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The Luminescence of Calcium Molybdate

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The luminescence properties of calcium molybdate are reported. Two emission bands are observed, one in the green and another in the orange spectral region. The shorter wavelength emission band is assigned to the $^3T_1 \rightarrow {}^1A_1$ transition in the tetrahedral molybdate group. The longer wavelength band is ascribed to a similar transition in a molybdate group lacking an oxygen ion, i.e. a MoO_3 group. Similar observations are made in the case of calcium tungstate.

Es werden die Lumineszenzeigenschaften von Kalziummolybdat mitgeteilt. Zwei Emissionsbanden werden beobachtet, eine im grünen, die andere im orangen Spektralbereich. Die Emissionsbande mit der kürzeren Wellenlänge wird dem $^3T_1 \rightarrow {}^1A_1$-Übergang in der tetraedrischen Molybdatgruppe zugeordnet. Die Bande mit der längeren Wellenlänge wird einem ähnlichen Übergang in einer Molybdatgruppe, in der ein Sauerstoffion fehlt, d. h. einer MoO_3-Gruppe, zugeschrieben. Ähnliche Beobachtungen werden für den Fall des Kalziumwolframats gemacht.

1. Introduction

After the early work of Kröger [1] and Botden [2] there has been a renewed interest in the molybdate and tungstate luminescence of scheelites during recent years. Beard et al. [3] reported on the temperature dependence of the quantum efficiency of $CaWO_4$ and $CdWO_4$. Van Loo [4, 5] discussed the luminescence of $PbWO_4$ and $PbMoO_4$. Treadaway and Powell [6, 7] and Grasser et al. [8, 9] have studied the $CaWO_4$ luminescence in detail. Blasse and Schipper [10] reported on the luminescence of $SrWO_4$ and $BaWO_4$. Recently Tyner and Drickamer [11] presented a study on the pressure and temperature dependence of the decay time and the intensity of the luminescence of several molybdates and tungstates.

Usually one emission band is found upon excitation into the optical band gap. In $CaWO_4$ [7, 9], $PbWO_4$ [4, 5], $SrWO_4$ [10], and $BaWO_4$ [10] an additional emission band at longer wavelengths was found upon excitation into the tail of the band gap. Such an additional emission band has not been reported for the molybdates, as far as we know.

Although the tungstates and the vanadates have been studied extensively, there has not been great interest in the molybdates. This work was undertaken to elucidate the luminescence of $CaMoO_4$, and especially the decay time of the emission, for this has been reported to be very long [12]. Further we report some additional observations on the luminescence of $CaWO_4$.

2. Experimental

Samples of doped and undoped $CaMoO_4$ were prepared by firing intimate mixtures of $CaCO_3$, MoO_3, Na_2MoO_4, and Y_2O_3 for 4 h at 850 °C in air, followed by milling and firing for 4 h at 1000 °C in air. The compositions of the starting mixtures for the Y- and Na-doped samples were $CaCO_3 + (1 + \delta)\, MoO_3 + \delta\, Y_2O_3$ ($\delta = 0.0025$) and $CaCO_3 + (1 + \delta)\, MoO_3 + \delta\, Na_2MoO_4$ ($\delta = 0.0025$), respectively. Samples of doped

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and undoped $CaWO_4$ were prepared by firing intimate mixtures of $CaCO_3$, WO_3, Na_2CO_3, and Y_2O_3 for 12 h at 950 °C in air, followed by milling and firing for 12 h at 1000 °C in air. Starting mixtures for the Y- and Na-doped samples were $CaCO_3 + (1 + 3\delta) WO_3 + \delta Y_2O_3$ ($\delta = 0.01$ and 0.0025) and $CaCO_3 + (1 + 2\delta) WO_3 + \delta Na_2CO_3$ ($\delta = 0.00375$, 0.0125, and 0.025), respectively.

The compounds were checked by X-ray analysis on a Philips diffractometer using the CuKα radiation. All samples appeared to be single-phased.

Emission and excitation spectra of their luminescence were recorded either on a Perkin-Elmer MPF-2A spectrofluorimeter, equipped with an Oxford Instruments CF 100 continuous flow He cryostat or on a Perkin-Elmer MPF-3L spectrofluorimeter, equipped with a cryoson XL2 liquid-nitrogen cryostat. Excitation spectra were taken with a combination of a Schott UG5 filter and a cuvet with a $NiSO_4$ solution in the excitation beam; in the emission beam Balzers K_1 to K_6 interference filters were used together with the standard mounted set of UV cut-off filters. Emission spectra were obtained using Baird Atomic broad-band interference filters with a maximum transmission at the excitation wavelength; in the emission beam the standard mounted set of UV cut-off filters was used.

