Two types of luminescence from Pb^{2+} in alkaline-earth fluorohalides with the PbFCl structure

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Abstract. The luminescence of the Pb^{2+} ion in the alkaline-earth fluorohalides with the PbFCl structure is reported. These systems show an ultraviolet emission at low temperatures, and a blue to yellowish emission at higher temperatures. This is ascribed to the (co-) existence of two different excited states, one typical for Pb^{2+}, and the other probably of charge-transfer nature.

1. Introduction

The luminescence of Pb^{2+} is quite diverse and depends strongly on the host lattice [1–4]. The energy level scheme of the free Pb^{2+} ion shows a ground state $^1S_0$ and triplet and singlet excited states $^3P_{0,1,2}$ and $^1P_1$. The possible excitation transitions are denoted by A, B, and C. Another excitation transition is possible when the s^2 ion is placed in a lattice; it is usually denoted as the D transition. Ranfagni *et al* [3] stated that, although the origin of the D band is not completely understood, a ligand-to-metal charge transfer seems to be the most plausible explanation.

Investigations over decades indicate a relation between the asymmetry of the s^2 ion in the lattice and the value of the Stokes shift of the emission [4–8]. The s^2 ion tends to occupy an off-centre position due to the lone pair of electrons. The excited state will be more symmetrical, which results in a large Stokes shift [9]. Recently, we reported on the Pb^{2+} luminescence in the alkaline-earth carbonates [10], a host lattice which offers the Pb^{2+} symmetrical surroundings. Surprisingly, an emission band with a small Stokes shift of the emission as well as an emission with a large Stokes shift have been found. These have been ascribed to a transition on the Pb^{2+} ion itself ($s^2 \leftrightarrow sp$), and a transition which is probably of charge-transfer nature, respectively. To investigate this luminescence further, we studied several alkaline-earth fluorohalides MFX (M = Ba, Sr, Ca and X = Br, Cl) with the PbFCl structure. Unlike in the alkaline-earth carbonates, this host lattice offers the Pb^{2+} ion very asymmetrical surroundings.

The alkaline-earth fluorohalides with the PbFCl (matlockite) structure crystallize in a tetragonal layered structure which consists of planes perpendicular to the c-axis [11]. The M ions are on one side coordinated by a plane of four fluorine ions and on the other side coordinated by five X ions of which one is on the c-axis out of the plane formed by the others. The site symmetry is C_{4v}. The MFX system seems to provide a suitable host lattice for luminescent materials, since several divalent ions substituted for the M ions luminesce in these systems [12–14].

2. Experimental details

Polycrystalline samples of the alkaline-earth fluorohalides were prepared by a solid-state reaction between the appropriate fluorides and bromides/chlorides. Pb^{2+} was incorporated using PbF_2. All of the starting materials were of high-purity quality. Since some of the *reactants are hygroscopic, a preheating step was used before preparation. Intimate mixtures of the reactants* were heated in air for five hours at 500 °C. All samples were found to be single-phase matlockite by x-ray powder diffraction (Cu Kα radiation)

Diffuse reflection spectra were measured with a Perkin–Elmer Lambda 7 spectrophotometer. Luminescence spectra were recorded with a Perkin–Elmer MPF-3L spectrofluorometer, equipped with a deuterium lamp and a liquid helium cryostat. Decay times were *measured using a Lambda Physik LPX 100 excimer laser (XeCl) as an excitation source.* The excimer laser pumps a tunable dye laser, Lambda Physik LPD 3000 (DMQ). A pulse generator triggered this laser and a Tektronix 2440 oscilloscope simultaneously.

Unactivated MFX compounds show luminescence also [15–19]. To exclude this luminescence from the luminescence of Pb^{2+} in the MFX compounds, an unactivated sample of BaFCl was prepared. Measurements with our set-up on this sample showed that the luminescence due to Pb^{2+} was dominant in the spectra.

3. Results

### 3.1. The luminescence of Pb^{2+} in the alkaline-earth fluorohalides

3.1.1. BaFCl:Pb^{2+}. The system BaFCl:Pb^{2+} was studied with different concentrations of Pb^{2+}. First the results on $Ba_{0.998}Pb_{0.002}FCl$ will be presented, then differences from those for 0.02%, 2% and 10% Pb^{2+} will be discussed.

