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Luminescent Properties and Energy Level Structure of CaZnOS:Eu²⁺

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Abstract

In this work it is shown that CaZnOS:Eu²⁺ has no Eu²⁺ emission even at low temperature. The observed and earlier reported red emission originates from a CaS:Eu²⁺ impurity phase. By means of washing the as-prepared samples with diluted nitric acid, we are able to remove the CaS impurity and get the pure CaZnOS. A clear relation was found between the red emission intensity, the CaS XRD line intensities and the nitric acid solution washing time, with zero intensity after prolonged washing. Later, a so-called VRBE (vacuum referred binding energy)-diagram was constructed showing the energy of the 4fⁿ and 4fⁿ⁻¹5d¹ states of the divalent and trivalent rare earth ions as dopants in CaZnOS with respect to the vacuum energy. This diagram shows that the 5d-levels of Eu²⁺ are located in the conduction band, which explains the absence of 5d→4f emission. By comparing the VRBE diagram with diagrams of other related compounds like CaO, CaS, ZnO and ZnS it becomes clear that the Eu²⁺ luminescence quenching is caused by a low lying conduction band, typical for Zn-based compounds.

1. Introduction

Red light emitting phosphors are of interest for their applications in white light-emitting diodes[1] and are considered for their potential to increase the rate of photosynthesis in algae systems[2, 3]. LEDs are energy efficient light sources that have found a wide range of applications since their discovery. Currently the most common method to produce white LEDs is by combining a blue LED chip (450-470 nm) with a yellow phosphor[3]. This however gives a cold white light and in order to produce a warmer colour of light a red emitting phosphor is needed. When Eu²⁺ is doped in a proper host lattice it is known to accommodate this red light emission[4].

The emission of Eu²⁺ arises from a 5d→4f transition. As the 5d electronic level is not shielded from the surrounding ligands[5], its energy varies widely with the lattice in which the Eu²⁺ ions are doped and is determined by the combined effect of the centroid shift and the crystal field splitting of the 5d states. The centroid shift is the lowering of average energy of the 5d states compared to a free ion. The centroid shift is larger when Eu is coordinated by S ions compared to O ions because it follows the nephelauxetic series[6]. The crystal field splitting is caused by the electron repulsion between the 5d states and the surrounding ligands and is therefore affected by the size and symmetry of the Eu lattice site.

CaS:Eu²⁺ is a commercially available red phosphor emitting at a maximum of 650nm. CaZnOS:Eu²⁺ has been reported to emit red luminescence that is practically the same as CaS:Eu²⁺ [3, 7]. In this article the two materials will be compared because it is not expected that two significantly difference between Eu lattice sites in CaS and CaZnOS

would give the same emission. A detailed analysis of phase pure Eu^{2+} , Eu^{3+} and Yb^{3+} doped CaZnOS powder samples will lead to the conclusion that CaZnOS:Eu^{2+} does not have Eu^{2+} emission and that the red emission accredited to CaZnOS:Eu^{2+} originates from a small quantity of CaS:Eu^{2+} impurity phase.

2. Experimental methods

CaZnOS has been synthesized by the following reaction: $\text{ZnS} + \text{CaO} \rightarrow \text{CaZnOS}$. The synthesis of pure phase CaZnOS is challenging because of the decomposition reaction above 1370 K: $\text{CaZnOS} \rightarrow \text{ZnO} + \text{CaS}$. Additionally ZnO easily decomposes to O_2 gas and Zn vapor when heated above 1205 K under reducing atmosphere[8], and this decomposition is accelerated by the presence of carbonate salts such as CaCO_3 [9]. Above 1180 K ZnS and CaO (i.e. CaCO_3 after thermal decomposition) react towards CaS and ZnO , which in time decomposes to zinc vapor[10]. Since a reducing environment is required when Eu_2O_3 is used as a starting material the synthesis towards a pure phase CaZnOS:Eu^{2+} is difficult because a small CaS phase is almost always present. Nevertheless several studies on CaZnOS report a pure phase without CaS impurities [3, 11, 12]. In this research, obtained CaZnOS samples were successfully purified by washing with a solution of water and nitric acid, a method not yet used for CaZnOS . With this method a series of CaZnOS:Eu^{2+} phosphors with decreasing CaS content was synthesized to investigate the luminescent properties as a function of the amount of CaS impurity.

