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Some New Observations on the Luminescence of $PbMoO_4$ and $PbWO_4$

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We report on the luminescence of doped and undoped $PbMoO_4$ and $PbWO_4$ single crystals; a red emission is found for the first time for $PbMoO_4$. The degree of polarization of both the emissions of $PbWO_4$ and of the shorter-wavelength emission of $PbMoO_4$ is measured. The shorter-wavelength emissions are assigned to the ${}^3T_1$–${}^1A_1$ transition in the tetrahedral $MoO_4{}^{2-}$($WO_4{}^{2-}$) group. It is assumed that the ${}^3T_1$ level is split due to spin-orbit coupling. The longer-wavelength emissions are assigned to a transition in a molybdate (tungstate) group lacking an oxygen ion, i.e., a MoO_3(WO_3) group.

1. Introduction

Since the early work of Kröger (*1*) the luminescence properties of lead molybdate ($PbMoO_4$) and lead tungstate ($PbWO_4$) have been considered exceptional compared to those of the various scheelite-structured molybdates and tungstates. The properties of these compounds have been reviewed by Van Loo (*2*) who also reported a large number of measurements on the luminescence of the lead scheelites (*3–6*). The green emission of $PbMoO_4$ and $PbWO_4$ was ascribed to the transfer of an electron occupying an orbital with mainly lead character to an empty orbital of an adjacent $XO_4{}^{2-}$ group with a predominantly *d* character. Van Loo also drew up a descriptive energy level scheme that consisted of two coupled four-level schemes and fitted the experimental results of his luminescence decay experiments.

Kröger (*1*) found two emission bands for $PbWO_4$, but only one for the alkaline-earth molybdates and tungstates and for lead molybdate. Recently an additional emission band at longer wavelengths has been found upon excitation into the tail of the absorption edge in the cases of $CaWO_4$ (*7, 8*), $CaMoO_4$ (*9*), $SrWO_4$ (*10*), and $BaWO_4$ (*10*). Bernhardt found a similar emission band in the case of $PbMoO_4$, but his description of this phenomenon is rather incomplete.

The present work has undertaken to elucidate the luminescence of $PbMoO_4$ and $PbWO_4$ further following the work done by Van Loo (*3-6*). We have studied samples doped with monovalent and trivalent cations. The polarization of the luminescence was measured and an additional emission was observed for $PbMoO_4$. These measurements show that the green emission of $PbMoO_4$ and $PbWO_4$ cannot be assigned to one and the same origin. We propose a model which, in our opinion, is valid for the alkaline-earth molybdates and tungstates as well as for the lead analogs.

2. Experimental

In nearly all cases the experiments were performed on polished or cleaved single-

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crystalline disks with an arbitrary crystallographic orientation. The preparation and the growth of the undoped and doped crystals have been described in a previous paper (*12*). The dopant concentrations in several crystals were analyzed by means of atomic absorption and emission spectrography. The results of the analysis are given in Table I.

Emission and excitation spectra as well as the temperature dependence of the emission intensity were recorded either on a Perkin–Elmer spectrofluorometer MPF-2A or MPF-3L as described in Ref. (*9*), or with the same experimental setup described by Van Loo (*3*).

The degree of polarization of the emission and absorption was measured in the following way. Crystals of undoped $PbMoO_4$ and $PbWO_4$ were aligned along the tetragonal *c*-axis. The polarization of the emission was measured by means of a Polaroid HN22 polarization filter and a single monochromator; we selected the excitation wavelength by combining an interference filter and an $NiSO_4$/UG5 filter which yields unpolarized radiation. The polarization of the excitation of the luminescence was recorded with the help of a Polacoat UV polarization filter and a double monochromator used in combination with a UG5 filter. A set of two Balzers interference filters and a UV cutoff filter were used to select the emission wavelength.

TABLE I

ANALYSIS OF THE CONCENTRATIONS FOR DELIBERATELY ADDED DOPANTS

	Concentration (mole %)	
	$PbMoO_4$	$PbWO_4$
Na	0.5	—
K	—	<0.1[a]
Bi	0.01	0.4
Y	0.7	0.77

[a] Detection limit.

The emission and excitation spectra were recorded with the electrical vector perpendicular and parallel to the *c*-axis. Corrections were made for the polarization of the monochromators, for the transmissions of the polarization filters and the $NiSO_4$/UG5 filter, for the relative intensity of the lamp, and for the sensitivity of the photomultiplier.

3. Results

3.1. $PbMoO_4$

All $PbMoO_4$ crystals exhibit the familiar green luminescence under excitation with radiation of energies above 3.40 eV. Measurements of the ionic conductivity, reported earlier (*12*), show that Na^+ and Y^{3+}, which are incorporated at Pb^{2+} lattice sites, increase or decrease the oxygen ion vacancy concentration, respectively. The incorporation of Na^+ and Y^{3+} did not influence the characteristics of the green emission. $PbMoO_4$–Na also shows a deep-red emission band when excited in an excitation band which peaks at 2.85 eV. This red emission was not observed in the case of the other $PbMoO_4$ samples.