The emission spectrum of $Ba_{0.998}Pb_{0.002}FCl$ at LHeT shows an ultraviolet (UV) band with maxima at 250 and 265 nm (see figure 1). The excitation spectra of the two bands are the same and consist also of two bands, with maxima at 205 and 220 nm. At about 70 K, the ultraviolet emission intensity decreases and a visible emission at about 450 nm emerges which does not quench up to room temperature. The excitation spectrum of this emission is the same as the excitation spectrum of the UV emission (within experimental error).

BaFCl activated with ten times less Pb^{2+} shows only one UV emission band with *the short-wavelength component at LHeT (see also table 1). Above 70 K, again the UV* emission intensity is quenched in favour of the visible emission. The excitation spectra of these emissions are the same as the spectra of $Ba_{0.998}Pb_{0.002}FCl$. A ten-times-higher concentration of Pb^{2+} ($Ba_{0.98}Pb_{0.02}FCl$) results in an intensity change of both maxima in the UV emission only. The longer-wavelength component is significantly more intense. For $Ba_{0.9}Pb_{0.1}FCl$ the UV emission band shows one maximum only, at 270 nm.

From the luminescence measurements for different concentrations of Pb^{2+} it is evident that the UV emission shifts to longer wavelengths when higher Pb^{2+} concentrations are involved. A similar phenomenon has been observed in the isoelectronic and isomorphous system $La_{1-x}Bi_xOCl$ [20]. In that previous work one emission was ascribed to isolated Bi^{3+} ions in LaOCl, and the other to a BiOCl-rich second phase. Since PbFCl shows its first absorption band at longer wavelength (245 nm) than observed here, we ascribe the longer-wavelength emission in $Ba_{1-x}Pb_xFCl$ to Pb^{2+} pairs. Detailed experiments were performed on the $x = 0.002$ sample only.

The double bands in the excitation spectrum have an energy difference which is too small to be due to excitations to the $^3P_1$ level (the A band) and the $^1P_1$ level (the C band).

BaFCl:Pb^{2+} (0.2%)
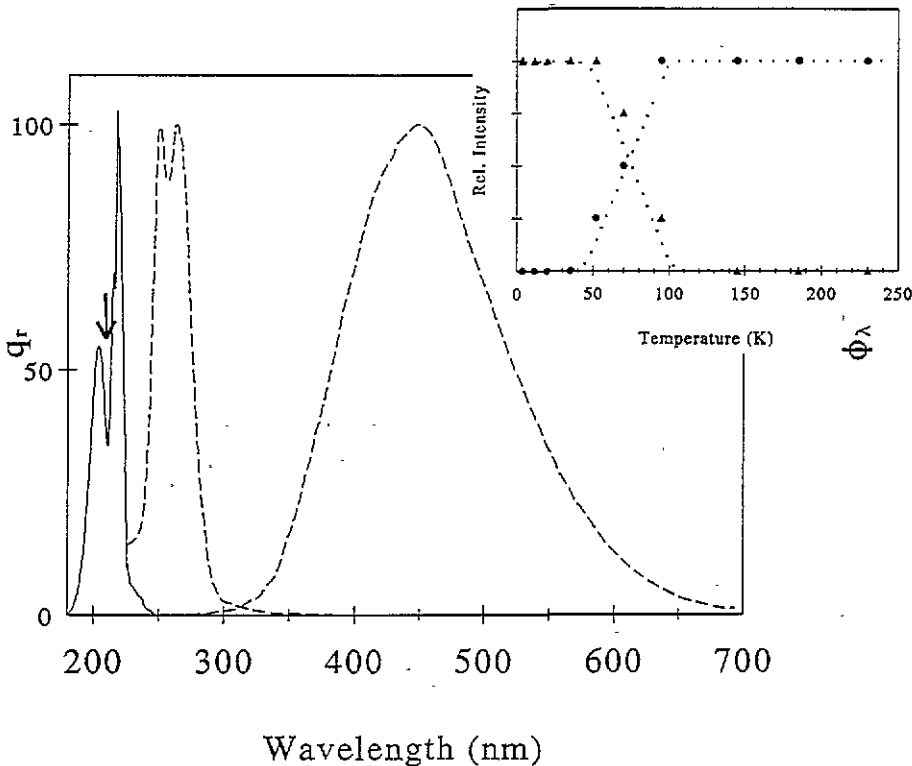
Figure 1. Excitation (the solid curve) and UV and visible emission (the dashed curves) spectra of the Ba$_{0.998}$Pb$_{0.002}$FCl luminescence at LHeT, LHeT and room temperature, respectively. The excitation wavelength is 220 nm; the monitored emission wavelength is 265 nm. Φ gives the radiant power per constant wavelength interval, and q_r gives the relative quantum output, both in arbitrary units. The inset shows the relative intensities of the UV emission (▲) and the visible emission (●) versus temperature.

