line with those for other titanates [5]. This, from a luminescent point of view, simple system shows unfortunately a rather low thermal quenching temperature. One of us has argued before that the position of the first absorption band of octahedral

groups like those under discussion seems to determine the thermal quenching temperature of the luminescence [9]. A comparison with existing data for luminescent compounds with octahedral titanate groups [1,5] shows that this relation is satisfied also in the case of $\text{BaTi}(\text{PO}_4)_2$.

The thermal quenching temperature of the titanate luminescence in the present compounds seems to be independent of the titanium concentration. This indicates that energy migration between the titanate groups in $\text{BaTi}(\text{PO}_4)_2$ does not occur. An important factor which prevents energy transfer will be the relatively large distance between the titanate octahedra in the yavapaiite structure. In most of the titanate systems studied before the shortest Ti-Ti is considerably less and, in addition, the probability of disorder is high (e.g. ordered perovskite, spinel, pyrochlore [5]). This results in a complicated luminescence behaviour due to the presence of several types of titanate octahedra and the possibility of energy migration among them. The luminescence of $\text{BaTi}(\text{PO}_4)_2$ shows that such a complicated behaviour is not characteristic of the titanate octahedron and that its luminescence can be compared directly with those of similar groups as vanadates and tungstates.

References

- [1] F.A. Kröger, *Some aspects of the luminescence of solids* (Elsevier, Amsterdam, 1948).
- [2] A.B. van Oosterhout, *J. Chem. Phys.* 67 (1977) 2412; *Phys. Stat. Sol.* 41a (1977) 607.
- [3] A. Wachtel, *J. Electrochem. Soc.* 111 (1964) 534.
- [4] G. Blasse, *Philips Res. Rept.* 23 (1968) 344.
- [5] A.J.H. Macke, *Phys. Stat. Sol.* 39a (1977) 117; *J. Solid State Chem.* 18 (1976) 337; thesis, Utrecht (1976).
- [6] R. Masse and A. Durif, *Compt. Rend. Acad. Sci. (Paris)* 274C (1972) 1692.
- [7] M.Th. Paques-Ledent, *J. Inorg. Nucl. Chem.* 39 (1977) 11.
- [8] J.Th.W. de Hair and G. Blasse, *J. Luminescence* 14 (1976) 307.
- [9] G. Blasse, *J. Chem. Phys.* 48 (1968) 3108; G. Blasse and A. Bril, *J. Solid State Chem.* 2 (1970) 291; 3 (1971) 69.