Excitation spectra of the luminescence of an undoped and of an Na- and a Y-doped crystal are presented in Fig. 1. The emission spectra (Fig. 2) consist of a broad band, the half-width of which is about 0.46 eV in the case of the green emission and about 0.34 eV in the case of the red emission. In Fig. 2 the emission spectrum of the green luminescence is given for only one excitation energy. As was observed before by Van Loo (*3*), excitation with higher energies causes a slightly shifted spectrum. From this observation and from the fact that the slope of the emission band is asymmetric and the half-width and maximum of the emission band exhibit an unusual temperature dependence (*3*), we conclude, in agreement with Van Loo, that the green emission consists of at least two strongly overlapping bands. The red emis-

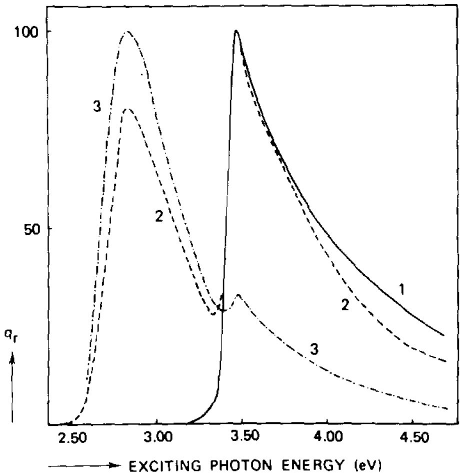

FIG. 1. Relative excitation spectra of the luminescence of several $PbMoO_4$ crystals at 77°K. q_r denotes the relative quantum output. (1) $PbMoO_4$, $PbMoO_4$-Na, $PbMoO_4$-Y, $E_{em} = 2.35$ eV. (2) $PbMoO_4$-Na, $E_em = 1.60$ eV. (3) $PbMoO_4$-Na, $E_{em} = 1.85$ eV.

sion is much weaker than the green emission. The maximum of the red emission band lies at about 1.65 eV, which is at a much lower energy than the orange emission band reported by Bernhardt (*11*).

As can be seen from Fig. 1, it is not possible to measure the excitation spectrum of the red emission without interference from the excitation band of the green emission; the reason is that the red emission is much weaker than the green emission. In the temperature region where the red emission occurs no effective energy transfer from the green to the red center is observed, since excitation in the green center (at energies above 3.40 eV) does not cause the red emission.

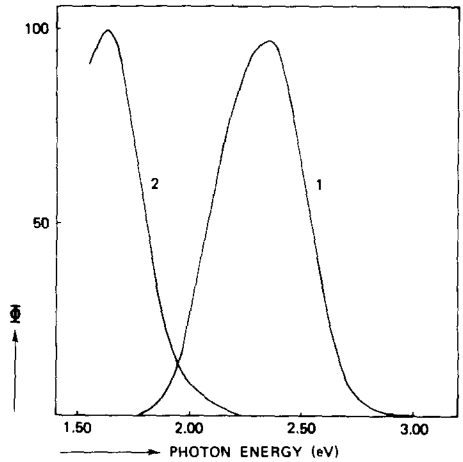

FIG. 2. Spectral energy distribution of the emission of several $PbMoO_4$ crystals at 4.2 K. Φ denotes the spectral radiant power per constant energy interval in arbitrary units. (1) $PbMoO_4$, $PbMoO_4$-Na, $PbMoO_4$-Y, $E_{exc} = 3.45$ eV. (2) $PbMoO_4$-Na, $E_{exc} = 2.85$ eV.

The present results suggest that the green emission, which has been reported before (*1, 3*), is the intrinsic molybdate emission. The red emission, which has not been reported before, must be due to a defect center, the concentration of which increases when the crystals are doped with monovalent ions (*9*). In view of its spectral position our red emission band must be different from the orange one reported by Bernhardt. The latter has not been observed by us.

Figure 3 shows excitation spectra of the luminescence of undoped $PbMoO_4$ for a cleaved and a polished crystal and for a powdered sample. The low-energy side of

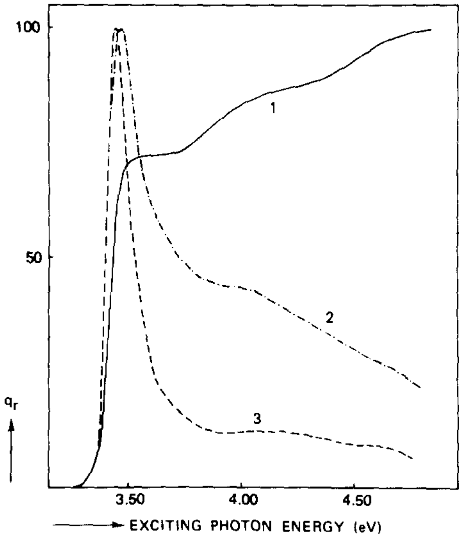

FIG. 3. Relative excitation spectra of the luminescence of several $PbMoO_4$ samples at 77°K. q_r denotes the relative quantum output. (1) Cleaved crystal. (2) Powdered crystal. (3) Polished crystal. $E_{em} = 2.35$ eV.

the spectra coincides with the optical absorption edge (Fig. 4). At higher energies (above 3.4 eV, where the optical density is very high, viz., of the order of 6–7), the efficiency of the luminescence depends on the nature of the sample. This suggests that the excitation energy is lost as a result of radiationless processes near the surface. It can be seen from Fig. 3 that the concentration of these killer sites increases in the sequence: cleaved crystal–powdered sample–polished crystal.

