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Journal of Alloys and Compounds 300–301 (2000) 193–198

Journal of ALLOYS AND COMPOUNDS

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Spectroscopic properties of $SrZnCl_4$:M^{2+} and $BaZnCl_4$:M^{2+} (M=Eu, Sm, Tm)

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Abstract

The emission spectra of the divalent rare-earth ions Eu^{2+}, Sm^{2+} and Tm^{2+}, doped into the new compounds $SrZnCl_4$ and $BaZnCl_4$, are reported. Eu^{2+} and Tm^{2+} show broad $4f^{n-1}5d \rightarrow 4f^n$ emission. Due to the smaller crystal-field splitting, the emission bands for $BaZnCl_4$:M^{2+} are shifted to higher energies when compared to $SrZnCl_4$:M^{2+}. For $SrZnCl_4$:Sm^{2+} at 298 K broad $4f^55d \rightarrow 4f^6$ emission is observed, while at 20 K additional lines due to the $^5D_0 \rightarrow {}^7F_J$ transition appear. $BaZnCl_4$:Sm^{2+} shows only line spectra at low temperature. At 298 K a weak $d \rightarrow f$ transition is observed. The results are discussed and compared with the corresponding measurements of $SrCl_2$ and $BaCl_2$ doped with the divalent rare-earth ions.

Keywords: Divalent lanthanides; Spectroscopy; Luminescence; Europium; Samarium; Thalium

1. Introduction

The luminescence characteristics of divalent europium with the $4f^7$ ground state configuration have been investigated in many halides [1]. It was shown that at a strong crystal-field strength and a high degree of covalency of the host lattice, broad $4f^65d \rightarrow 4f^7(^8S)$ emission appears while in the other case narrow lines of $^6P_{7/2} \rightarrow {}^8S$ transitions are observed. $KMgF_3$:Eu^{2+} is the only example, that shows also emission lines from the next higher energetical level $^6I_{7/2}$ [2].

Investigations of Sm^{2+} doped in different host lattices are not so frequent [1]. In this case, the lowest excited ^5D_J level of the $4f^6$ configuration is at comparable or at lower energy than the $4f^55d$ potential even at relatively strong crystal-fields, so that in most cases at low temperature line emission is observed.

As far as we know the luminescence of Tm^{2+} was investigated in a few host lattices only, CaF_2 [3] and SrB_4O_7 [4], which are very suitable host lattices for divalent ions. The reason may be the difficulties in the preparation and the handling of Tm^{2+} due to its high reduction potential and the extreme oxygen and moisture sensitivity of Tm^{2+} compounds.

In this work, the recently prepared compounds $SrZnCl_4$ and $BaZnCl_4$ are doped with divalent rare-earth ions and the emission spectra are measured. These host lattices are excellent for a comparative investigation. First, it is possible to prepare large crystals of pure phases. The lattice site of the two cations differs, and only the site of the alkaline earth is occupied by the rare-earth ion. The M^{2+} sites in the Ba and Sr compound possess comparable coordination polyhedra which are only different with respect to their crystal-field splitting. The mean Sr^{2+}–Cl^- distance in $SrZnCl_4$ is very similar to that found in $SrCl_2$. In the latter, however, the M^{2+} point symmetry is higher, so the crystal-field splitting of the *d*-orbital is different in the two compounds.

2. Crystal structure

Recently, $SrZnCl_4$ and $BaZnCl_4$ were prepared for the first time [5]. The crystal structures are shown in Fig. 1. $SrZnCl_4$ (tetragonal, $I4_1/a$, $Z=4$, $a=650.40(7)$, $c=1437.0(2)$ pm) crystallizes with the scheelite ($CaWO_4$) type of structure [5], which frequently occurs with mono- and trivalent cations with $LiGdCl_4$ [6] as a prominent example. $BaZnCl_4$ (orthorhombic, *Pnna*, $Z=4$, $a=724.15(6)$, $b=986.2(2)$, $c=947.71(8)$ pm) belongs to the β-$GaCl_2$ type of structure [5].