On the other hand, this energy difference is too large to be due to the crystal-field splitting of the $^3P_1$ level. Most probably the splitting originates from the strong absorption of excitation radiation, so a dip instead of a maximum occurs at the absorption maximum in the spectrum. This has been observed earlier [10].

3.1.2. SrFCl:Pb^{2+}. In the emission spectrum of Sr$_{0.998}$Pb$_{0.002}$FCl at LHeT (figure 2), a UV emission band with a maximum at 235 nm is observed. At about 130 K, the UV emission intensity decreases and a visible emission emerges which is still present at room temperature. The UV emission can also be observed at room temperature, but with a lower emission intensity. The two emissions have the same excitation spectrum, with a maximum at 220 nm.

3.1.3. CaFCl:Pb^{2+}. For CaFCl:Pb^{2+} the luminescence of Pb^{2+} is not very strong, but is dominant in the spectra. Emission at low temperatures is observed, with a maximum at 240 nm. At a temperature which could not be established well—but that was higher than

Table 1. Emission maxima of the Pb^{2+} luminescence in MFX compounds with the PbFCl structure. The Stokes shift of the emission, and the temperature at which the UV emission intensity decreases and the visible emission intensity increases, are also presented.

| Composition	Emission maxima UVE (nm)	Emission maximum VE (nm)	$T_{UVE \rightarrow VE}$ (K)	Stokes shift (cm^{-1})
BaFCl:Pb (0.2%)	250, 265		70	7.000
		445		24.000
SrFCl:Pb (0.2%)	235		130	3.000
		400		20.000
CaFCl:Pb (0.2%)	235		> 130	2.000
		360		16.000
BaFBr:Pb (0.2%)	260, 290		—	8.000
		520		27.000
SrFBr:Pb (0.2%)	260, 300		—	8.000
		440		24.000

$SrFCl:Pb^{2+}$ (0.2%)
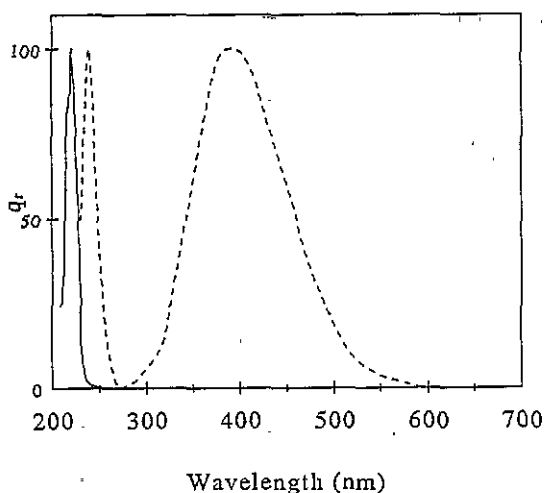
Wavelength (nm)

Figure 2. Excitation (the solid curve) and UV and visible emission (the dashed curves) spectra of the $Sr_{0.998}Pb_{0.002}FCl$ luminescence at LHeT, LHeT and room temperature, respectively. The excitation wavelength is 220 nm; the monitored emission wavelength is 380 nm. Φ gives the *radiant power per constant wavelength interval*, and q_r gives the *relative quantum output*, both in arbitrary units.

130 K—a weak visible emission can be observed. The UV emission is still intense at room temperature. The excitation maximum is at 235 nm for both emissions.