Polarized emission spectra of the green luminescence of $PbMoO_4$ were recorded at 77°K at several excitation energies. The ratio of the emission intensities of the two components varies with the excitation energy, viz., $I_\perp/I_\parallel = 0.75$, 0.85, and 1.08 for $E_{\text{exc}} = 3.44$, 3.85, and 4.13 eV, respectively. The degree of polarization of the emission, however, should not be affected by the energy of excitation for two reasons. In the first place, no difference in peak position and half-width was observed for the two components of the emission, perpendicular and parallel to the c-axis. From this we conclude that the same emission is measured in both cases. Second, the excitation and the emission occur via transitions to and from different levels (*4*). We believe, therefore, that the measured polarization of the emission is due to some trivial effect, the nature of which is still unclear. We have, therefore, no firm indication that the green emission of $PbMoO_4$ is polarized. This is in contradiction with the model evaluated by Van Loo, which predicts that the green emission will be polarized in the xy plane.

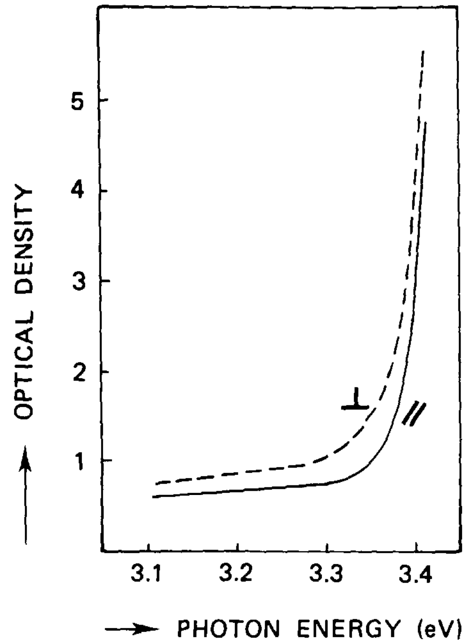

FIG. 4. Optical absorption spectra of $PbMoO_4$ at 77°K.

The temperature dependence of the luminescence intensity was measured for both emissions of $PbMoO_4$. Results are presented in Fig. 5.

3.2. $PbWO_4$

In the case of $PbWO_4$, the situation is more complicated. We found, as reported earlier (*1, 3*), two emission and two excitation bands. In contrast to $PbMoO_4$, the two emission bands in $PbWO_4$ overlap considerably.

In a previous paper (*12*) we concluded from measurements of the ionic conductivity that K^+ is incorporated at Pb^{2+} sites, while Y^{3+} is introduced at W^{6+} sites. In both cases, this leads to an increase in the concentration of the oxygen ion vacancies. The intro-

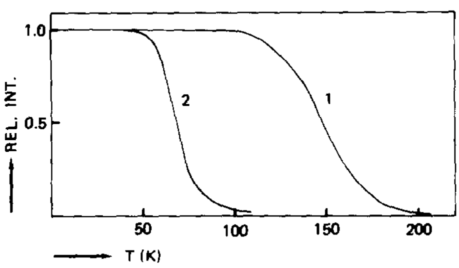

FIG. 5. Temperature dependence of the emission intensity of the green and red emission of $PbMoO_4$–Na. (1) Green emission, $E_{\text{exc}} = 3.45$ eV. (2) Red emission, $E_{\text{exc}} = 2.85$ eV.

duction of K^+ and Y^{3+} did not greatly affect the position of half-width of the emission bands or the intensity ratio of the blue and the green emission. In the case of $PbWO_4$-Y, however, the excitation band of the green emission peaks at somewhat lower energy and has a larger half-width.

The oxygen ion vacancy concentration is decreased by the incorporation of Bi^{3+} at Pb^{2+} sites (*12*). The optical absorption by Bi^{3+}, however, prevents conclusions about the relative intensities of the blue and the green emissions from being drawn from the excitation and emission spectra of $PbWO_4$-Bi. In contrast to $PbMoO_4$, $CaMoO_4$, and $CaWO_4$ (*9*), it is not possible in the case of $PbWO_4$ to draw conclusions, from the doping experiments only, about the nature of the center responsible for the green emission.