The coordination polyhedra of the alkaline earth cations are shown in Fig. 2, for comparison those of the neat alkaline earth chlorides are added. In $SrZnCl_4$ Sr^{2+} is surrounded by eight Cl^- ions in the form of a trigon-

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0925-8388/00/$ – see front matter
PII: S0925-8388(99)00722-7

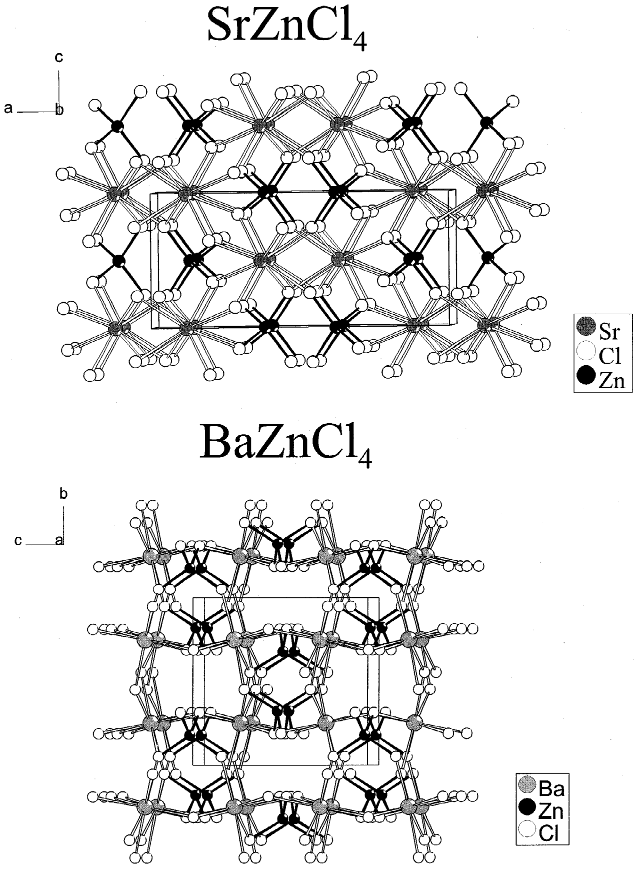

Fig. 1. Crystal structures of $SrZnCl_4$ (above) and $BaZnCl_4$ (below) [5].

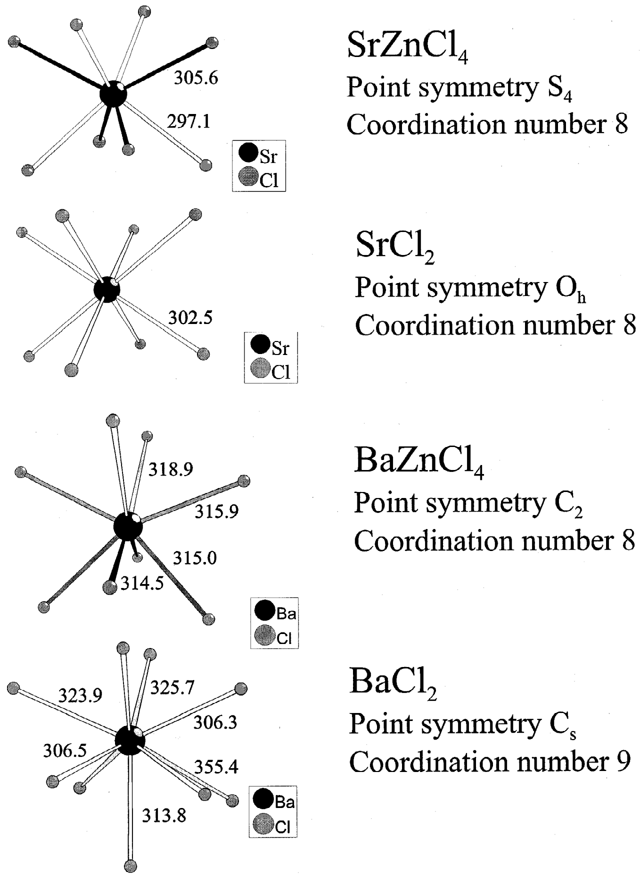

Fig. 2. Coordination polyhedra, point symmetries and coordination numbers of $SrZnCl_4$, $SrCl_2$, $BaZnCl_4$ and $BaCl_2$.

dodecahedron with two different Sr^{2+}–Cl^- distances. The point symmetry of the Sr^{2+} site is S_4. In $SrCl_2$ Sr^{2+} is again eightfold coordinated but with a regular cube as the coordination polyhedron (point group O_h) [7]. The Sr^{2+}–Cl^- distances in $SrCl_2$ are very close to the average distance Sr^{2+}–Cl^- in $SrZnCl_4$ so that the crystal-field strength is similar in both compounds.

