

The Influence of Crystal Structure on the Luminescence of Tantalates and Niobates*

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The luminescence of MgTa_2O_6 (trirutile structure) and ZnTa_2O_6 (tri- α - PbO_2 structure) are reported and discussed in connection with the luminescence of related compounds, especially the niobates with columbite structure. The maximum of the excitation band of the luminescence of the two tantalates is at 280 nm, a value lower in energy than that for the niobates. The emission band has its maximum at 500 nm (MgTa_2O_6) and 450 nm (ZnTa_2O_6). The quantum efficiency is low, reaching 15% (MgTa_2O_6) and 30% (ZnTa_2O_6) at 4.2 K. It is argued that the phenomena observed for these compounds indicate that the excitons, formed upon photoexcitation, are mobile, whereas in the columbite niobates they are localized due to self-trapping. © 1988 Academic Press, Inc.

Introduction

The luminescence of closed-shell highly charged transition-metal ion complexes, as for instance, titanates, vanadates, niobates, tungstates, and tantalates, has been studied for many decades (1, 2). Nevertheless, this type of luminescence is still not well understood. The difficulties are of a divergent nature. The experimental data give only a restricted amount of information due to the fact that the spectra consist of very broad emission and excitation bands which do not show vibrational structure. If more than one optically active center is present, spectral resolution is usually not possible, because the bands are so broad.

If we consider the excited state of one isolated center, the knowledge of this state

appears to be restricted. We have proposed that the emission consists essentially of a triplet-singlet transition (3). Recently this has been convincingly confirmed by van der Waals and co-workers (4) using electron paramagnetic resonance with optical detection in a magnetic field. They also showed that the excited state of the tetrahedral complexes is subject to a strong Jahn-Teller distortion.

In addition to the structure of the excited state, there are other factors which determine the luminescence properties. One of these is the occurrence of extrinsic centers which may quench the intrinsic luminescence. These extrinsic centers may be due to anion deficiency (e.g., WO_3 centers in CaWO_4 (2)) or to cation disorder (e.g., Sc^{3+} and Nb^{5+} disorder in ScNbO_4 (5)).

Another factor is the delocalization of the excited state, i.e., energy band formation. A good example is TiO_2 , for which we

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recently observed free exciton emission (6). This is also the case for CsVO_3 (7). However, there is a series of examples which lie in between a semiconductor like TiO_2 and an insulator like CaWO_4 . In KTiOPO_4 we observed self-trapped exciton emission with a low thermal activation energy (8). The compounds LaNb_3O_9 (9) and NbPO_5 (10) are examples of compositions which occur in two different crystal structure: the wolframite MgWO_4 and the columbite CaNb_2O_6 are examples of luminescence is strong (9, 10).

A well-known class of luminescent compounds is that based on the $\alpha\text{-PbO}_2$ structure: the wolframite MgWO_4 and the columbite CaNb_2O_6 are examples of luminescent materials with high quantum efficiencies for photoluminescence (11). Cation disorder can spoil this efficiency considerably (5, 11). The tantalates within this family were less thoroughly investigated than the niobates (12). Recently Müller-Buschbaum and co-workers reported the crystal structure of several tantalates of MTa_2O_6 and discussed their crystal chemistry (13). We have now studied the luminescence of these tantalates. At room temperature their luminescence efficiency is negligible. At low temperatures, however, luminescence appears. The experiments indicate a certain amount of delocalization of the excited state which influences the luminescence properties in a decisive way. Several other compounds are also discussed in this connection.

Experimental

Samples of ZnTa_2O_6 and MgTa_2O_6 were prepared using conventional solid state techniques. They were fired several times at 1450°C in air. Samples were checked by X-ray powder diffraction using $\text{CuK}\alpha$ radiation. The diffractometer patterns showed ZnTa_2O_6 to have tri- $\alpha\text{-PbO}_2$ structure and MgTa_2O_6 to be of trirutile structure, in agreement with literature data (13).

Optical measurements were performed on a Perkin-Elmer MPF-3 spectrofluorometer equipped with an Oxford helium cryostat, as described in earlier papers (3, 9).