Excitation spectra of the blue and the green luminescence are presented in Figs. 6 and 7, respectively. In both of them the excitation spectra shift to lower energies at higher temperatures. This is due to a shift of the optical absorption edge, viz., from 4.09 eV at 4.2°K to 3.91 eV at 266°K (*3*). At room temperature, where the emissions are almost entirely quenched, the green and the blue emission cannot be excited separately: the excitation spectrum of the emission at 2.40 eV (green emission) coincides with that of the emission at 3.10 eV (blue emission). The emission spectrum at room temperature shows only the green emission band, irrespective of the excitation energy. This points to energy transfer from the blue-emitting centers to the green-emitting centers. In order to determine whether the quenching of the blue emission of $PbWO_4$ is due to thermal quenching via nonradiative processes within the blue-emitting center, or to concentration quenching via energy migration along the blue center subsystem, we measured the temperature dependence of the blue emission of the system $Ca_{1-x}Pb_xWO_4$, in which x varies from 0 to 0.2. The results are presented in Fig. 8. This figure shows dramatically the well-known enormous increase in the thermal quenching temperature of the blue tungstate emission

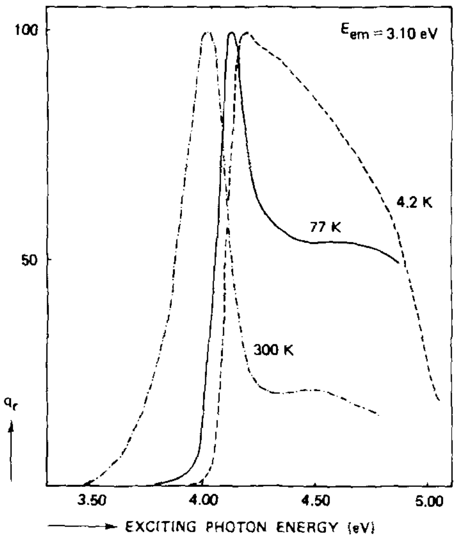

FIG. 6. Relative excitation spectra of the blue emission of $PbWO_4$ at several temperatures.

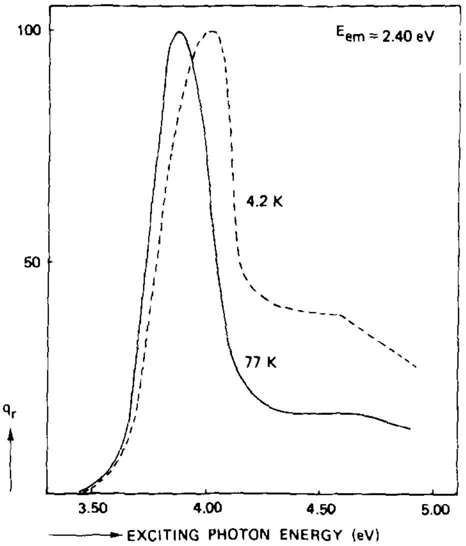

FIG. 7. Relative excitation spectra of the green luminescence of $PbWO_4$ at several temperatures.

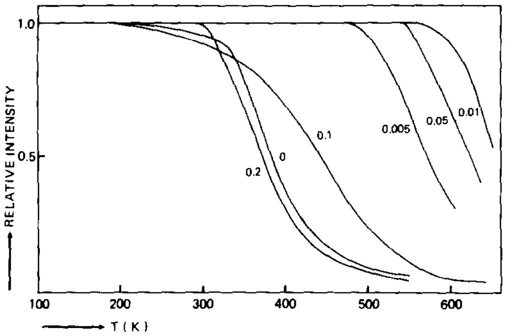

FIG. 8. Temperature dependence of the intensity of the blue emission of $Ca_{1-x}Pb_xWO_4$ for several values of x.

upon the addition of lead (*1*). These effects must be due to the electron configuration of the Pb^{2+} ion, since we did not observe such changes when small amounts of calcium were replaced by barium.

We also recorded the polarization of the absorption and emission spectra of $PbWO_4$. The green emission of $PbWO_4$ is strongly polarized, in striking contrast to the green emission of $PbMoO_4$. The polarization is temperature dependent: at 77°K the ratio of the intensities of the components perpendicular and parallel to the c-axis is about 0.55 ($I_\perp/I_\parallel$), while at 4.2°K this ratio is about 0.85. The polarization of the green emission of $PbWO_4$ is not dependent on the energy of excitation (excitation at 3.80 and 4.0 eV yields the same degree of polarization) although it was in the case of $PbMoO_4$. Although it was difficult to measure the degree of polarization of the blue emission, we could not find any indication of polarization within the experimental accuracy.

The absorption spectrum (Fig. 9) shows that the component perpendicular to the c-axis is absorbed more strongly in the region where the green luminescence is excited. This can also be seen in the excitation spectrum of the green emission (Fig. 10). In the excitation spectra the ratio between the two components was independent of temperature.

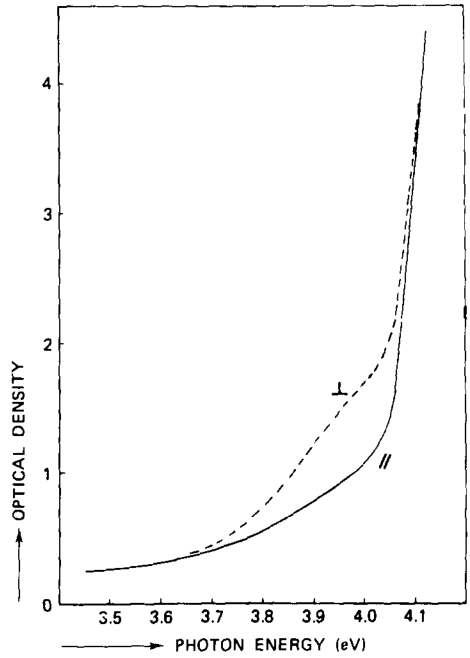

FIG. 9. Optical absorption spectra of $PbWO_4$ at 77°K.