The coordination polyhedron of Ba^{2+} in $BaZnCl_4$ is again a trigon-dodecahedron but Ba^{2+} is surrounded by eight Cl^- with four different distances. The point symmetry is C_2. Unfortunately, the coordination polyhedron of Ba^{2+} in $BaCl_2$ is not comparable; the coordination number (CN) is nine in this case with the very low point symmetry of C_s [8].

When doping alkaline earth lattices with divalent rare-earth ions, the radii of the ions have to be considered. Eu^{2+} which has a radius of 139 pm in compounds with a CN of eight [9,10] fits well the lattice site of Sr^{2+} (140 pm, CN=8) [9,10] but is a slightly smaller than Ba^{2+} (156 pm, CN=8) [9,10]. The same is true for Sm^{2+} (141 pm, CN=8), while the Tm^{2+} radius (123 pm, CN=8) [9,10] is significantly smaller. The second cation in the tetrachlorozincate, Zn^{2+}, occupies much smaller lattice sites: the radius of Zn^{2+} is only 74 pm for CN=4 [9,10]. So it can be assumed that the doped rare-earth cations M^{2+} occupy only the sites of the alkaline earth ions.

3. Experimental

3.1. Preparation

The dihalides of Eu^{2+}, Sm^{2+} and Tm^{2+} were prepared by reduction of the respective trihalides. For that purpose the trichlorides MCl_3 were synthesized following the ammonium chloride route [11]. $EuCl_2$ was obtained by reducing $EuCl_3$ in a hydrogen–argon stream at 500°C. $SmCl_2$ and $TmCl_2$ were prepared via synproportionation with the respective metals in a ratio of 2:1 at 750°C in tantalum containers. To obtain products of high purity, the dichlorides were sublimed in vacuo (10^{-6} mbar) at 850°C.

Large crystals of $SrZnCl_4$ and $BaZnCl_4$ were prepared from $ZnCl_2$ and the respective alkaline earth dichloride in a molar ratio of 1:1 using the Bridgman technique. As a dopant 0.05 mol% of the rare-earth dichloride MCl_2 was added. The reactions were carried out in silica (M=Eu, Sm) or tantalum (M=Tm) containers at 550°C. The samples are extremely moisture sensitive and must be handled under inert and anhydrous conditions. The purity of all products was checked by powder X-ray diffraction methods (Stoe and Cie., Stadi P). No phase transitions were detected in the range from 400 K to 140 K [5].

3.2. Spectroscopic measurements

Photoluminescence measurements of $SrZnCl_4:Eu^{2+}$ and $BaZnCl_4:Eu^{2+}$ were performed on a SPEX DM3000F spectrofluorometer equipped with 0.22 m SPEX 1680 double monochromators, a 450 W xenon lamp and a liquid helium flow cryostat (Oxford LF 205). The Sm^{2+} and Tm^{2+} doped samples were investigated using a frequency doubled Nd:YAG laser (Spectra Physics, GCR11) as an excitation source. Cooling down to 20 K was achieved by a closed cycle cryostat (Air Products Displex). The emission signal was focused on the entrance slit of a 0.27 m single monochromator (Spectroscopy Instruments). The signal of a photomultiplier (Hamamatsu, R2949) was preamplified (Stanford, SR445) and measured using a photon counting system (Stanford, SR400). All emission spectra were corrected for the photomultiplier sensitivity.