The excitation spectra were corrected for the lamp intensity and the UG5-$NiSO_4$ filter using lumogen as a standard. The emission spectra were corrected for the sensitivity of the photomultiplier according to the curve given by the manufacturer.

The performance of the luminescence decay measurements has been described in detail by van Loo and Wolterink [13]. As a light source we used an EG & G Xe flash lamp; excitation and emission wavelengths were selected with the set of filters mentioned above and a filter which cuts off radiation above 2.03 eV.

The temperature dependence of the emission intensity was measured on the MPF-2A spectrofluorimeter from LHeT to 300 K and on the MPF-3L spectrofluorimeter from 100 to 430 K.

3. Results

All the samples under examination were white powders. The $CaMoO_4$ samples show a green luminescence under short wavelength (4.0 to 5.0 eV) UV excitation. Under 3.9 eV excitation, undoped $CaMoO_4$ and $CaMoO_4$ doped with Na show an orange emission, while in the case of $CaMoO_4$ doped with Y the maximum of the emission band is in between these two (Fig. 1). Doping with Na or Y does not introduce new emission bands, but increases or decreases the intensity of the orange emission, respectively. The emission spectra consist of a broad band, the halfwidth of which is about 0.45 eV in the case of the green emission, and about 0.35 eV in the case of the orange emission.

Excitation spectra of the luminescence of undoped $CaMoO_4$ are presented in Fig. 2. Recording the excitation spectrum of the green emission (at 2.58 eV) yields a broad

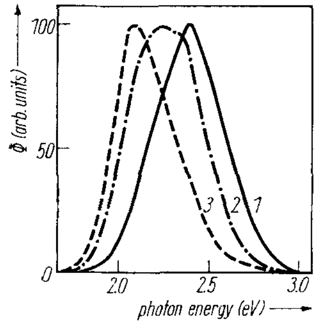

Fig. 1. Spectral energy distribution of the emission of several $CaMoO_4$ samples at 77 K. Φ denotes the spectral radiant power per unit energy. (1) Undoped, Na- and Y-doped, $E_{exc} = 4.51$ eV; (2) Y-doped, $E_{exc} = 3.85$ eV; (3) undoped and Na-doped, $E_{exc} = 3.85$ eV

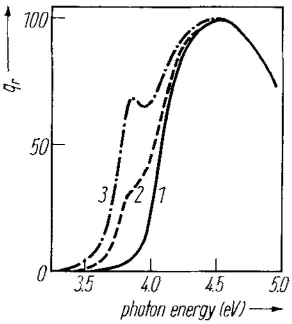

Fig. 2

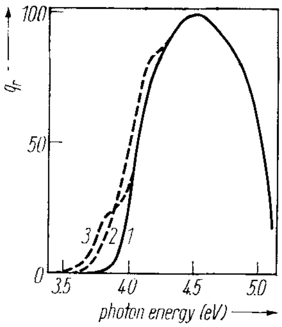

Fig. 3

Fig. 2. Relative excitation spectra of the luminescence of $CaMoO_4$ at several emission energies at 77 K. q_r denotes the relative quantum output. (1) $E_{em} = 2.21$, (2) 1.94, (3) 1.82 eV

Fig. 3. Relative excitation spectra of the luminescence of several $CaMoO_4$ samples at 77 K. q_r denotes the relative quantum output. (1) Undoped, Na- and Y-doped, $E_{em} = 1.94$ eV; (2) Y-doped, $E_{me} = 1.94$ eV; (3) undoped and Na-doped, $E_{em} = 1.94$ eV

excitation band. At lower emission energies an additional excitation band appears at lower energy. The considerable spectral overlap of the green and the orange emission (Fig. 1) causes the simultaneous presence of the excitation band of the green emission, when recording the excitation spectrum of the orange emission.

Excitation spectra of the luminescence of undoped, Na- and Y-doped $CaMoO_4$ samples are presented in Fig. 3. As can be seen from Fig. 1 to 3 we observed two emission bands, which can be excited separately. The present results suggest that the green emission which has been reported before [1, 9] is the intrinsic molybdate emission. The orange emission, which has not been reported earlier, must be due to a defect centre the concentration of which changes by doping with aliovalent ions.