4. Discussion

4.1. $PbMoO_4$

4.1.1. *The Nature of the Red Emission*

The luminescence of $PbMoO_4$ shows similarities with the luminescence of $CaMoO_4$, the nature of which is discussed

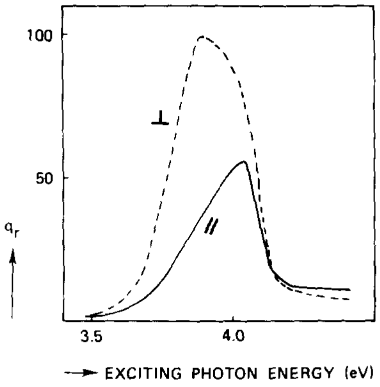

FIG. 10. Relative excitation spectra of the green emission of $PbWO_4$ at 77°K. $E_{em} = 2.40$ eV.

elsewhere (*9*). Two emission bands are observed in both compounds. Doping of $CaMoO_4$ with Na^+ increased the intensity of the longer-wavelength emission. This was also observed in the case of $PbMoO_4$. As with $CaMoO_4$, this points to luminescence from a center associated with an oxygen ion vacancy. It seems obvious, therefore, to ascribe the red emission in $PbMoO_4$–Na also to transitions in a MoO_3 group.

The excitation spectrum of the red luminescence of $PbMoO_4$ almost coincides with the absorption band which causes the yellow coloration of most crystals (*13*). This suggests that the color center is essentially the same as the red-emitting center. Several authors have disagreed about the nature of this color center. The coloration has been ascribed to deviations from stoichiometry or molecularity (*13–15*) or to presence of impurities (*11, 16*). Van Loo (*13*) and Bernhardt (*11*) both ascribe the coloration to the presence of oxygen ion vacancies which are associated either with one or two electrons (*13*) or with Mn^{3+} at Pb^{2+} lattice sites (*11*), respectively.

We agree with Van Loo and Bernhardt that oxygen ion vacancies influence the coloration, but the present measurements do not allow further conclusions to be drawn about the constitution of the color center.

4.1.2. *The Nature of the Green Emission*

The nature of the shorter-wavelength emission of $CaMoO_4$ is discussed in another paper (*9*). We assigned the emission to a transition from the crystal-field split $^3T_1$ state of the MoO_4^{2-} group to the ground state. In this model we did not take spin-orbit coupling into account. We suppose, as did Van Loo (*4*), that in $PbMoO_4$, too, the shorter-wavelength (green) emission is an intrinsic emission. In the case of the lead scheelites, however, one has to take the role of the lead ion into account. The oxygen orbitals of the molybdate group will probably be strongly mixed with the antibonding 6*s* orbitals of the Pb^{2+} ions (*4, 17*). The influence of this mixing becomes apparent from the smaller Stokes shift and the lower energy of the maxima of the emission and especially the excitation bands in $PbMoO_4$ and $PbWO_4$, compared to the alkaline-earth molybdates and tungstates.

Until now the crystal field has been considered to be responsible for the splitting of the $^3T_1$ state of the MoO_4^{2-} group. The model evaluated by Van Loo (*4*) for $PbMoO_4$ predicts that there will be polarized emission and a splitting of about 100 cm^{-1} of the first excited state. This seems rather high compared to the crystal-field splitting of about 4.5 cm^{-1} of the $^3T_1$ state in $CaMoO_4$ (*9*), of a few wavenumbers in the vanadates, and compared to the splitting of less than 10 cm^{-1} of the $^1T_1$ state in $LiClO_4 \cdot 3H_2O/LiMnO_4 \cdot 3H_2O$ (*19*) and of 6 cm^{-1} in the case of K_2CrO_4 (*20*). Further, we did not observe the predicted polarization of the emission. For these reasons we conclude that Van Loo (*4*) overestimated the effect of the crystal field.

Nevertheless, the temperature dependence of the decay time of the green emission of $PbMoO_4$ (*5, 6*) can only be explained by a four-level energy scheme. We evaluated such an energy level scheme in which spin-orbit coupling, due to the presence of the lead ions, lifts the degeneracy of the emitting $^3T_1$ state.

In T_d symmetry, the ground state of the molybdate group is $^1A_1$, while the first excited configuration consists of four states probably ordered thus: $^3T_1 \approx {}^3T_2 < {}^1T_1 < {}^1T_2$ (*21*). As in the case of $CaMoO_4$ (*9*), we assume that the $^3T_1$ state will be the lowest one. If we take spin-orbit coupling into account, the emitting $^3T_1$ state splits into four levels, viz., A_2, E, T_1, and T_2. The ground state is an A_1 state. The transitions from A_2, E, and T_1 to A_1 are orbitally forbidden, while $T_2 \rightarrow A_1$ is orbitally allowed as an electric dipole transition. This scheme makes it possible to explain both the temperature dependence of the decay time and the absence of polarization of the emission. One of the levels from which the transition to the ground state is forbidden will be the lowest level. The T_2 level lies a few wavenumbers above this level. This configuration yields the sharp decrease in the decay time with increasing temperature at very low temperatures. The remaining two levels lie above T_2. When these are thermally populated at higher temperatures there is an increase in the total decay time with increasing temperature if p_{34} and $p_{43} > p_{31} > p_{41}$ (Fig. 11). In the case of $PbMoO_4$ ε was found to be about 60 cm^{-1} (*5*). This means that the splitting of the $^3T_1$ state due to spin-orbit coupling is some 100 cm^{-1} in the case of $PbMoO_4$. This is in fact much larger than the crystal-field splitting of this state reported for $CaMoO_4$ (4.5 cm^{-1}, Ref. (*9*)).