Results

At room temperature the trirutile MgTa_2O_6 shows no photoluminescence at all. This is in striking contrast with the efficient luminescence of MgNb_2O_6 (5), which, however, has columbite structure. Below 200 K MgTa_2O_6 shows weak luminescence. The quantum efficiency at 4.2 K is only $15 \pm 5\%$ and decreases more or less linearly to 200 K. The broad emission band has its maximum at about 500 nm; the corresponding excitation band is at 280 nm. The Stokes shift is about $17,000\text{ cm}^{-1}$. The excitation spectrum shows a weak shoulder on the longer wavelength side. The emission spectrum shows a weak shoulder on the shorter wavelength side, suggesting the presence of another emission band with a maximum at about 420 nm. The excitation maximum corresponds to the absorption edge in the diffuse reflection spectrum. These results are summarized in Fig. 1.

The tri- $\alpha\text{-PbO}_2$ ZnTa_2O_6 also does not luminesce at room temperature. This is in

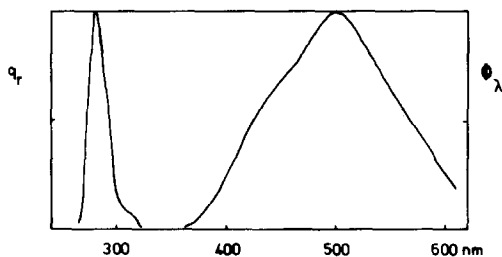


FIG. 1. Emission spectrum (right) and excitation spectrum (left) of the luminescence of MgTa_2O_6 at 4.2 K. The relative quantum output (q_r) and the spectral radiant power per constant wavelength interval (ϕ_λ) are given in arbitrary units.

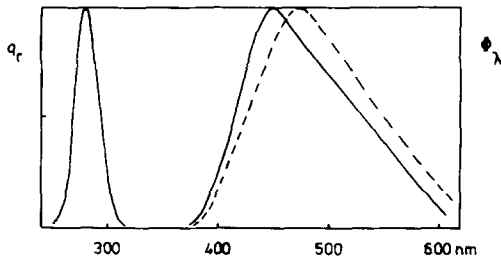


FIG. 2. Luminescence spectra of ZnTa_2O_6 at 4.2 K. See legend to Fig. 1.

contrast to ZnNb_2O_6 with columbite structure (12). Below 150 K, however, ZnTa_2O_6 shows photoluminescence with a quantum efficiency reaching a value of about 30% at 4.2 K. The broad emission band has its maximum at about 450 nm, with a corresponding excitation maximum at 280 nm (in agreement with the reflection spectrum). The Stokes shift amounts to $14,000 \text{ cm}^{-1}$. The emission band carries a lower wavelength shoulder. This corresponds to another emission band with a maximum around 530 nm. It was not possible to resolve the spectra any better or to obtain a more or less selective excitation. However, this longer wavelength component becomes stronger at higher temperature and has a higher quenching temperature ($\sim 150 \text{ K}$) than the main emission band ($\sim 125 \text{ K}$). The spectra at 4.2 K are given in Fig. 2.

The Transition between Free and Self-Trapped Excitons

As argued in the Introduction, we may expect to observe in the luminescence of the type of compounds under discussion free exciton emission (e.g., TiO_2 , CsVO_3) or self-trapped exciton emission (e.g., CaWO_4 , $\text{La}_2\text{MgTiO}_6$, YVO_4 (2)) as well as all features between these extremes. A beautiful example of the transition of free to self-trapped exciton emission occurs in the system $\text{AgBr}_{1-x}\text{Cl}_x$ (14). Theories have been outlined by Toyozawa (15) and, for the simple rare-gas solids, by Fugol (16)

and Schwentner *et al.* (17). Let us summarize the results.

Imagine a system of luminescent centers, each with a two-level energy scheme. After excitation we can distinguish two extreme situations. In general the radiative lifetime τ_r is much longer than the electron-lattice relaxation time τ_{lr} , so that after excitation the excited state relaxes to the equilibrium state of the excited state. The relaxation lowers the energy of the system by E_{lr} . If E_{lr} is large enough, the excitation energy stays at that particular site accompanied by a distortion of the surroundings (self-trapped state, S). However, there exists another energy effect: the excitation energy can be transferred from one center to another, forming an exciton band of width $2B$, where $2B = 2\nu|J|$. Here ν is the number of nearest neighbors and J is the transfer energy between the nearest neighbors. The total energy of the system is lowered by B if the excitation propagates through the crystal without lattice distortion (nearly free state, F).

Excitonic emission from the F state should be a sharp line (almost resonant with the absorption peak), whereas emission from the S state should be a Stokes-shifted broad band, characteristic of localized de-excitation. Closer consideration suggests that the stable state changes abruptly from F -like to S -like when the ratio $g \equiv E_{lr}/B$ exceeds a certain value ($g \approx 1$).