For both emissions the decay time and the intensity of the emission were recorded as a function of temperature. The decay curves appeared to be single exponentials at

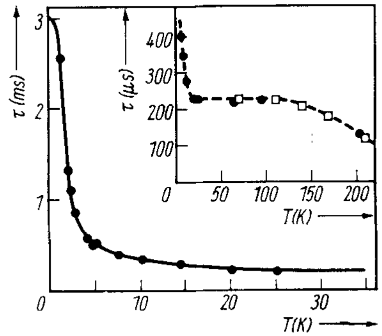

Fig. 4

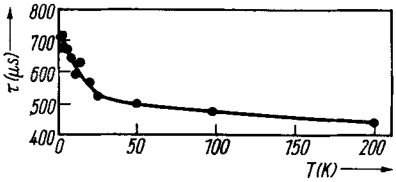

Fig. 5

Fig. 4. Temperature dependence of the decay time of the green emission of $CaMoO_4$. $E_{exc} = 4.47$ eV; circles this work, squares [11]. The solid line represents a fitted curve (see text)

Fig. 5. Temperature dependence of the decay time of the orange emission of $CaMoO_4$. $E_{exc} = 3.85$ eV; the solid line represents a fitted curve (see text)

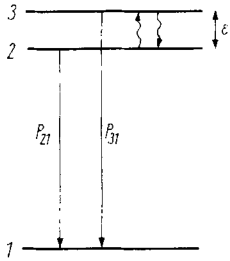

Fig. 6. Three-level energy scheme

all temperatures. The experimental points are given in Fig. 4 and 5. The decay time of both emissions decreases with increasing temperature in the low-temperature region. This points to an energy level scheme as given in Fig. 6, with $p_{21} < p_{31}$, so that level 2 acts as an optical trap [14].

The solid line in Fig. 4 and 5 represents a fit of the measured decay times to $\tau = [1 + \exp(\varepsilon/kT)]/[p_{31} + p_{21} \exp(\varepsilon/kT)]$. This equation gives the temperature dependence of the decay time of the three-level scheme in Fig. 6, under the assumption of thermal equilibrium between the levels 2 and 3 [14]. Further we assume that energy transfer is absent. This is fairly reasonable because excitation into the green centre does not yield the orange emission. The parameters, p_{21}, p_{31}, and ε for the two emissions are presented in Table 1.

Table 1

Parameters used for fitting the experimental decay curves of $CaMoO_4$

	ε (meV)	p_{31} (10^3 s^{-1})	p_{21} (10^3 s^{-1})
green emission	0.6 ± 0.1	8.0 ± 0.2	0.33 ± 0.03
red emission	2.0 ± 0.5	3.1 ± 0.3	1.43 ± 0.04

The temperature dependence of the intensity of both emissions is given in Fig. 7. The increase of the emission intensity of the orange emission in the low-temperature region is probably due to an increasing absorption strength. Because excitation took place in the low-energy side (at 3.69 eV) of the spectrum, a thermal shift of the absorption edge effects the emission intensity strongly. Excitation at higher energies yields also the green emission and can, therefore, not be applied.

In the case of $CaWO_4$ also excitation and emission spectra were recorded. We found in all samples two emission bands, a blue emission band resulting from excitation at energies higher than about 4.8 eV, and a green emission band, resulting from excitation at energies of about 4.6 eV. These two emission bands have been observed earlier by Grasser and Scharmann [9] and Treadaway and Powell [7].

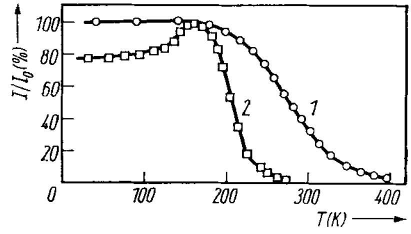

Fig. 7. Temperature dependence of the emission intensity of the green and the orange emission of $CaMoO_4$. (1) Green emission, $E_{exc} = 4.27$ eV; (2) orange emission, $E_{exc} = 3.69$ eV

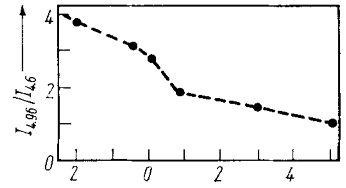

Fig. 8. Ratio of the emission intensity of $CaWO_4$ at 2.48 eV excited at 4.96 and 4.6 eV as a function of the nominal Na and Y-concentration, measured at 77 K

The blue emission band consists of a broad band with a halfwidth of about 0.7 eV and a maximum at 2.75 eV. The green emission band has its maximum at 2.38 eV and a halfwidth of about 0.44 eV. The green emission was quenched at room temperature.