The luminescence decay of $PbMoO_4$ was found to have two components (*5*). Van Loo (*4*) could explain this phenomenon by assuming that a hyperfine interaction is induced by the presence of ^{207}Pb (natural abundance 22.6%, nuclear spin $\frac{1}{2}$). This hyperfine interaction increases the energy separation between the two lowest levels, giving rise to a longer total decay time. This model holds also for the energy level scheme given above.

In our model, the emission originates from the T_2 level at all temperatures, and no polarization of the emission is expected. It is, however, unlikely that noncubic crystal-field components are totally absent. Such a crystal-field component would lift the degeneracy of the T_2 level and cause polarized emission at very low temperatures.

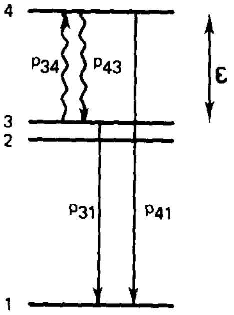

FIG. 11. Four-level energy scheme. Wavy arrows: nonradiative transitions; drawn arrows: radiative transitions; level 3: T_2 level; level 4; stands for the two upper levels.

We shall now compare these results with those reported for other molybdates, tungstates, and vanadates. The decay characteristics of the different vanadates (*18*) and $CaMoO_4$ (*9*) could be explained if a site symmetry of the tetrahedral group lower than T_d was taken into account. This symmetry lowering causes the $^3T_1$ state to split into two or three levels, separated by a few wavenumbers. For the tungstate luminescence, however, the situation is more complicated. The temperature dependence of the decay time of $CaWO_4$ (*22*) shows a great resemblance at low temperatures to that of $CdWO_4$ (*22*) and Ba_2CaWO_6 (*23*), viz., there is a sharp decrease in the decay time at increasing temperatures. This temperature dependence can be explained in the usual way by a three-level scheme in which the lowest level above the ground state acts as an optical trap. The energy separation between the emitting level and the optical trap level appears to be of the order of 20 cm^{-1} for $CaWO_4$, $CdWO_4$, as well as Ba_2CaWO_6. These three compounds have a different crystal structure, and the tungstate ions have a different site symmetry. In fact, $CdWO_4$ and Ba_2CaWO_6 both contain tungstate octahedra. Further, the site symmetry of this octahedron in Ba_2CaWO_6 deviates only slightly from pure cubic symmetry. It seems unlikely that the constant energy separation of about 20 cm^{-1} for different site symmetries can be ascribed to crystal-field effects. This constant energy separation strongly suggests that spin-orbit coupling plays a dominant role in the splitting of the $^3T_1$ state of the tungstate group. We suppose, therefore, that in the case of the tungstate group the splitting of the $^3T_1$ state by spin-orbit coupling is larger than the splitting by the crystal field. In the case of the vanadates and $CaMoO_4$, the crystal-field effect is supposed to be the dominant one. This is not unreasonable, since spin-orbit coupling increases strongly in the sequence V, Mo, and W, whereas crystal-field effects will not vary very strongly.

In the case of $CaWO_4$, spin-orbit coupling produces the same levels as mentioned before for $PbMoO_4$. The decay characteristics show that in the case of $CaWO_4$ the separation between the lowest level and the emitting T_2 level is about 20 cm^{-1}. At higher temperatures no increase in the decay time is observed. This means that the other two levels must be situated at less than about 10 cm^{-1} above T_2. If they are, then no increase in the decay time at higher temperatures is expected. An energy level scheme explaining the results of the decay measurements of $CaWO_4$ is presented in Fig. 12. This figure also shows the energy level schemes constructed for the cases of $CaMoO_4$ and $PbMoO_4$.

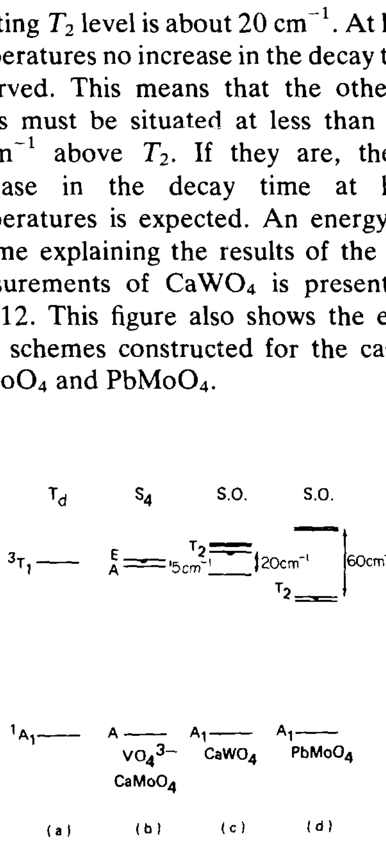

FIG. 12. Several possibilities for the splitting of the $^3T_1$ level in the case of crystal-field splitting or splitting due to spin-orbit (S.O.) coupling (schematical). The half circle indicates the emitting level. (a) Cubic symmetry without S.O. coupling. (b) S_4 symmetry without S.O. coupling (examples: $CaMoO_4$, vanadate group in certain lattices). (c) Cubic symmetry with S.O. coupling (level sequence as deduced from decay time measurements on $CaWO_4$). (d) as (c) (level sequence as deduced from decay time measurements on $PbMoO_4$).