The emission of TiO_2 and CsVO_3 is an example of the F state, the emission of YVO_4 and CaWO_4 of the S state (2). In Refs. (16) and (17) it has been argued that coexistence of free and localized excitons is possible. This situation occurs if the free and self-trapped exciton states are separated by a potential barrier $H_M = 4B^3/27E_{lr}^2$. This is presented schematically in Fig. 3. The barrier H_M prolongs the localization time of the free excitons. This localization can occur by tunneling or by activated barrier transitions.

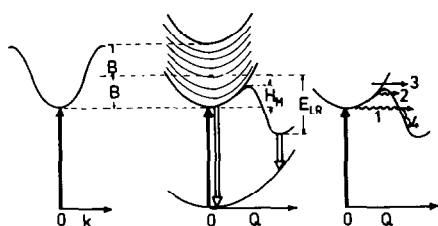


FIG. 3. Schematic representation for the dispersion of free excitons vs wavevector k (left-hand side), for self-trapping in a configurational coordinate diagram (center), and for several transitions through or over the barrier height H_M (right-hand side). Also see text.

For a very pure TiO_2 crystal we have observed a free exciton line at 412 nm, but also a broad band with a maximum at 485 nm (6). This emission might be ascribed to self-trapped excitons, but it cannot be excluded that it is due to titanate groups near defects after free-exciton trapping (as suggested in Ref. (6)). Let us now turn to a discussion of the present results.

Discussion

Let us first consider the position of the optical absorption edge of the compounds. It should be realized that strong delocalization, i.e., a high value of B , results necessarily in a low-energy position of the optical absorption edge. This is well illustrated

by the titanates where the following values have been reported and compared: TiO_2 3.0 eV; SrTiO_3 3.2 eV; MgTiO_3 3.7 eV; $\text{BaTi}(\text{PO}_4)_2$ 3.8 eV (2, 18). The latter compound contains isolated titanate octahedra. In the sequence given the coupling between the titanate octahedra decreases, i.e., B decreases. The compound $\text{BaTi}(\text{PO}_4)_2$ shows titanate emission with a large Stokes shift (1.4 eV), as expected for a self-trapped exciton with a large relaxation (19). Such a dramatic shift has also been observed for Bi^{3+} compounds, e.g., $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ with 4.6 eV and $\text{Bi}_{12}\text{GeO}_{20}$ with 3.4 eV, the former with self-trapped exciton emission, the latter with semiconductor behavior (7). From this we can conclude that a low-energy position of the optical absorption edge strongly suggests electronic delocalization.

Table I contains some values of optical absorption edges from reflection spectra and/or excitation spectra of the emission relating to the compounds under discussion. Tantalates with isolated tantalate groups have the optical absorption transition at much higher energy than the corresponding niobates in agreement with the values of the fifth ionization potential ($I_5(\text{Nb})$ 52 eV; $I_5(\text{Ta})$ 45 eV (23)). The value of I_5 is of decisive importance, since we are dealing with charge-transfer transitions (2).

TABLE I
Value of the Optical Absorption Edge of Some Niobates and Tantalates

Compound	Optical absorption edge (nm)	Ref.
Tantalates with isolated tantalate groups (YTao_4 , $\text{Mg}_4\text{Ta}_2\text{O}_9$, Li_3TaO_4)	220 ± 5	2, 20
Niobates with isolated niobate groups (YNbO_4 , $\text{Mg}_4\text{Nb}_2\text{O}_9$, Li_3NbO_4)	250 ± 5	2, 21
MgTa_2O_6	280	This work
ZnTa_2O_6	280	This work
ScNbO_4	260	5
MgNb_2O_6	275	5, 11
LiNb_3O_8	300	22