4. Results and discussion

4.1. $SrZnCl_4:Eu^{2+}$ and $BaZnCl_4:Eu^{2+}$

Under photoexcitation, the divalent europium doped in the tetrachlorozincate host lattices shows the violet emission typical for many Eu^{2+} doped chlorides in contrast to the line emission observed in many fluorides [1]. Fig. 3a shows the emission spectra of $SrZnCl_4:Eu^{2+}$ for 26 315 cm^{-1} excitation. The broad bands can be assigned to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+}. No fine structure is observed. The maxima of the emission bands are located at 24 845 cm^{-1} (4.2 K) with $\Delta_{1/2} = 675$ cm^{-1} (full width at half maximum; FWHM) and at 24 747 cm^{-1} (200 K) with $\Delta_{1/2} = 886$ cm^{-1}, showing a red shift of the maximum with increasing temperature. The fact that the bands show a smooth structure without any shoulder confirms that Eu^{2+} occupies only the alkaline earth sites.

The maxima of the emission bands of $SrCl_2:Eu^{2+}$ are at 24 630 cm^{-1} (78 K) and 24 390 cm^{-1} (293 K) [12]. This is a shift to lower energy compared with the spectra of $SrZnCl_4:Eu^{2+}$. Because the strengths of the two crystal-fields are similar due to the comparable ligand distances, this observation can be attributed to the higher point symmetry of the alkaline earth site. The splitting of the lowest lying d-orbitals due to the S_4 point symmetry in $SrZnCl_4$ is fourfold ($A_g + 2B_g + E_g$) while there is only a twofold splitting ($E_g + T_{2g}$) due to O_h symmetry in $SrCl_2$. This different splitting may be the reason for the emission band in $SrZnCl_4:Eu^{2+}$ being located at higher energy.

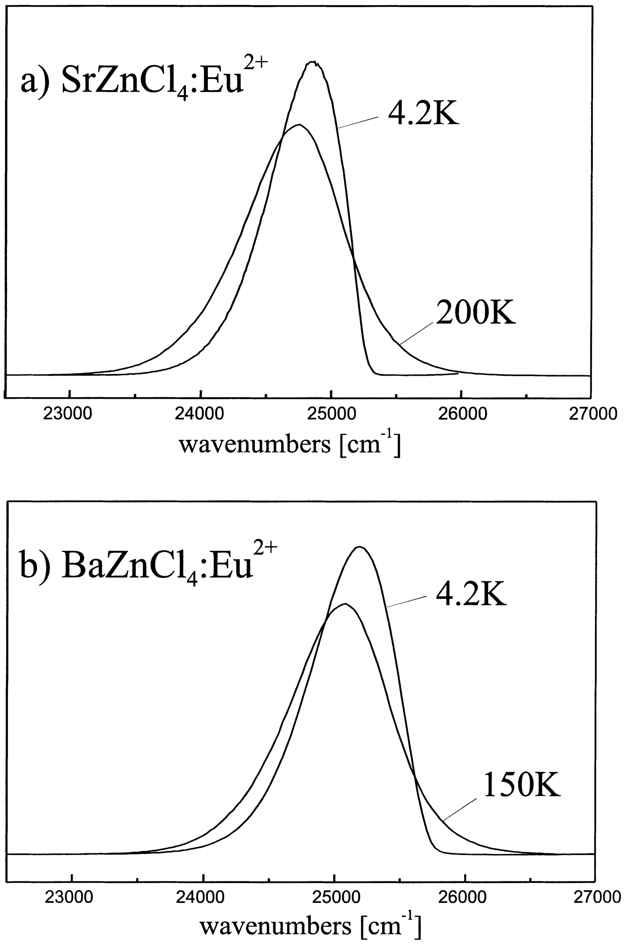

Fig. 3. (a) Emission spectra of the $4f^65d \rightarrow 4f^7$ transition of $SrZnCl_4:Eu^{2+}$ at different temperatures. Excitation wavenumber was $\lambda_{ex} = 26\,315$ cm^{-1}. (b) Emission spectra of the $4f^65d \rightarrow 4f^7$ transition of $BaZnCl_4:Eu^{2+}$ at different temperatures. Excitation wavenumber was $\lambda_{ex} = 27\,777$ cm^{-1}.