4.1.3. The Temperature Dependence of the Emissions

The red emission of $PbMoO_4$ is quenched at a relatively low temperature, viz., $T_q \approx$ 68°K (T_q is the temperature at which the intensity of the emission has decreased to half of its original value). Since there are no possibilities for energy transfer, we assume that the quenching of the emission is due to nonradiative transitions in the center.

The red emission is completely quenched before the intensity of the green emission starts to decrease (see Fig. 5). Kröger (*24*) performed quenching experiments on the system $Ca_{1-x}Pb_xMoO_4$ ($0 \leq x \leq 1$). He found that for $x > 0.25$ the quenching temperature (T_q) of the green emission decreases and approaches gradually that of pure $PbMoO_4$. This suggests quenching due to energy transfer, whereby the excitation energy is finally lost at killer sites. This idea is supported by measurements by Botden (*25*) on the temperature dependence of the quantum efficiency of the molybdate and the Sm^{3+} emission of the system $Ca_{1-x}Pb_xMoO_4$–Sm^{3+} ($0.25 \leq x \leq 0.75$). He observed that the Sm^{3+} emission starts to increase with increasing temperatures in the quenching region of the molybdate emission; this is in contradiction to the situation in $CaMoO_4$ itself (compare the discussion in Ref. (*9*)). We conclude, therefore, that the green emission of $PbMoO_4$ is quenched due to energy transfer through the lattice and that this process starts at about 100°K. We cannot be certain whether the excitation energy is finally lost at MoO_3 groups or at other killer sites, since the luminescence of the MoO_3 group is quenched completely at 100°K.

The measurements of Kröger (*24*) also show that at low lead concentrations ($x <$ 0.25) the quenching temperature (T_q) of the green emission excited at 3.40 eV (the $PbMoO_4$ emission) is much higher than that of the emission excited at 4.93 eV (the pure $CaMoO_4$ emission). In this concentration region concentration quenching does not occur. Obviously the quenching temperature of the green $PbMoO_4$ emission is at a temperature higher than that of the $CaMoO_4$ emission. This is, however, not surprising in view of the much smaller Stokes shift in the case of $PbMoO_4$, viz., about 1.1 eV for the green emission of $PbMoO_4$ compared to about 2.2 eV for the green emission of $CaMoO_4$. The smaller Stokes shift should correspond to a smaller parabola offset in the configurational coordinate system. This, in turn, is in line with the smaller change in the bonding character due to the antibonding character of the s^2 configuration of the Pb^{2+} ions.

4.2 $PbWO_4$

4.2.1. The Nature of the Green Emission

We observed, as did Kröger (*1*) and Van Loo (*3*) earlier, two emissions in $PbWO_4$, viz., one emission band in the blue and another in the green spectral region. On account of the similar decay characteristics of the green emissions of $PbMoO_4$ and $PbWO_4$, Van Loo (*4*) concluded that these two emissions originated from the same kind of center. We found, however, the degree of polarization of these emissions to be different: the green emission of $PbMoO_4$ is almost unpolarized, while the green emission of $PbWO_4$ is strongly polarized. The excitation spectra of both emissions are also very different. The green emission of $PbMoO_4$ is excited at energies above the optical band edge, whereas the green emission of $PbWO_4$ is excited in a band at energies below the optical band edge.

In view of the similarity between the luminescence of $PbMoO_4$, $PbWO_4$, $CaMoO_4$, and $CaWO_4$, viz., the presence of two emissions in all compounds, we suppose that the green emission in $PbWO_4$ is also due to transitions in a center associated with an oxygen ion vacancy, i.e., a WO_3 group. In the case of $PbWO_4$, however, the situation is different. The green emission of $PbWO_4$ is not quenched at a lower temperature than the shorter-wavelength emission, as it is in the case of the longer-wavelength emission of $PbMoO_4$, $CaMoO_4$, and $CaWO_4$ (*3*). Furthermore, no noticeable difference was observed between the doped and the undoped crystals.

The measurements of the ionic conductivity reported in Ref. (*12*) show that in undoped $PbWO_4$ extrinsic conductivity is present in the whole temperature region measured, whereas in the case of $PbMoO_4$ at higher tempeatures intrinsic conductivity is observed. From this one might conclude that in $PbWO_4$ the concentration of the mobile defects, i.e., the oxygen ion vacancies, is higher than in $PbMoO_4$. Furthermore, doping with K^+ did not greatly increase that concentration, whereas the introduction of Y^{3+} was found to increase the oxygen ion vacancy concentration. In the latter case the oxygen ion vacancies are associated with Y^{3+} ions. This implies that the concentration of WO_3 groups is not enhanced by doping with Y^{3+}. This may explain why the green emission of $PbWO_4$ is present at approximately the same relative intensity in both the doped and the undoped crystals, and why it is much more pronounced than the long-wavelength emission in the other scheelites.