For the synthesis of CaZnOS:Eu^{2+} , CaCO_3 (99.95%, Alfa Aesar), ZnS (99.99%, Alfa Aesar) and Eu_2O_3 (99.99%, Sigma Aldrich) were weighted in stoichiometric quantities and extensively ground with a pestle and mortar and placed in an Al_2O_3 crucible which was placed in a larger crucible and heated at 900°C for 32 hours under a 7% H_2 / 93% N_2 reducing atmosphere in a tube furnace and subsequently cooled down to room temperature. For the undoped CaZnOS host an 8-hour reaction time was used at the same conditions. The doping concentration of Eu was 4 mol%. The CaS:Eu^{2+} was obtained as a commercial product from Intematix. The washing of the product was performed by adding a 1% nitric acid solution of water to the sample, followed by stirring, filtration and washing with acetone. For the synthesis of the Eu^{3+} doped pure phase CaZnOS , the host lattice was synthesized first. After that, Eu_2O_3 was added in the as-prepared CaZnOS and re-annealed at the same temperature for 4 hours in the N_2 atmosphere.

The XRD measurements were performed by a PANalytical XPert Pro XRD spinner between a 2θ value of 5° and 80° in a 1-hour measurement. The radiation source is a $\text{Cu K}\alpha$ anode at 45 kV and 40 mA with $\lambda(\text{K}\alpha_1) = 0.154060$ nm and $\lambda(\text{K}\alpha_2) = 0.154443$ nm. The background determination was performed with Highscore software. Emission spectra were recorded of powder samples that were compressed to pills and placed in a rotating sample holder to minimize any effects from sample holder displacement. Sample were excited by a monochromatic Expla OPO laser and the emission spectra were collected with an Ocean Optics QE65000 Spectrometer. For low temperature measurements, spectra were obtained by pelletizing the sample and irradiated with a 150W Xenon arc lamp (Hamamatsu L2273). A Gemini 180 Monochromater was used to tune the excitation wavelength. The emission spectra were obtained by an Acton Sp2300 Spectrometer. The excitation spectra were calibrated by the Xe lamp spectrum and the emission spectra were calibrated by the detector response curve. Diffuse reflection spectra were obtained by placing the sample in a sample holder and irradiating it with an Acton Deuterium lamp. The reflection spectra were measured by

102 an Ocean Optics QE65000 Spectrometer. BaSO₄ was used as a reference for the
103 reflection measurement.

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105 3. Results

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107 In Figure 1 the XRD spectra of four samples are presented: (a) CaZnOS (washed), (b)
108 CaZnOS:Eu²⁺ (unwashed), (c) CaZnOS:Eu²⁺ (washed) and (d) CaS:Eu²⁺. Spectra (a) and
109 (d) show the same lines as the reference spectra for CaZnOS and CaS obtained from the
110 Pearson's Crystal Database[13]. Many peaks of CaS overlap with those of CaZnOS,
111 however the peak at 45° is unique for CaS and is therefore considered the best indicator
112 to determine the amount of CaS impurity phase within the CaZnOS samples.

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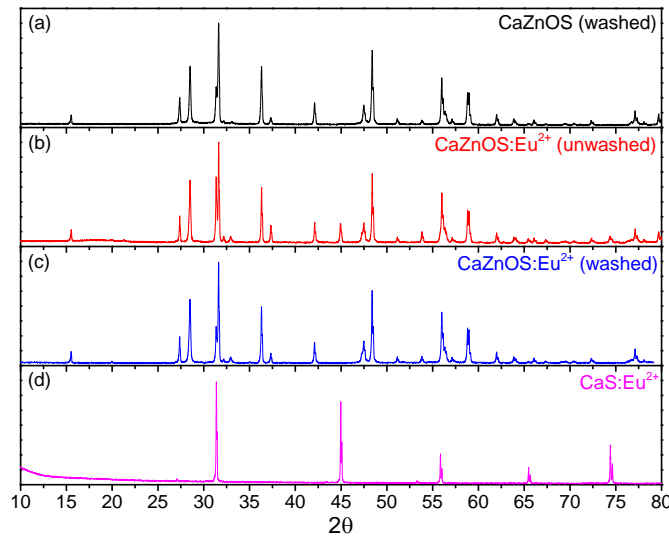
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133 **Figure 1.** XRD spectra of : (a) CaZnOS (washed), (b) CaZnOS:Eu²⁺ (unwashed) , CaZnOS:Eu²⁺ (washed)
134 and (d) commercial CaS:Eu²⁺.

