

Influence of Local Charge Compensation on Site Occupation and Luminescence of Apatites

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The apatite structure contains two different sites for the larger cations. It is shown that the principle of local charge compensation can predict the site occupation. This is especially important for an interpretation of the luminescence properties of a number of apatites. The predictions are compared with experimental data. The agreement is satisfactory.

1. Introduction

Compounds with apatite structure have been used extensively as a host lattice for luminescent ions. The most well-known example is Sb^{3+} - and Mn^{2+} -coactivated calcium halophosphate which material has found application in fluorescent lamps (1). The Sb^{3+} ion shows efficient luminescence in alkaline earth lanthanide apatite silicates too (2). These compounds can also be activated by luminescent lanthanide ions, for example by Eu^{3+} (3). The apatite lattice has two sites available for cations of this type, viz (4f) with nine-coordination and (6h) with seven-coordination. A very clear picture of these coordinations is given in Ref (4). One might expect that the nature of the site will influence the luminescence of the emitting cation. Many studies have, therefore, dealt with the problem which of the two sites is occupied by the emitting cations. We propose here a simple method to predict this site. It is based upon the same idea as Pauling's electrostatic valence rule (5). Our approach differs from that of Felsche (4) who tried to derive cation site occupation in several oxyapatites from the variation of the lattice parameters of the apatite unit cell with the ionic radius of the constituting lanthanides. For the apatites $\text{M}^+\text{Ln}_9(\text{SiO}_4)_6\text{O}_2$ ($\text{M} = \text{Li}, \text{Na}$) the M^+ ion is

supposed to be in (6h), because the a vs $r_{\text{Ln}^{3+}}$ curve shows a kink at a place where the Na^+ radius becomes competitive with the lanthanide radius. For lithium, however, there is a kink at the same value of $r_{\text{Ln}^{3+}}$. Also the Mg^{2+} and Ca^{2+} ions in $\text{M}_2^+\text{Ln}_8(\text{SiO}_4)_6\text{O}_2$ ($\text{M} = \text{Mg}, \text{Ca}$) are placed in (6h) for the same reasons. Our procedure gives other results which seem to agree with the luminescence data published for these compounds. We will first discuss the oxyapatites (silicates) of the lanthanides and after that the fluoro (chloro)-apatites (phosphates).

2. Oxyapatites of the Lanthanides

A striking detail of the oxyapatites is the coordination of the O(4) ion. This is the oxygen ion that does not belong to any silicate tetrahedron. It is sometimes called the free oxygen ion. It is coordinated triangularly by three (6h) cations. Even if these are trivalent lanthanide ions, the sum of the electrostatic bond strength of the cations towards O(4), ζ , is only 9/7, considerably less than 2 as required by Pauling's electrostatic valence principle (4). This results in a very short Ln–O distance (5). Further calculation shows that ζ for the other oxygen ions does not differ significantly from 2. From this it follows that it must be very

unfavourable to have cations with large radius and/or low charge in the (6*h*) sites in these compounds. Let us see what we can learn from this simple statement.

a. Binary Compounds $\text{Ln}_{9.33}\square_{0.67}(\text{SiO}_4)_6\text{O}_2$

It will be clear that we expect that the (6*h*) sites are completely filled and that the (4*f*) sites contain the lanthanide vacancies. This has also been found from crystallographic investigations (6).

b. Ternary Compounds $M^+\text{Ln}_9(\text{SiO}_4)_6\text{O}_2$ ($M = \text{Li, Na}$)

From our considerations we expect the monovalent ions to be in (4*f*) in contrast with Felsche's proposal (5). This author has also shown that samples LiLaSiO_4 studied earlier by us must be $\text{LiLa}_9(\text{SiO}_4)_6\text{O}_2$ in view of the crystallographic data. In Ref. (7) we reported on the Eu^{3+} luminescence of these compounds. Since Eu^{3+} is smaller than La^{3+} we expect the activator ions in (6*h*). In view of the low value of ζ for the surrounding anions the Eu^{3+} charge-transfer band is expected at relatively low energy (8). This is found indeed, viz 280 nm (7), a very low value for Eu^{3+} in silicates. Furthermore, the ${}^5D_0\text{--}{}^7F_0$ emission of Eu^{3+} in this compound is rather intense indicating a strong linear crystal-field component at the Eu^{3+} ion (9). It is quite obvious that this is the case in the (6*h*) site. The site symmetry is C_s with one free oxygen ion in the symmetry plane.

c. Ternary Compounds $M_2^+\text{Ln}_8(\text{SiO}_4)_6\text{O}_2$ (M is Alkaline Earth)

Our model predicts the alkaline-earth ions in (4*f*). Only if the Ln^{3+} ions are relatively large (e.g., La^{3+}) and the M^{2+} ions small (e.g., Mg^{2+}) it is not excluded that the M^{2+} ions are also in (6*h*). Luminescence of the Eu^{3+} ion in some of these compounds has been reported by Isaacs (3) and we will try to relate his results with the present discussion.

We expect Eu^{3+} in the compounds used in the following sites.