In Fig. 3b emission spectra of $BaZnCl_4:Eu^{2+}$ are depicted. The spectra show the same transition of Eu^{2+} at an excitation energy of 27 777 cm^{-1}. The position of the maxima is at 25 221 cm^{-1} (4.2 K) with $\Delta_{1/2} = 753$ cm^{-1} and 25 072 cm^{-1} (150 K) with $\Delta_{1/2} = 913$ cm^{-1}. Again, the band shifts towards lower energies with increasing temperature. The spectra are comparable to those of $SrZnCl_4:Eu^{2+}$. This is expected because both crystal structures are very similar. The blue shift in the spectra of the barium compounds can be explained by the larger radius of Ba^{2+} compared to Sr^{2+}. This results in a smaller crystal-field splitting for Eu^{2+} at the Ba^{2+} sites so that the lowest d-orbital is located at higher energy. The increasing FWHM in $BaZnCl_4:Eu^{2+}$ compared to $SrZnCl_4:Eu^{2+}$ is due to lower energies of the phonons to which the electronic states couple. The Eu^{2+}–Cl^- distances are larger in $BaZnCl_4$, which lowers the vibrational energy and results in a broadening of the potential curves.

The maxima for $BaCl_2$:Eu^{2+} are at similar positions: 25 125 cm^{-1} at 78 K and 25 062 cm^{-1} at 293 K [12]. In this case a detailed comparison is difficult because of the lower crystal-field strength due to larger Eu^{2+}–Cl^{-} distances, the lower point symmetry and the higher CN of the dichlorides (see Crystal structures).

4.2. $SrZnCl_4$:Sm^{2+} and $BaZnCl_4$:Sm^{2+}

The Sm^{2+} doped compounds show a different behavior. Fig. 4 depicts the emission spectra of $SrZnCl_4$:Sm^{2+} at 20 K and 298 K for an excitation energy of 18 796 cm^{-1}. At room temperature a broad band is observed which can be assigned to the $4f^5 5d \rightarrow 4f^6$ emission of Sm^{2+}. The maximum is located at 14 685 cm^{-1} with $\Delta_{1/2} = 1108$ cm^{-1}. At 20 K the $4f^5 5d \rightarrow 4f^6$ band with a maximum at 14 609 cm^{-1} ($\Delta_{1/2} = 801$ cm^{-1}) can be detected. Additionally, emission appears at low temperature which is due to luminescence from the $^5D_0$ state to the ^7F_J manifold (intraconfigurational $4f^6$ emission). The $^5D_0 \rightarrow {}^7F_0$ transition is located at 14 580 cm^{-1}, other positions are given in Table 1. Each line with $J = 1,2$ is split into several transitions due to the different crystal-field components of the S_4 symmetry. Only one crystal-field splitting component is observed for the $^5D_0 \rightarrow {}^7F_3$ emission.

Electric dipol as well as magnetic dipol selection rules predict that transitions with $J = 0 \rightarrow J = 0$ are strongly forbidden in S_4 point symmetry. Nevertheless, a weak $^5D_0 \rightarrow {}^7F_0$ emission line was observed in $SrZnCl_4$ at 20 K (Fig. 4) and can probably be attributed to J mixing of the $^5D_0$ and $^7F_0$ wave functions with mainly $^5D_2$ and $^7F_2$ by the crystal-field. The assumption that the occupation of sites with lower symmetry can cause this observation is improbable because the other $^5D_0 \rightarrow {}^7F_J$ emissions indicate S_4 symmetry. For comparison, in the spectra of the scheelite type $LiYF_4$ doped with Eu^{3+} which is also located at a S_4 site symmetry no $^5D_0 \leftrightarrow {}^7F_0$ transitions were observed [13].