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135 In Figure 2, a close-up of the 45° peak in the XRD spectra of a series of CaZnOS samples
136 with increasing washing time is presented to demonstrate the decreasing CaS line at
137 45°. The CaZnOS:Eu²⁺ samples are labelled 1 through 4 referring to the unwashed
138 (spectrum 4), the once washed (3), and the thrice washed (2) sample. Sample (1) was
139 washed until a pure phase CaZnOS was obtained.

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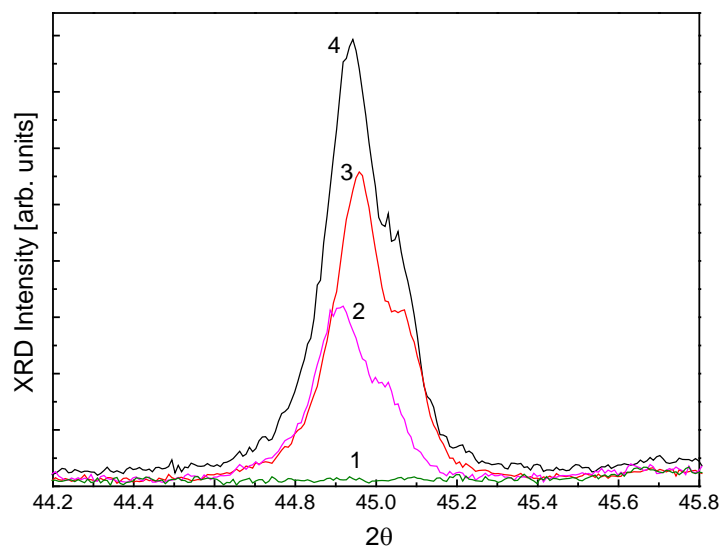
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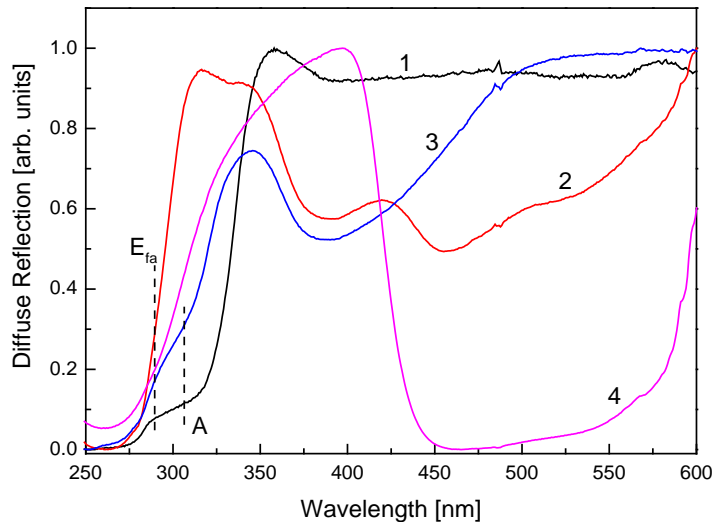
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160 **Figure 2. Zoom in on the 45° XRD peak intensity as a function of washing time for the unwashed (4),**
161 **once washed (3) and thrice washed (2) sample. Sample (1) was washed until a pure phase CaZnOS**
162 **was obtained.**