3.1.4. BaFBr:Pb^{2+}. In the emission spectrum of BaFBr:Pb^{2+} the UV and visible emissions are present over the whole temperature domain which is investigated (LHeT to room temperature); see figure 3. The excitation spectra of the two bands are alike, each with a maximum at 215 nm (see the arrow in figure 3)

BaFBr:Pb²⁺
20K
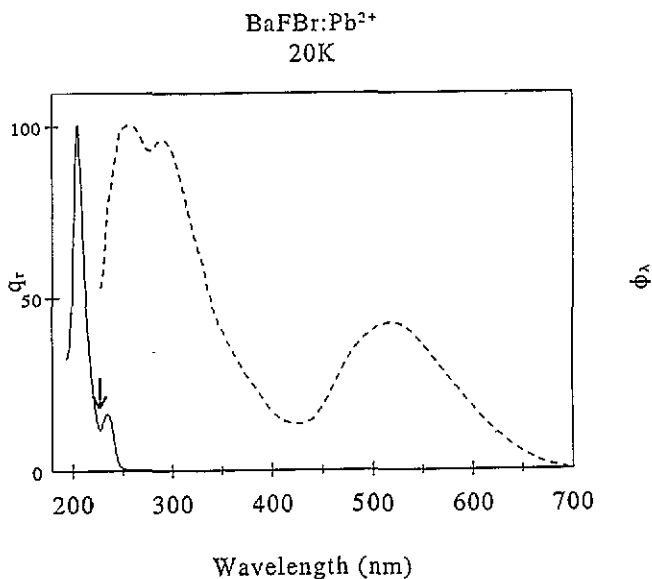
Wavelength (nm)

Figure 3. Excitation (the solid curve) and emission (the dashed curve) spectra of the $Ba_{0.998}Pb_{0.002}FBr$ luminescence at 20 K. The excitation wavelength is 210 nm; the monitored emission wavelength is 520 nm. Φ gives the radiant power per constant wavelength interval, and q_r gives the relative quantum output, both in arbitrary units.
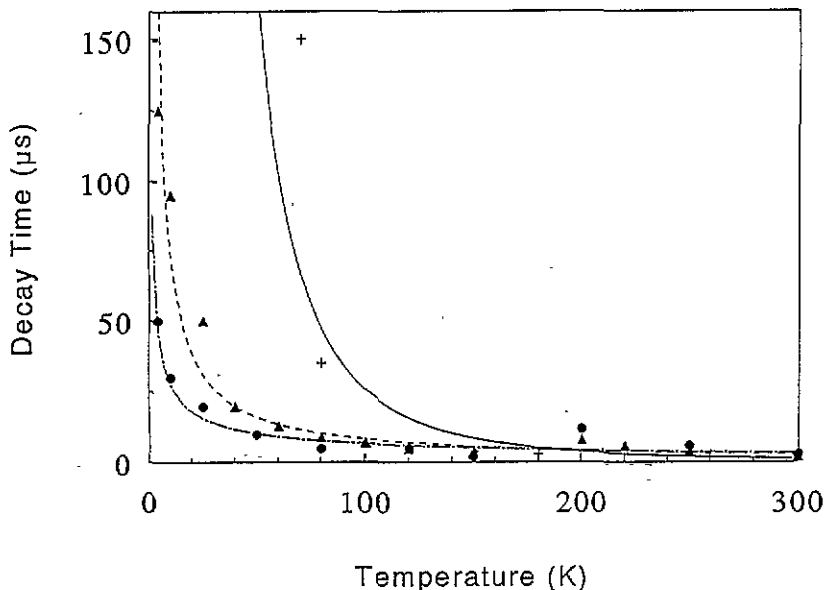
Temperature (K)

Figure 4. The decay time of the visible emission as a function of temperature of $Ba_{0.998}Pb_{0.002}FCl$ (+, monitored at 450 nm), $Ba_{0.998}Pb_{0.002}FBr$ (▲, monitored at 510 nm) and $Sr_{0.998}Pb_{0.002}FBr$ (■, monitored at 440 nm).

3.1.5. SrFBr:Pb²⁺. Like in BaFBr:Pb²⁺, the UV as well as the visible emission is present from LHeT up to room temperature, with maxima at 300 and 440 nm. The excitation spectra are the same, with a maximum at 215 nm. The spectral data are summarized in table 1.

3.2. Decay kinetics of the emission

Decay times were measured for the emissions of $Ba_{0.998}Pb_{0.002}FCl$, $Ba_{0.998}Pb_{0.002}FBr$ and $Sr_{0.998}Pb_{0.002}FBr$.