Table 1
Fluorescence lines of $SrZnCl_4$:Sm^{2+} and $BaZnCl_4$:Sm^{2+} at 20 K

Assignment	$SrZnCl_4$:Sm^{2+} (cm^{-1})	$BaZnCl_4$:Sm^{2+} (cm^{-1})
$^5D_0 \rightarrow {}^7F_0$	14 580	14 567
$^5D_0 \rightarrow {}^7F_1$	14 282	14 306
	14 245	14 275
		14 245
$^5D_0 \rightarrow {}^7F_2$	13 751	13 803
	13 726	13 784
		13 746
		13 699
$^5D_0 \rightarrow {}^7F_3$	13 057	13 106
$^5D_0 \rightarrow {}^7F_4$		12 338
		12 315
		12 300
		12 285
		12 270

This temperature depended behavior can be explained as follows: The $d \rightarrow f$ emission is parity allowed and the transition probability is about five orders of magnitude higher than that of the $f \rightarrow f$ emission which is parity forbidden [14]. In $SrZnCl_4$:Sm^{2+} the $4f^5 5d$ potential is located at slightly higher energy than the $^5D_0$ state (Fig. 5). At high temperature the $4f^5 5d$ potential is thermally occupied and fast $d \rightarrow f$ emission will occur while at low temperature there is only a small degree of thermal occupation of the d state and additional $f \rightarrow f$ emission is observed.

Investigations on $SrCl_2$:Sm^{2+} show similar results [15]. At room temperature only a broad $d \rightarrow f$ emission band is observed, while at 4.2 K the behavior is different and only $f \rightarrow f$ transitions were detected. This means that the $4f^5 5d$ potential must be located at higher energy when compared to $SrZnCl_4$:Sm^{2+} so that there is no thermal occupation at low temperature. The maximum is at about 13 900 cm^{-1},

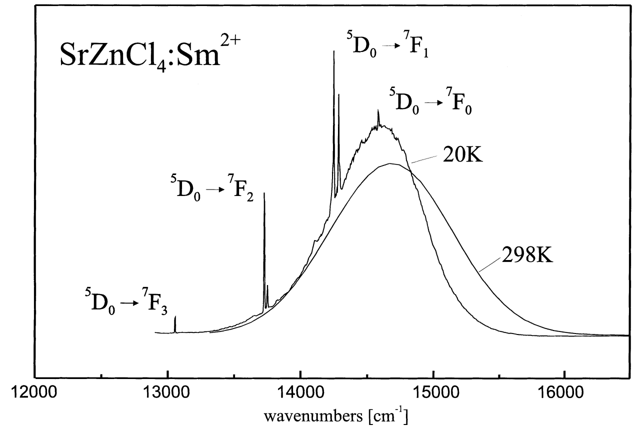

Fig. 4. Emission spectra of $SrZnCl_4$:Sm^{2+} at different temperatures. Excitation wavenumber was $\lambda_{ex} = 18\ 796$ cm^{-1}. $^5D_0 \rightarrow {}^7F_J$ spin orbit components are indicated.

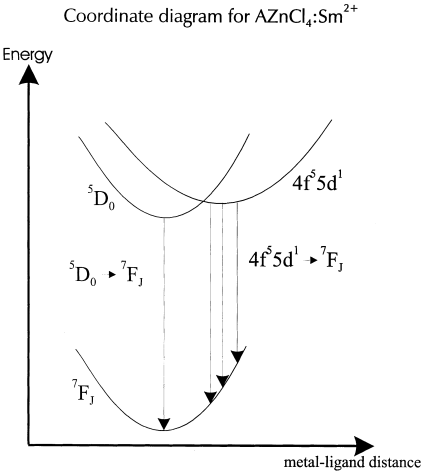

Fig. 5. Schematic configurational coordinate diagram for Sm^{2+} in $AZnCl_4$.

again at lower wavenumbers as in the $SrZnCl_4$:Sm^{2+}. In the spectrum at low temperature, only $^5D_0 \rightarrow {}^7F_J$ ($J=$ 1,3,4) transitions are observed.

In $BaZnCl_4$:Sm^{2+} the $4f^55d$ and the $^5D_0$ potentials are again located at comparable energy. Fig. 6 depicts an emission spectrum at 20 K with an excitation wavenumber of 18 796 cm^{-1}. In contrast to $SrZnCl_4$:Sm^{2+} only line emission is detected. The $4f^55d$ state is, therefore, located at higher energy (because of the lower crystal-field strength) and no thermal occupation of the fd state will occur at 20 K. At 298 K the $d \rightarrow f$ emission is observed as a very weak broad band with a maximum approximately at 15 300 cm^{-1} in addition to the line emission, about 600 cm^{-1} higher than in the strontium compound.