163 A comparison between the optical properties of CaZnOS (washed), CaZnOS:Eu²⁺
164 (unwashed), pure phase CaZnOS:Eu²⁺ (washed) and CaS:Eu²⁺ was made. In Figure 3 the
165 diffuse reflection spectra of the four samples are presented. An absorption band
166 between 400 and 600 nm in CaS is clearly visible in spectrum labelled 4 as expected. No
167 Eu-related absorption bands can be seen in the undoped CaZnOS sample (spectrum 1).
168 The phase pure CaZnOS:Eu²⁺ sample shows an absorption band peaking at 380nm as
169 can be seen from spectrum 3. We assign this band to 4f→5d absorption by Eu²⁺ in
170 CaZnOS. The absorption features of the unwashed CaZnOS:Eu²⁺ sample (spectrum 2)
171 of which the XRD spectra has shown that it contained CaS:Eu²⁺, can nicely be explained by
172 a combination of bands due to Eu²⁺ in CaS and CaZnOS. Spectra were not plotted beyond
173 600 nm as the measured diffusely reflected light was too much contaminated with the
174 red luminescence from Eu²⁺. This can already be seen from the too high diffuse
175 reflection values for spectrum 2 towards 600 nm. Spectra 1, 2, and 3 have a short
176 wavelength absorption onset near 280-290nm that marks the fundamental absorption
177 onset E_{fa}. An additional absorption band marked A for spectra 1 and 3 has unknown
178 origin.

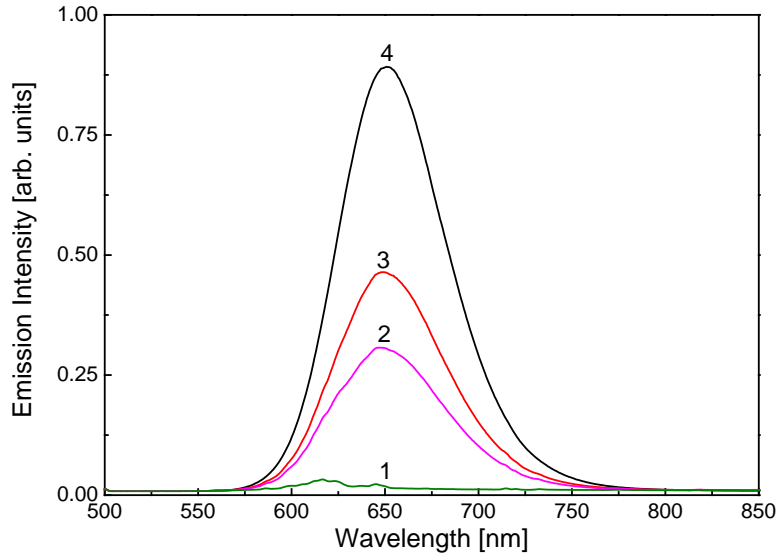


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195 **Figure 3. Normalized diffuse reflection spectra for CaZnOS (black curve labelled 1), CaZnOS:Eu²⁺with**
196 **CaS:Eu²⁺ (red curve labelled 2), CaZnOS:Eu²⁺ (blue curve labelled 3) and CaS:Eu²⁺ (purple curve**
197 **labelled 4).**

198 In Figure 4 the emission of the four samples with decreasing CaS phase is presented
199 under 500 nm laser excitation in the absorption band of Eu²⁺ in CaS:Eu²⁺. The intensity
200 of emission decreases rapidly with decreasing CaS content.

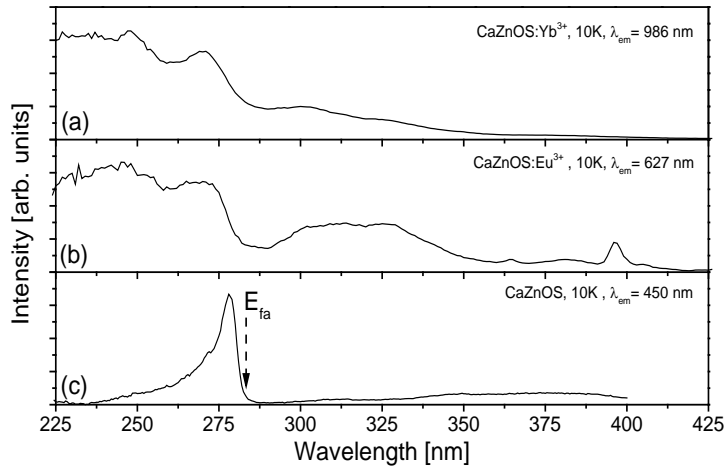
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233 **Figure 4. Emission spectra excited at 500 nm for the unwashed (4), once washed (3), and thrice (2) washed samples. Sample (1) was washed until a pure phase CaZnOS was obtained.**