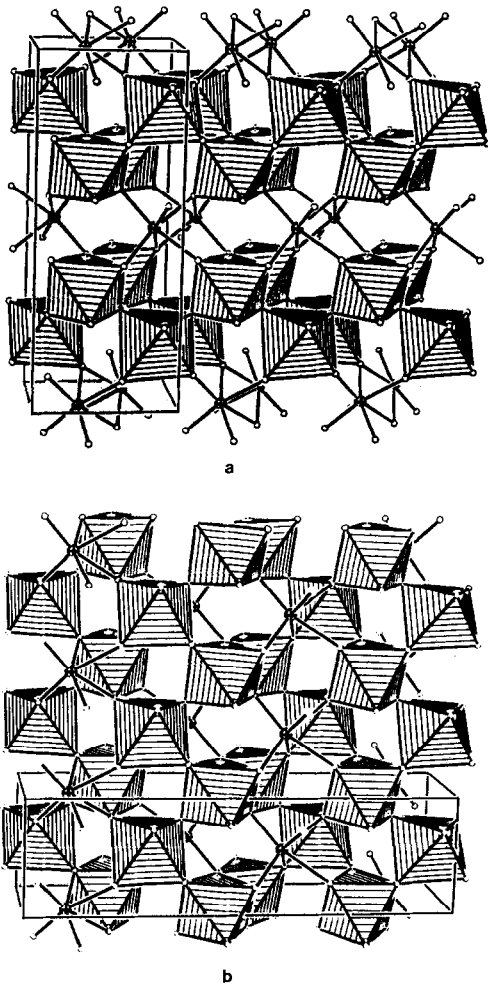


FIG. 4. (a) The columbite structure. (b) The tri- α - PbO_2 structure. The general formula for both cases is AB_2O_6 . The coordination octahedra around the pentavalent B ions (Nb^{5+} in a, and Ta^{5+} in b) are hatched. The coordination octahedra around the divalent A ions are open. Reprinted, by permission of the publisher, from Ref. (13).

In ScNbO_4 the niobate groups form linear zig-zag chains by edge-sharing of octahedra (ScNbO_4 has wolframite structure). This does not influence the position of the niobate absorption much. In MgNb_2O_6 with related structure (columbite) two of such niobate chains are coupled resulting in a lower absorption edge than ScNbO_4 . This

probably indicates a small amount of delocalization. The luminescence, however, is clearly of the self-trapped exciton type with a large Stokes shift (5). The columbite structure is given in Fig. 4a. In LiNb_3O_8 all the niobate zigzag chains are connected to each other by niobate octahedra, since this structure can be derived from the wolframite structure (e.g., ScNbO_4) by replacing the trivalent ions in an ordered way with Li^+ and Nb^{5+} ions (24). The absorption edge shifts to energies which are new considerably lower than those for the isolated niobate group (see Table I). The stronger the connections between the niobate groups, the lower the absorption edge will be. This has drastic consequences for the luminescence: LiNb_3O_8 is only a weak emitter, probably because the excitation energy is now mobile and can reach quenching sites in the lattice.

The value of the optical absorption edge of the tantalates MTa_2O_6 under discussion is at low energy: not only much lower than the values of the edge of the compounds with isolated tantalate groups, but even lower than the value of the corresponding niobate MgNb_2O_6 (see Table I). From this comparison of optical absorption edges we conclude that the possibility of electronic delocalization occurring in the excited state in the MTa_2O_6 tantalates cannot be neglected.

Let us now consider the crystal structures of these tantalates. They confirm a very old rule that the structures of tantalates are in between those of niobates and antimonates, a phenomenon which can be explained from the difference in electron configuration of the pentavalent ions (25). The structure of MgTa_2O_6 is trirutile (13, 26), contrary to that of MgNb_2O_6 . The compound MgSb_2O_6 has also trirutile structure (26). This structure, shown in Fig. 5, contains linear chains of edge-sharing octahedra filled in the sequence $\text{Mg}-\text{Ta}-\text{Ta}$. The tantalate pairs in the chains are con-

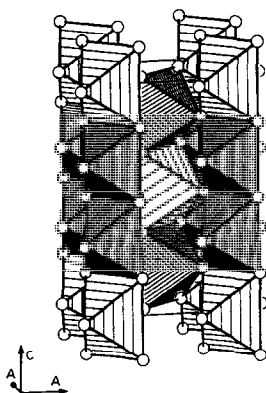


FIG. 5. The trirutile structure of MgTa_2O_6 . The TaO_6 octahedra are densely hatched; the MgO_6 octahedra are widely hatched. Reprinted by permission of the publisher from Ref. (13).

nected via corner-sharing to other pairs. This three-dimensional coupling is probably responsible for the low-energy value of the optical absorption edge, i.e., for electronic delocalization or a high value of B .

The structure of ZnTa_2O_6 is also different from ZnNb_2O_6 (columbite), but also from that of ZnSb_2O_6 (trirutile) (13, 26): ZnTa_2O_6 has tri- α - PbO_2 structure (13, 27) (Fig. 4b). This structure has the same arrangement of octahedra as the columbite structure, but the occupation is different (see Fig. 4). In columbite the zigzag chains are occupied by metal ions of one type; in tri- α - PbO_2 one-third of the chains contain one type of ion (Ta^{5+}) and two-thirds is filled up by equal and ordered amounts of both (Zn^{2+} and Ta^{5+}) ions. As a consequence there is again a three-dimensional coupling of the tantalate groups. This suggests that in ZnTa_2O_6 the delocalization is more pronounced than in ZnNb_2O_6 .