$\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ and $\text{Mg}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$. Eu^{3+} is expected to enter the (6*h*) sites because Eu^{3+} is smaller than La^{3+} . Because the (4*f*) sites are occupied statistically by equal amounts of

alkaline earth and lanthanum ions the crystal field at Eu^{3+} will vary from site to site. This is confirmed by the luminescent spectra. The Eu^{3+} emission from the lanthanum compounds resembles that of the lithium compound mentioned above (3, 7): the excitation band peaks at about 285 nm due to the coordination by a free oxygen ion. Furthermore the ${}^5D_0\text{--}{}^7F_0$ emission is stronger than in the corresponding yttrium compounds. The strongest emission line peaks at 626 nm and the ${}^5D_0\text{--}{}^7F_4$ emission has medium intensity.

$\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ and $\text{Mg}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$. Here Eu^{3+} is expected to enter the (4*f*) site because Eu^{3+} is larger than Y^{3+} . The luminescent properties differ significantly from those of the lanthanum compounds. The excitation band peaks at about 230 nm (3) indicating a coordination by strongly bound oxygen anions. Since the (4*f*) site lacks a pronounced linear crystal field term the ${}^5D_0\text{--}{}^7F_0$ emission is very weak. Furthermore, the ${}^5D_0\text{--}{}^7F_4$ emission is very weak and the strongest emission line peaks at about 611 nm.

$\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$. Since Eu^{3+} is about as large as Gd^{3+} we expect a statistical distribution of Eu^{3+} among the Gd^{3+} sites. These are (6*h*) and the half of the (4*f*) sites (the other half is occupied by calcium), so that there are three times more (6*h*) than (4*f*) lanthanides. We expect, therefore, that the luminescence of Eu^{3+} in the gadolinium compound can be described by a superposition of the spectra of the lanthanum and the yttrium compounds with a dominant contribution by the former. This is in fact the case. The emission spectrum of the Gd compound resembles closely that of the La compound with one marked difference, viz a strong line at 612 nm. This is the dominating line in the Y compounds. There is a strong excitation band around 265 nm which is ascribed to Eu^{3+} in (6*h*). We cannot exclude, therefore, a certain preferential excitation of the Eu^{3+} ions in (6*h*). There is another band at about 220 nm which is also present in the other compounds. This band is not discussed further because it is impossible to derive from the data in Ref. (3) whether this is a host-lattice band or an activator band.

Since the model works well up till here we now turn to other activators in the oxyapatites.

Wanmaker *et al.* (2) have reported Sb^{3+} emission from apatites $\text{M}_2^{2+}\text{Ln}_8(\text{SiO}_4)_6\text{O}_2$. The emission consists of a broad band peaking in the region 450–540 nm. Our model predicts the Sb^{3+} ion (which is smaller than the lanthanides) in (6*h*). This cannot be verified from the luminescent data, the bands being broad and their structural dependence unknown. It is striking that the position of the maximum of the Sb^{3+} emission depends markedly on the choice of Ln^{3+} and practically not on that of M^{2+} (2). For Sb^{3+} in (4*f*) this would not be expected, the (4*f*) sites forming linear chains parallel to the hexagonal *c* axis. For Sb^{3+} in (6*h*) this dependence is more conceivable, since then the Sb^{3+} coordinates the free oxygen ion together with two other (6*h*) site ions, i.e., Ln^{3+} ions. Let us now turn to the calcium halophosphates.

3. Calcium Halophosphates $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$.

In $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ζ for the F^- ion is found to be 6/7, whereas ζ for the O^{2-} ions is very near to 2. This means that we have in principle the same situation as in the oxyapatites discussed above, but that the lack of charge compensation is less pronounced. We expect, therefore, that trivalent cations in fluorophosphate will mainly occupy the (6*h*) sites. The luminescence data confirm this expectation as will be shown now.

Luminescence from Eu^{3+} in fluorapatite has been reported by Chafaï *et al.* (10). From the fact that the relative peak intensities in the emission spectrum are constant for different Eu^{3+} concentrations they conclude that Eu^{3+} occupies only one of the sites. The authors conclude that this must be the (4*f*) site. This conclusion is based upon the fact that they observe the ${}^5D_0\text{--}{}^7F_0$ emission which should be allowed for Eu^{3+} in (4*f*), and forbidden for Eu^{3+} in (6*h*). This is obviously incorrect (see Table I). As argued above this emission is allowed for both sites, but should be even stronger for the (6*h*) site. They further observe that the ${}^5D_0\text{--}{}^7F_4$ emission is weak and that the ${}^5D_0\text{--}{}^7F_2$ emission dominates strongly. The latter fact is not expected for a fluorophosphate (11). We are, therefore, inclined to believe that the Eu^{3+} ion occupies a (6*h*) site, as expected

TABLE I
NUMBER OF LINES EXPECTED FOR ${}^5D_0\text{--}{}^7F_n$ ($n = 0, 1, 2$)
TRANSITIONS FOR Eu^{3+} UNDER C_3 AND C_s SYMMETRY

Site symmetry	${}^5D_0\text{--}{}^7F_0$	${}^5D_0\text{--}{}^7F_1$	${}^5D_0\text{--}{}^7F_2$
C_3	1	2	3
C_s	1	3	5

from our model, and that it is charge-compensated by an oxygen ion on the fluorine site. This explains the presence of the ${}^5D_0\text{--}{}^7D_0$ emission and the intensity of the ${}^5D_0\text{--}{}^7F_2$ emission.