The positions of the $^5D_0 \rightarrow {}^7F_J$ transitions are given in Table 1. The $^5D_0 \rightarrow {}^7F_0$ line is located at 14 567 cm^{-1}. Again, emission to all ^7F_J spin orbit components was observed. The appearance of additional peaks with respect to the $SrZnCl_4$:Sm^{2+} spectra can be explained by the lower point symmetry of the Ba^{2+} site (C_2).

To the best of our knowledge there are no investigations of $BaCl_2$:Sm^{2+}, so that a comparison is not possible.

4.3. $SrZnCl_4$:Tm^{2+} and $BaZnCl_4$:Tm^{2+}

Photoemission spectra of the Tm^{2+} doped samples show a deep red luminescence. In Fig. 7a the emission spectra of $SrZnCl_4$:Tm^{2+} at different temperatures are shown. The excitation energy was 18 796 cm^{-1}. Again, a broad band is observed. This can be assigned to the $4f^{12}5d \rightarrow 4f^{13}(^2F_{7/2})$ transition of Tm^{2+}. The spectra do not show vibrational structure. The maxima of the emission bands are located at 14 662 cm^{-1} (20 K) with $\Delta_{1/2}=785$ cm^{-1} and at 14 700 cm^{-1} (298 K) with $\Delta_{1/2}=$ 1070 cm^{-1}, respectively. As in the Sm^{2+} doped samples there is a blue shift of the maximum of the $d \rightarrow f$ emission with increasing temperature. Because Tm^{2+} is isoelectronic with Yb^{3+}, a second emission band $4f^{12}5d \rightarrow 4f^{13}(^2F_{5/2})$ is expected. In SrB_4O_7:Tm^{2+} the energy of this band is at 8410 cm^{-1} [4]. In this work, infrared detection of this band was outside the instrumental sensitivity.

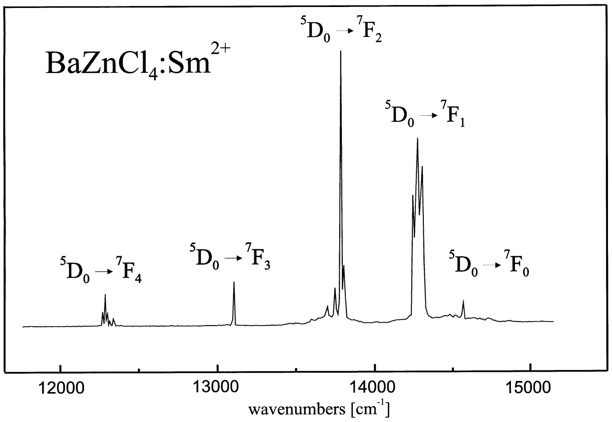

Fig. 6. Emission spectrum of $BaZnCl_4$:Sm^{2+} at 20 K. Excitation wavenumber was $\lambda_{ex}=18\ 796$ cm^{-1}. $^5D_0 \rightarrow {}^7F_J$ spin orbit components are indicated.