In the case of the Na-doped samples, the green emission was stronger than in the case of the undoped and the Y-doped samples. This is shown in Fig. 8 where the ratio of the intensity of the 2.48 eV emission (which is in between the blue and the green emission) at excitation energies of 4.96 and 4.6 eV is plotted versus the nominal Na or Y content. The higher this ratio, the weaker the green emission will be and the lower the concentration of green emitting centres. We realize that this is a rough and artificial method to estimate the concentration of the green emitting centres, but in view of the overlap of the emission and excitation bands involved we have no other possibility.

4. Discussion

4.1 The temperature dependence of the emissions

The temperature dependence of the green emission of $CaMoO_4$ is given in Fig. 7. Fig. 9 presents a plot of $\ln[(I/I_0) - 1]$ versus $1/T$. In this figure the results of Botden [2] on $CaMoO_4$ are presented, too. In both cases one observes two regions, with a higher slope in the higher temperature region. In addition, we made the following observations: a) Excitation into the green centre yields never the orange emission, independent of temperature. b) When doped with Sm^{3+} (1%), the Sm^{3+} emission starts to increase in the high-temperature region in Fig. 9, which has also been observed by Botden [2]. c) Experiments on mixed crystals of $CaWO_4$ and $CaMoO_4$ show no increase of the quenching temperature of the MoO_4^{2-} emission at low MoO_4^{2-} concentrations [2].

In view of the observations mentioned above we conclude, in agreement with [2], that the decrease of the emission intensity in the low-temperature region (150 to 320 K) is due to thermal quenching of the molybdate luminescence. At a certain temperature (about 320 K) the probability of energy transfer between the molybdate groups exceeds the probability of the non-radiative transitions in the centre itself. This is concluded from the increase of the Sm^{3+} emission intensity and the higher slope

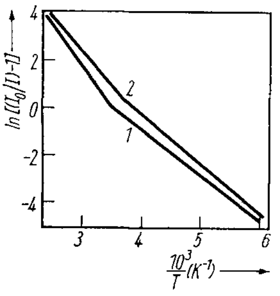

Fig. 9. Temperature dependence of the intensity of the green emission of $CaMoO_4$, plotted as $\ln[(I_0/I) - 1]$ vs. $1/T$. (1) This work, (2) Botden [2]

in the high-temperature region in Fig. 9. This model implies that the temperature dependence of the energy transfer probability must be more pronounced than the temperature dependence of the non-radiative transitions. This is in line with a recent theoretical analysis by Fonger and Struck [15].

The temperature dependence of the orange emission of $CaMoO_4$ is shown in Fig. 7. The slight temperature dependence at low temperatures was discussed in Section 3. At high temperatures the quenching can be described by $I_0/I = [1 + c \exp(\Delta E/kT)]^{-1}$ which represents thermal quenching in the centre itself.

Botden [2] and Treadaway and Powell [6, 7] have reported on the temperature dependence of the luminescence of $CaWO_4$ and $CaWO_4$: Sm^{3+}. Their studies reveal that the decrease of the intensity of the blue tungstate emission occurs simultaneously with the increase of the Sm^{3+} emission. This implies energy transfer between the tungstate groups and finally to the samarium ions. The model for the energy transfer processes proposed in [6] can, however, not completely account for the observed temperature dependence of the emission. It was supposed, therefore, that thermal quenching processes in the tungstate group itself are playing a role, too. The situation in $CaWO_4$ is, therefore, different from that in $CaMoO_4$, because there is no temperature region in which the thermal quenching processes dominate the temperature dependence of the emission.

It is interesting to compare YVO_4:Eu^{3+} and $CaMoO_4$:Sm^{3+} in this respect. Whereas in the case of YVO_4 [16] energy migration starts at much lower temperatures than thermal quenching, we have the reversed situation in $CaMoO_4$. The experiments mentioned above suggest that $CaWO_4$ is in between these extremes.