The Sb^{3+} ion is also expected on the (6*h*) sites. From the work of Soules *et al.* (12) it is clear that Sb^{3+} is not in (4*f*) sites, neither in compensated nor in uncompensated fluorophosphate.

For Mn^{2+} in fluorophosphate the charge compensation principle predicts a slight preference for (6*h*) sites, because the Mn^{2+} ion is somewhat smaller than the Ca^{2+} ion. Optical and EPR measurements (13, 14) are, however, not very conclusive. Reference (14) reports Mn^{2+} in (4*f*) only, Ref. (13) reports also large amounts of Mn in (6*h*) associated with an oxygen vacancy.

The chloroapatite $\text{Ca}_{10}(\text{PO})_4)_6\text{Cl}_2$ has a slightly different monoclinic crystal structure, where each Cl^- ion is surrounded by six Ca^{2+} ions so that ζ for Cl^- is 1.5 which is much too high. The value of ζ for oxygen is slightly less than 2. We therefore expect Sb^{3+} on (4*f*) sites unless it is charge-compensated by O^{2-} on chlorine sites. The behaviour of Sb^{3+} in chloro- (and also fluoro-) apatite has been studied thoroughly by Davis *et al.* (15). We are especially interested in their results on samples without oxygen compensation. They find an emission at about 400 nm for these samples. This is at much shorter wavelengths than the emission of oxygen-compensated samples which emit at about 490 nm. The authors hesitate to assign the 400 nm emission to Sb^{3+} in one of the two sites. It seems to us that it is not likely that the 400 nm emission in the fluoro- and chloroapatite is due to Sb^{3+} in (6*h*), because the nature of the neighbouring halogen ion will influence the spec-

tral position of the electronic transitions as is well known (16). We are, therefore, left with the conclusion that Sb^{3+} in the chloroapatites is in (4f), if it is not oxygen-compensated. We realize that the experimental evidence for this conclusion is not very strong, so that the agreement with our expectation is not very convincing.

For Mn^{2+} we expect a weak preference for (4f). Experimental data (14) indicate a statistical distribution of manganese among the calcium sites, so that we conclude that the change in manganese distribution going from fluoro- to chloroapatite is predicted correctly. The difference between Mn^{2+} and Ca^{2+} is so small that this is the best result to be expected.

We conclude that an extremely simple model can predict site occupations correctly in the apatite structure. A more general applicability will be investigated.

References

1. See, e.g., J. L. OUWELTJES, "Luminescence and Phosphors, in Modern Materials," Vol. 5, p. 161, Academic Press, New York, 1965.
2. W. L. WANMAKER, J. W. TER VRUGT, AND J. G. VERLIJSDONK, *J. Solid State Chem.* **3**, 452 (1971).
3. T. J. ISAACS, *J. Electrochem. Soc.* **120**, 654 (1973).
4. L. PAULING, "The Nature of the Chemical Bond", 2nd ed. chapter 48b. Oxford University Press, London.
5. J. FELSCHÉ, *Structure and Bonding* **13**, 99 (1973); *J. Solid State Chem.* **5**, 266 (1972).
6. YU. I. SMOLIN AND YU. F. SHEPELEV, *Izv. Akad. Nauk SSSR, Inorg. Mater.* **5**, 1823 (1969).
7. G. BLASSE AND A. BRIL, *J. Inorg. Nucl. Chem.* **29**, 2231 (1967).
8. G. BLASSE, *J. Chem. Phys.* **45**, 2356 (1966); G. BLASSE AND A. BRIL, *Z. Physik. Chemie N.F.* **57**, 187 (1968).
9. W. C. NIEUWPORT AND G. BLASSE, *Solid State Comm.* **4**, 227 (1966).
10. M. CHAFAÏ, J. C. HEUGHEBAERT, C. LINARÈS, F. GAUME-MAHN, AND G. MONTEL, *C.R. Acad. Sci. Paris Série C* **272**, 1804 (1971).
11. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **50**, 2974 (1969).
12. T. F. SOULES, T. S. DAVIS, AND E. R. KREIDLER, *J. Chem. Phys.* **55**, 1056 (1971).
13. F. M. RYAN, R. C. OHLMANN, J. MURPHY, R. MAZELSKY, G. R. WAGNER, AND R. W. WARREN, *Phys. Rev. B2*, 2341 (1970).
14. W. W. PIPER, *J. Luminescence* **1-2**, 669 (1970).
15. T. S. DAVIS, E. R. KREIDLER, J. A. PARODI, AND T. F. SOULES, *J. Luminescence* **4**, 48 (1971).
16. C. K. JØRGENSEN, "Absorption Spectra and Chemical Bonding in Complexes", chapter 10, Pergamon Press, New York.