3.2.1. The ultraviolet emissions. For the UV emissions of BaFCl:Pb^{2+}, BaFBr:Pb^{2+} and SrFBr:Pb^{2+} decay times equal to or shorter than the pulse duration of the excimer laser (<15 ns) are obtained. In contrast to the fluorobromides, BaFCl:Pb^{2+} gives a slow component as well. This emission has been measured as a function of temperature. Up to 75 K, the decay time amounts to a millisecond; above 75 K it decreases exponentially. Because the UV emission is quenched at that temperature, no measurements could be performed at higher temperatures.

3.2.2. The visible emissions. The temperature dependence of the decay time of the visible emission of BaFCl:Pb^{2+}, BaFBr:Pb^{2+} and SrFBr:Pb^{2+} is presented in figure 4.
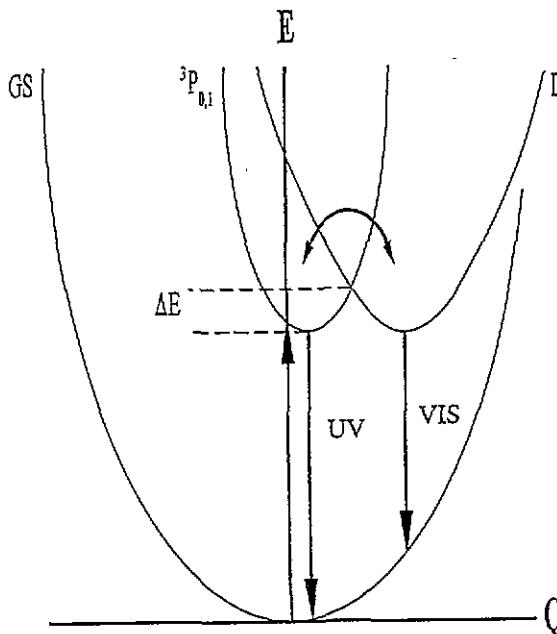

Figure 5. The configuration coordinate model describing the ground state and two excited states of Pb^{2+}. See also the text.

4. Discussion

4.1. The luminescence of Pb^{2+} in the alkaline-earth fluorohalides

Since the UV emission intensity of BaFCl:Pb^{2+} is quenched in favour of the visible emission intensity above 70 K, and the two emissions have the same excitation spectrum, the excited states from which these emissions originate must be related. However, the different decay times indicate different excited states. This behaviour has been observed before, for example for the alkaline-earth carbonates [10]. In that work, a model was proposed which is also

valid in the present case. The UV emission is due to a transition on the Pb^{2+} ion, namely $^3P_{0,1} \rightarrow {}^1S_0$. The visible emission originates from a higher level, the so-called D level, which is probably of charge-transfer nature. Figure 5 illustrates the model of two emitting states within the configurational coordinate diagram. One should bear in mind that this is a very simplified and limited model. For example, it cannot be excluded that the minima of the excited states are on different sides of $Q = 0$. Excitation into the A band yields UV emission, but on passing the energy barrier to the D band by thermal activation above 70 K, visible emission can also be obtained. The occurrence of this D-band emission depends on the position of the D level relative to the position of the A level. This seems to depend on the host lattice.

In SrFCl:Pb^{2+}, the same behaviour is observed, but the temperature at which the visible emission appears is higher. In CaFCl:Pb^{2+}, this temperature is even higher, and the visible emission intensity remains weak. Obviously, the energy barrier separating the A and the D states becomes higher when smaller cations are involved. A relationship between $T_{UV \rightarrow VE}$ and the cationic radius has also been observed in the case of the alkaline-earth carbonate system [10]. Obviously, the D level lies lower if the s^2 ion occupies a larger site.

In the alkaline-earth fluorobromides (BaFBr:Pb^{2+} and SrFBr:Pb^{2+}) both emissions can be observed even at LHeT. Obviously, the energy barrier between the two states has decreased. Since the electronegativity of one of the ligands is found to have decreased when we compare this system with the alkaline-earth fluorochlorides, the positions of the D band and the energy barrier will be lowered.