4.2 The nature of the shorter wavelength emission

It is well accepted that the shorter wavelength emission in these compounds is due to optical transitions within the MoO_4^{2-} or WO_4^{2-} group. In the known closed-shell tetrahedral tetroxo-transition metal complexes the highest completely filled MO, and the lowest unfilled MO are supposed to be t_1 and $2e_1$, respectively. This gives rise to a $^1A_1$ ground state. The first excited configuration t_12e_1 gives rise to four states viz. $^1T_1$, $^1T_2$, $^3T_1$, and $^3T_2$. The most probable ordering of these states is $^3T_1 \approx {}^3T_2 < < {}^1T_1 < {}^1T_2$ [17]. The emission in these compounds is ascribed to transitions from the lower lying triplets $^3T_{1,2}$ to the $^1A_1$ ground state [9, 12].

In T_d-symmetry the $^3T_1 \rightarrow {}^1A_1$ transition is orbitally forbidden as an electric dipole transition, while $^3T_2 \rightarrow {}^1A_1$ is an orbitally allowed transition. Both $^3T_1 \rightarrow {}^1A_1$ and $^3T_2 \rightarrow {}^1A_1$ are spin forbidden. The actual site symmetry in $CaMoO_4$, however, is S_4. Due to the symmetry lowering from T_d to S_4, T_1 will split into an A- and an E-state, and T_2 into a B- and an E-state. The ground state repesentation is now A. Under the selection rules in S_4, A → A is forbidden, whereas E → A and B → A are allowed transitions. Note that the $^3T_1 \rightarrow {}^1A_1$ transition contains under S_4 a forbidden and an allowed component.

The decay parameters (Table 1) show that the emission transition from the higher emitting level has a roughly 25 times higher probability than the emission from the lower lying level. From this we conclude that the green emission of $CaMoO_4$ originates from the split $^3T_1$ level, because this level gives rise to an allowed and a forbidden transition. On the basis of similar arguments Ronde and Blasse [18] concluded that the emission of the isoelectronic VO_4^{3-} complex originates from the $^3T_1$ level, too. It is not very surprising that the splitting of the $^3T_1$ level is about 4.5 cm^{-1}, because Ronde and Blasse found for the splitting of this level also a few cm^{-1}. Furthermore, Ballhausen and Trabjerg [19] suggest a splitting of the $^1T_1$ level in the case of $LiClO_4$ ·

$\cdot$ 3 H_2O/$LiMnO_4 \cdot$ 3 H_2O of less than 10 cm^{-1}, while Butowiez [20] reports 6 cm^{-1} for this splitting in the case of K_2CrO_4.

In view of the similarities between the decay times as a function of temperature of the shorter wavelength emissions in $CaWO_4$ and $CaMoO_4$, and in view of the "isoelectronic" configuration of the tetrahedral groups, we suppose that in $CaWO_4$, too, the intrinsic blue emission corresponds to a transition from the split $^3T_1$ level to the $^1A_1$ level.

A comparison of the decay times, measured in the temperature-independent region, of the "isoelectronic" VO_4^{3-}, MoO_4^{2-}, and WO_4^{2-} complexes reveals that in that sequence the decay time decreases: for VO_4^{3-} about 10^{-3} s [18], for MoO_4^{2-} about 10^{-4} s (this work, [11]), and for WO_4^{2-} about 10^{-5} s [7, 9, 11]. The emission corresponds in all three cases to a transition which is orbitally allowed, but spin forbidden. The decrease of the decay time in the sequence vanadate, molybdate, and tungstate can be ascribed to the increase of the spin–orbit coupling in this sequence.

4.3 The nature of the longer wavelength emission

Our experiments on Na- and Y-doped samples of $CaMoO_4$ and $CaWO_4$ reveal that the concentration of the centre, responsible for the longer wavelength emission increases in the sequence: Y-doped, undoped, and Na-doped samples. Doping with Na will increase, doping with Y will decrease the oxygen ion vacancy concentration, and, therefore, the concentration of MoO_3 (WO_3) groups.

On the basis of quenching experiments, Grasser and Scharmann suggest that the green emission band in $CaWO_4$ originates from WO_3 groups. Our doping experiments give additional chemical evidence for this model. It is obvious, therefore, to ascribe the green emission in $CaWO_4$ and the orange emission in $CaMoO_4$ to a transition on a WO_3 and a MoO_3 group, respectively.