Let us now turn to the luminescence properties. The luminescence of the trirutile MgTa_2O_6 has a low quantum efficiency, even at 4.2 K. This excludes quenching due to disorder or quenching centers, since there are no indications that the concentration of these defects is high and energy

migration must be strongly hampered at that temperature. In the case of MgNb_2O_6 , where a low efficiency at 300 K may be due to disorder, the efficiency increases to high values if the temperature is lowered (5, 12). In view of the low-energy position of the absorption edge of MgTa_2O_6 (below MgNb_2O_6), we propose that excitation into the absorption edge creates mobile excitons. It cannot be excluded that the weak 420-nm emission presents self-trapped exciton emission. The main emission band at 500 nm cannot be due to this type of emission in view of the large Stokes shift (18). In our opinion this emission is due to exciton recombination at defect sites. The low efficiency is, therefore, due to the fact that the free excitons have three modes to decay: (i) after crossing the barrier H_M as self-trapped excitons (420 nm); (ii) after trapping by defects as deep-center emission (500 nm); (iii) nonradiatively at quenching centers. Obviously mode iii prevails. The centers responsible for the 500-nm emission might well be due to a small amount of Mg^{2+} - Ta^{5+} disorder. The weak feature in the excitation spectrum corresponds in that case to direct excitation of these centers. The trirutile MgTa_2O_6 can be considered as an intermediary situation between rutile (TiO_2) and the columbite MgNb_2O_6 .

The tri- α - PbO_2 shows a quantum efficiency which is higher than that of MgTa_2O_6 , but still there is a considerable amount of nonradiative loss. Actually the spectral characteristics of ZnTa_2O_6 and MgNb_2O_6 are not too different, although the tantalate spectra lie at somewhat lower energy than the niobate spectra. Therefore, we assume that ZnTa_2O_6 presents a case which is close to the border line between localization and delocalization. The longer wavelength emission (530 nm) may again be due to recombination at centers due to disorder.

Recalling the three modes, i-iii mentioned above, the situation may be characterized in a qualitative way as follows: In

MgTa_2O_6 , $\text{iii} > \text{ii} > \text{i}$, the notation "ni" now indicating the rate of the process concerned. In ZnTa_2O_6 , $\text{iii} > \text{i} > \text{ii}$, and in MgNb_2O_6 $\text{i} > \text{iii} > \text{ii}$. The shift in the rates is mainly due to the change in crystal structure.

It seems very hard to prove this model in an unambiguous way. In view of the spectra (broad bands), not much help can be expected from there. Perhaps energy level calculations might be of help, but these are not easy to perform. Therefore a consideration of many experimental facts might confirm these ideas further. It is interesting to note that in bismuth compounds similar phenomena have been observed (7).

In this connection it is noteworthy that the compounds ATiBO_6 ($A = \text{La, Gd, Y, Lu, Sc}$; $B = \text{Nb, Ta}$) show luminescence only at 300 K if they have columbite structure; those with CaTa_2O_6 or rutile structure luminesce only weakly at lower temperatures (28). Note that GdTiNbO_6 (columbite) has the absorption edge at 280 nm, but GdTiTaO_6 (CaTa_2O_6) at 320 nm. Again the columbite structure shows the smallest amount of delocalization.

The tantalates La_3TaO_7 and Y_3TaO_7 do not show luminescence with reasonable efficiency (29). These compounds have a crystal structure in which tantalate octahedra form chains by corner-sharing (30). Such a configuration facilitates delocalization, so that the exciton can easily reach quenching centers. The same is true for Ba_2WO_5 (31). Interestingly enough, the linear chain of corner-sharing niobate octahedra in $\alpha\text{-NbPO}_5$ leads to efficient luminescence below 150 K (10). The corner-sharing O^{2-} ions are far away from one of the two Nb^{5+} ions, but close to the other. This configuration explains the localization.

The model sketch shows a pronounced analogy to the concept of a critical internuclear separation (R_c) in discussing localized versus collective electrons. This separation is defined in such a way that outer electrons

are best described as high-mobility collective electrons if the interatomic separation $R < R_c$, and as low-mobility localized electrons if the interatomic separation $R > R_c$ (32). However, we cannot translate our model in just one critical parameter, since many bond distances and angles are involved. The case of ZnTa_2O_6 is obviously near the border line between the two regimes.