Evaluation of a descriptive energy level scheme for the observed temperature dependence of the decay time is not very meaningful, since one has to take into account not only a strong spin-orbit coupling (due to Pb^{2+} as well as W^{6+}), but also a strong crystal field (in the trigonal WO_3 group). The latter is necessary to explain the polarization of the green emission. Let us suppose, for instance, that the emission of the trigonal WO_3 group is polarized along its trigonal axis. The trigonal axis is oriented along the body diagonals of the cube around the original WO_4^{2-} tetrahedron (with the oxygen ions on four of the corners of the cube, see Fig. 13). The tetragonal c-axis of the crystal is parallel to the z-axis of these cubes. Since

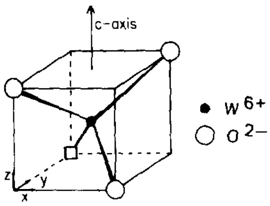

FIG. 13. The position of a WO_3 group in the lattice, in the absence of relaxation.

the sum of the components of the electrical vector parallel to the c-axis differs from the sum of the components perpendicular to the c-axis, we should observe polarized emission under our experimental conditions. More experiments, for instance, measurements on crystals oriented in all three directions and measurements of the azimuthal dependence of the polarization, are necessary to obtain a better description of the structure and polarization characteristics of the WO_3 center.

In Section 4.1.1 we showed that the excitation spectrum of the red emission of $PbMoO_4$ coincides with the absorption band which causes the yellow coloration. Crystals of $PbWO_4$ are also often yellowish in color, and show practically the same absorption band as crystals of $PbMoO_4$ (*13*). In the case of $PbWO_4$, however, the excitation band of the green emission does not coincide with the absorption band. This is in line with our conclusion in another paper (*12*) where we deduced from conductivity measurements that there are certain indications that the coloration in $PbMoO_4$ and in $PbWO_4$ is not due to centers with the same constitution. The present measurements, however, do not allow further conclusions to be drawn about the constitution of the color center in $PbWO_4$.

4.2.2. *The Nature of the Blue Emission*

Van Loo (*4*) assigned the blue emission to transitions is the isolated WO_4^{2-} groups. From the foregoing we conclude that the blue emission of $PbWO_4$ is due to transitions in the regular WO_4^{2-} group in which the lead ions play a role.

In Section 4.1.2 we showed that in the case of $PbMoO_4$ and several tungstates the role of spin-orbit coupling in lifting the degeneracy of the $^3T_1$ state is dominant We can be sure that this will be the case for $PbWO_4$ also. One should expect an even larger splitting due to spin-orbit coupling, since both lead and tungsten are very heavy atoms. Van Loo (*5, 6*) reported on the temperature dependence of the decay time of the blue emission. He did not observe an increase in the decay time at higher temperatures, such as he had observed with $PbMoO_4$. In the low-temperature region, the decrease of the decay time for increasing temperatures is not so pronounced as in the case of the green emission of $PbMoO_4$. This points to a larger energy separation between the two lowest levels. The larger splitting would also result in a larger separation between the T_2 level and the higher levels. The increase in the decay time is, therefore, expected at higher temperatures than in the case of $PbMoO_4$.

As will be shown in Section 4.2.3, the excition energy of the blue emission becomes mobile at moderate temperatures. Due to the occurrence of energy transfer the decay time of the system will decrease. This is another reason why it will be difficult to observe the increase of the decay time at higher temperatures for the blue emission of $PbWO_4$.

Finally we note that the absence of polarization of the blue emission fits the model, as explained above for $PbMoO_4$.

4.2.3. *The Temperature Dependence of the Emissions*

Kröger (*1*) measured the temperature dependence of the intensity of the blue emission of the system $Ca_{1-x}Pb_xWO_4$. His results show a great resemblance with our results for the same system, which are presented in Fig. 8. The increase in the quenching temperature for increasing lead concentrations (up to $T_q = 650°K$ for $x = 0.01$), points, as in the case of the green emission of $PbMoO_4$, to a very high thermal quenching of the blue emission (see Section 4.1.3). In the case of higher concentrations, the same explanation as mentioned in Section 4.1.3 is valid for the blue emission of $PbWO_4$. We therefore ascribe the quenching of the blue emission of $PbWO_4$ to energy transfer through the lattice.

The green emission is quenched in the same temperature region as the blue emission. At room temperature, at which both emissions are almost entirely quenched, excitation into the blue center causes only weak emission from the green center. This points to energy transfer from the blue center to the green center. However, at this temperature, most of the excitation energy is lost by nonradiative processes.

The temperature dependence of the green emission has not been investigated systematically, but in view of the fact that we are dealing with isolated WO_3 groups, we suppose that the quenching is due to nonradiative processes in the WO_3 group.

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