The presence of a UV emission at low temperatures and a visible emission at higher temperatures has been observed before. For the isostructural and isoelectronic systems LaOX (X = Br$^-$, Cl$^-$) doped with Bi^{3+} (6s^2) the same behaviour has been observed [20, 21]. The similarity in luminescence to the alkaline-earth fluorohalides is striking. In LaOCl:Bi^{3+}, in contrast to LaOBr:Bi^{3+}, no visible emission was observed. This illustrates the influence of the electronegativity of the ligands in the same way as is observed for the alkaline-earth fluorohalides. Other nice examples have been published recently on the luminescence of Pb^{2+} in CdCl$_2$ [22] and CdI$_2$ [23]; the present work runs parallel with these cases.

However, in several alkali halide systems doped with s^2 ions the two emissions are ascribed to a transition from the A_T and A_X minima on the adiabatic potential energy surface due to the dynamical Jahn–Teller effect [3, 24, 25]. This effect requires symmetrical surroundings for the s^2 ion. But on comparing for example the luminescence of BaCl$_2$:Pb^{2+} [26] and SrCl$_2$:Pb^{2+} [27] with the luminescence of s^2-doped alkali halide systems, it becomes obvious that the luminescences are similar, although BaCl$_2$ does not offer a symmetrical environment for Pb^{2+}. Moreover, the spin–orbit coupling is considerable for 6s^2 ions, so the dynamical Jahn–Teller effect may play a minor role. It can, therefore, not be excluded that the same explanation as given for the alkaline-earth fluorohalides holds also for SrCl$_2$:Pb^{2+} and BaCl$_2$:Pb^{2+}.

4.2. Decay kinetics of the emission

The UV emission of BaFCl:Pb^{2+} consists of a slow and a fast component. When the $^3P_0$ and $^3P_1$ excited states are not in thermal equilibrium (the non-radiative transition probability of the $^3P_1 \rightarrow {}^3P_0$ transition being smaller than the radiative transition probability of the $^3P_1 \rightarrow {}^1S_0$ transition), decay from both the $^3P_1$ state and the $^3P_0$ state may occur [28]. Van der Steen and Dijcks [5] studied the decay behaviour of Bi^{3+} (6s^2) to investigate in which cases emission from the $^3P_1$ state, the $^3P_0$ state or both is favourable. Defining R as the ratio of the energy difference between $^3P_1$ and $^3P_0$ (ΔE) and the highest phonon

frequency of the lattice, it was shown that when $R \simeq 2$, only the slow $^3P_0$ decay is found, when $R \simeq 3$ both emissions are found and when $R \simeq 4$ only the fast $^3P_1$ decay is found. From the temperature-dependent decay measurements for $BaFCl:Pb^{2+}$, it is hard to make an estimation of the energy difference between the $^3P_1$ and $^3P_0$ levels because only a small temperature domain could be studied. A rough estimation yields about 500 cm^{-1}. The highest phonon frequency of the alkaline-earth fluorohalides is at about 300 cm^{-1} [29]. Since Van der Steen and Dijcks studied transitions with weak coupling, whereas the present case involves strong coupling, their results may not be completely transferable to our case. Nevertheless, they indicate that the different decays are due to emission from the $^3P_1$ and $^3P_0$ states. For the bromine compounds only the fast $^3P_1$ emission is observed.

Since the nature of the D state is unknown, no prediction of the decay time of the emission from this state can be made. In the isomorphous and isostructural $LaOBr:Bi^{3+}$ a comparable 'long' decay time has been observed for the UV and the visible emission, decreasing with temperature [21]. However, the fast decay component for the UV emission is not found. A fast decay for the UV emission and a slow one for the visible emission has also been found in $CdI_2:Pb^{2+}$ [23]. To find the origin of this behaviour, the decay kinetics of the UV and the visible emissions of several other compounds are now under investigation.

5. Conclusions

The luminescence of Pb^{2+} in the alkaline-earth fluorohalides originates from two types of excited state. The UV emission is ascribed to the $^3P_{0,1} \rightarrow {}^1S_0$ transition of Pb^{2+} (the so-called A transition). The visible emission is ascribed to a transition from a higher level, probably of charge-transfer nature (the so-called D transition). Among the factors which determine the position of the D state relative to the A state, the radius of the cation for which the Pb^{2+} is substituted and the electronegativity of the ligands seem to be important.

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