We suppose that the symmetry of such a MoO_3 (WO_3) group is C_{3v}. Relaxation to a planar MoO_3 (WO_3) group is very unlikely, because this would lead to very immobile oxygen ion vacancies. This is contradicted by various experiments which show that oxygen is a rather mobile species in these compounds [21 to 23].

If we consider now the nine 2p orbitals on the three O^{2-} ions, the group theoretical representations of the combinations of these orbitals are $\Gamma_\sigma = A_1 + E$ and $\Gamma_\pi = A_1 + A_2 + E$. None of the s-, p-, or d-orbitals of the metal ions have the A_2-representation. The combination with representation A_2 is, therefore, non-bonding. We assume that it will be the highest filled orbital in the ground state of the MoO_3(WO_3) complex. It seems also reasonable to assume that the d_{z^2} orbital (directed along the trigonal axis) will be the lowest unoccupied d-orbital, since it points to the effectively positive oxygen ion vacancy. The d_{z^2} orbital transforms as a_1.

It is this simple picture which is able to show that at low temperatures the emission transition is orbitally forbidden. The ground state will be $^1A_1$, while the first excited configuration a_2a_1 gives rise to $^1A_2$ and $^3A_2$. The latter one will be the lower. The selection rules in C_{3v} show that transitions between A_2 and A_1 are orbitally forbidden and between A_1 or E and A_1 allowed. All possible transitions at higher energy are, therefore, orbitally allowed, since only A_1- and E-representations are involved. The decay parameters show that the probability of the transition from the lowest excited level to the ground state is smaller than that from the higher level (Table 1). This is in accordance with the model given above.

The difference between the transition probabilities is not as great as may be expected for an allowed and a forbidden transition. It should be realized, however, that we considered the isolated MoO_3(WO_3) complex by assuming C_{3v} symmetry. The actual site symmetry is only C_1 without any symmetry selection rules at all. Our results show, nevertheless, that C_{3v} symmetry is a reasonable first-order approximation.

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References

[1] F. A. KRÖGER, Some Aspects of the Luminescence of Solids, Elsevier Publ. Co., Amsterdam 1948.
[2] TH. P. J. BOTDEN, Philips Res. Rep. **6**, 425 (1951).
[3] G. B. BEARD, W. H. KELLEY, and M. L. MALLOY, J. appl. Phys. **33**, 144 (1962).
[4] W. VAN LOO, phys. stat. sol. (a) **27**, 565 (1975).
[5] W. VAN LOO, phys. stat. sol. (a) **28**, 227 (1975).
[6] M. J. TREADAWAY and R. C. POWELL, Phys. Rev. B **11**, 862 (1975).
[7] M. J. TREADAWAY and R. C. POWELL, J. chem. Phys. **61**, 4003 (1974).
[8] R. GRASSER, E. PITT, A. SCHARMANN, and G. ZIMMERER, phys. stat. sol. (b) **69**, 359 (1975).
[9] R. GRASSER and A. SCHARMANN, J. Lum. **12**, 473 (1976).
[10] G. BLASSE and W. J. SCHIPPER, phys. stat. sol. (a) **25**, K163 (1974).
[11] C. E. TYNER and H. G. DRICKAMER, J. chem. Phys. **67**, 4103 (1977).
[12] G. BLASSE and A. BRIL, J. Lum. **3**, 109 (1970).
[13] W. VAN LOO and D. J. WOLTERINK, Phys. Letters A **47**, 83 (1974).
[14] W. VAN LOO, J. Lum. **10**, 221 (1975).
[15] W. H. FONGER and C. W. STRUCK, J. Lum. **17**, 241 (1978).
[16] G. BLASSE, Philips Res. Rep. **23**, 344 (1968).
[17] C. J. BALLHAUSEN, Theor. chim. Acta (Berlin) **1**, 285 (1963).
[18] H. RONDE and G. BLASSE, J. inorg. nuclear Chem. **40**, 215 (1978).
[19] C. J. BALLHAUSEN and I. B. TRABJERG, Mol. Phys. **24**, 689 (1972).
[20] B. BUTOWIEZ, C.R. Acad. Sci. (France) **B267**, 1234 (1968).
[21] M. A. RIGDON and R. E. GRACE, J. Amer. Ceram. Soc. **56**, 475 (1973).
[22] K. NASSAU and G. M. LOIACONO, J. Phys. Chem. Solids **24**, 1503 (1963).
[23] J. A. GROENINK and H. BINSMA, J. Solid State Chem., accepted.

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