Acknowledgments

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References

1. F. A. KRÖGER, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam 1948.
2. G. BLASSE, *Struct. Bonding* **42**, 1 (1980).
3. H. RONDE AND G. BLASSE, *J. Inorg. Nucl. Chem.* **40**, 215 (1978); G. BLASSE, *Chem. Phys. Lett.* **63**, 441 (1979).
4. W. BARENDSSWAARD, J. VAN TOL, AND J. H. VAN DER WAALS, *Chem. Phys. Lett.* **121**, 361 (1985); J. H. VAN DER WAALS, *Int Rev. Phys. Chem.* **5**, 219 (1986); W. BARENDSSWAARD AND J. H. VAN DER WAALS, *Mol. Phys.* **59**, 337 (1986).
5. G. BLASSE, G. J. DIRKSEN, AND L. H. BRIXNER, *Mat. Chem. Phys.* **14**, 485 (1986).
6. L. G. J. DE HAART AND G. BLASSE, *J. Solid State Chem.* **61**, 135 (1986).
7. G. BLASSE, *Rev. Inorg. Chem.* **5**, 319 (1983).
8. G. BLASSE, G. J. DIRKSEN, AND L. H. BRIXNER, *Mater. Res. Bull.* **20**, 989 (1985).
9. H. C. G. VERHAAR, H. DONKER, M. J. J. LAMMERS, G. J. DIRKSEN, G. BLASSE, C. C. TORARDI, AND L. H. BRIXNER, *J. Solid State Chem.* **60**, 20 (1985).
10. G. BLASSE AND G. J. DIRKSEN, *Phys. Status Solidi A* **87**, K181 (1985).
11. G. BLASSE AND M. G. J. VAN LEUR, *Mater. Res. Bull.* **20**, 1037 (1985).
12. A. WACHTEL, *J. Electrochem. Soc.* **111**, 534 (1964).
13. M. WABURG AND Hk. MÜLLER-BUSCHBAUM, *Z. Anorg. Allg. Chem.* **508**, 55 (1984); Hk. MÜLLER-

- BUSCHBAUM AND R. WICHMANN, *Z. Anorg. Allg. Chem.* **536**, 15 (1986).
14. H. KANZAKI, S. SAKURAGI, AND K. SAKAMOTO, *Solid State Commun.* **9**, 999 (1971).
 15. Y. TOYOZAWA, *J. Lumin.* **12/13**, 13 (1976).
 16. J. Y. FUGOL, *Adv. Phys.* **27**, 1 (1978).
 17. N. SCHWENTNER, E. E. KOCH, AND J. JORTNER, in "Energy Transfer Processes in Condensed Matter" (B. DiBartolo, Ed.), p. 417, Plenum, New York (1984).
 18. L. G. J. DE HAART, A. J. DE VRIES, AND G. BLASSE, *J. Solid State Chem.* **59**, 291 (1985).
 19. G. BLASSE AND G. J. DIRKSEN, *Chem. Phys. Lett.* **62**, 19 (1979).
 20. G. BLASSE AND A. BRIL, *J. Solid State Chem.* **3**, 69 (1970).
 21. G. BLASSE AND A. BRIL, *Z. Phys. Chem. N.F.* **57**, 187 (1968).
 22. G. BLASSE, *Phys. Status Solidi A* **20**, K99 (1973).
 23. L. H. AHRENS, *Geochim. Cosmochim. Acta* **2**, 155 (1952).
 24. M. LUNDBERG, *Acta Chem. Scand.* **25**, 3337 (1971).
 25. G. BLASSE, *J. Inorg. Nucl. Chem.* **26**, 1191 (1964).
 26. G. BAYER, thesis, ETH Zürich (1962).
 27. J. SENEGAS AND J. GALY, *J. Solid State Chem.* **10**, 5 (1974).
 28. G. BLASSE, *Mater. Res. Bull.* **2**, 497 (1967); G. BLASSE AND A. BRIL, *Philips Res. Rep.* **22**, 46 (1967).
 29. M. J. J. LAMMERS AND G. BLASSE, unpublished results; L. H. BRIXNER, private communication.
 30. H. J. ROSSELL, *J. Solid State Chem.* **27**, 115 (1979).
 31. G. BLASSE, *Inorg. Chim. Acta* **129**, 115 (1987).
 32. J. B. GOODENOUGH, "Magnetism and the Chemical Bond," Interscience Wiley, New York (1963).