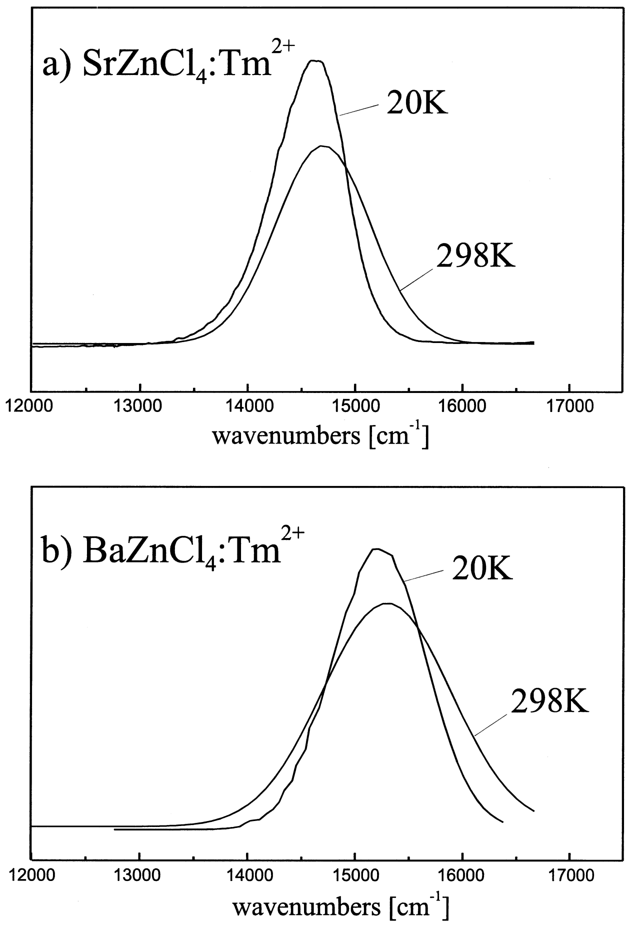

Fig. 7. (a) Emission spectra of the $4f^{12}5d \rightarrow 4f^{13}$ transition of $SrZnCl_4$:Tm^{2+} at different temperatures. Excitation wavenumber was $\lambda_{ex}=18\ 796$ cm^{-1}. (b) Emission spectra of the $4f^{12}5d \rightarrow 4f^{13}$ transition of $BaZnCl_4$:Tm^{2+} at different temperatures. Excitation wavenumber was $\lambda_{ex}=18\ 796$ cm^{-1}.

As expected, the $BaZnCl_4$:Tm^{2+} samples show the same red luminescence detectable by eye. The emission spectra are depicted in Fig. 7b excited again at 18 796 cm^{-1}. The maxima are at 15 218 cm^{-1} (20 K) and at 15 290 cm^{-1} (298 K) with $\Delta_{1/2}=1025$ cm^{-1} and $\Delta_{1/2}=1450$ cm^{-1}, respectively. The expected shift to higher energy when compared to $SrZnCl_4$:Tm^{2+} is again observed. The bands are much broader than in the strontium compound. Due to the large difference in ionic radii for the large Ba^{2+} ion and the small Tm^{2+} ion the increase of the equilibrium nuclear distance in the excited state is larger, so that the bands become broader. The increase of the broadening with increasing temperature is also stronger in $BaZnCl_4$:Tm^{2+}. The reason for this is the lower phonon energy which couples to the electronic states because of the larger Ba^{2+}–Cl^- distance of this compound.

Because there are no investigations of Tm^{2+} doped chlorides no comparison with other measurements is possible.

5. Conclusion

Emission spectra of the divalent rare-earth ions Eu^{2+}, Sm^{2+} and Tm^{2+} doped in the new host lattices $SrZnCl_4$ and $BaZnCl_4$ are reported. The thulium and the europium compounds show broad $d \rightarrow f$ luminescence with maxima at shorter wavelengths in the case of the $BaZnCl_4$ host lattice. In $SrZnCl_4$:Sm^{2+} additional $^5D_0 \rightarrow {}^7F_J$ emission lines appear at low temperatures. In $BaZnCl_4$:Sm^{2+} only line emission is detectable at low temperature. At room temperature, a weak $d \rightarrow f$ band is observed. The results are discussed and compared with the investigations on Eu^{2+} and Sm^{2+} doped $SrCl_2$ and $BaCl_2$ samples.

For a more detailed analysis with respect to the position of the potentials further investigations are necessary and will follow. Emission spectra will be measured at different temperatures as well as lifetimes. To get some knowledge of the Huang–Rhys factor and the positions of the d-orbital components which split in the crystal-field, excitation spectra will be recorded. Furthermore, other divalent lanthanides, like Yb^{2+} and Dy^{2+}, will be doped into the tetrachlorozincates. Another excellent host lattice for comparison, $SrZnF_4$, which is isotypic with $SrZnCl_4$ will be used.

Acknowledgements

Generous support by Prof. Dr. G. Meyer is gratefully acknowledged. The author is also indebted to Prof. Dr. A. Meijerink for the possibility to use his experimental equipment and for helpful discussions.

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