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252 **Figure 5. Luminescence excitation spectra of CaZnOS:Yb³⁺ (a), CaZnOS:Eu³⁺ (b) and undoped CaZnOS (c).**

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We did not observe any luminescence on excitation in the 380nm 5d absorption band of CaZnOS, not even at 10K. Such absence can be explained when the lowest energy 4f⁶5d excited state of Eu²⁺ is located close or above the conduction band bottom[14]. In order to verify this, luminescence excitation spectra were recorded on samples doped with Eu³⁺ and Yb³⁺ to obtain the VB→Ln³⁺ charge transfer energies of these ions as well as an undoped sample to obtain the exciton- and bandgap energy of CaZnOS. These energies can be used to construct a so-called vacuum referred binding energy diagram (VRBE) that provides the location of all lanthanide ground and excited states and the host valence band and conduction band states with respect to the vacuum level. All samples were washed and free from any CaS impurity phase. The results are presented in Figure 5.

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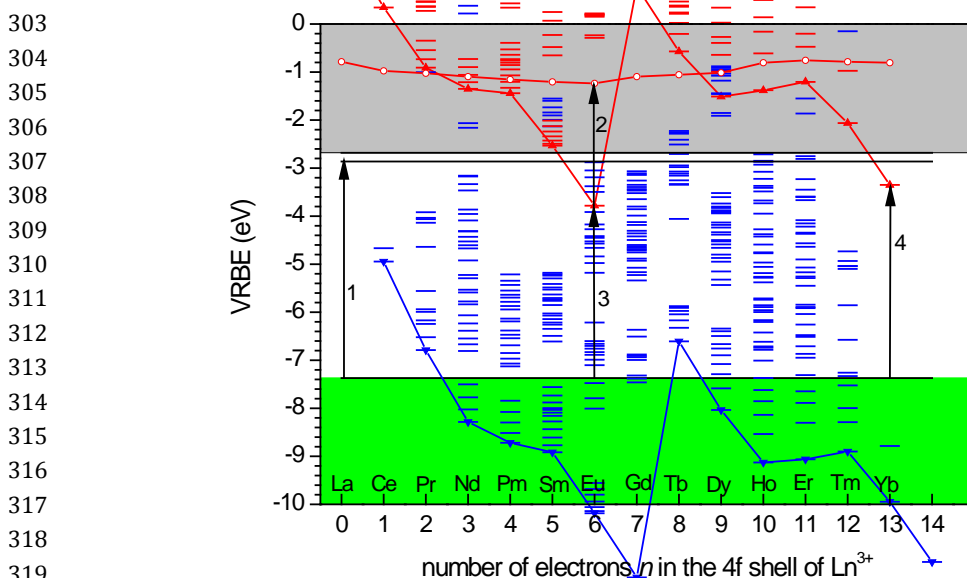
Figure 5b shows the excitation spectra of 627 nm Eu³⁺ emission at 10K. The 0.55 eV broad band at 315 nm (3.9 eV) is attributed to the valence band to Eu³⁺ charge transfer (CT) transition. At 270 nm (4.6 eV) the host exciton band is observed. This peak can be observed more clearly in the undoped sample of Figure 5c when monitoring host-related emission at 10 K around 450nm. This onset of this peak near 285 nm is the optical bandgap or fundamental absorption threshold E_{fa} of CaZnOS. The energy agrees

272 with the absorption band onset found for CaZnOS:Eu²⁺ in the diffuse reflection spectra of
 273 Figure 3. The optical bandgap of CaZnOS is reported in literature with different values
 274 between 3.7 and 4.3 eV[11-13]. The bandgap of CaS is reported at 4.9 eV[15]. The CT-
 275 band of Yb³⁺ is always expected at about 0.4 eV higher energy than that of Eu³⁺ [16] and
 276 is therefore anticipated at 288 nm. Figure 5a shows the excitation spectrum monitoring
 277 the 4f_{5/2}→4f_{7/2} emission of Yb³⁺. Besides the host exciton band at 275 nm a broad band
 278 centred around 300 nm (4.2 eV) is observed within an acceptable range of the predicted
 279 value.
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281 4. Discussion

282 The experimental data presented in this work strongly suggest that the 650 nm
 283 emission that was accredited to CaZnOS:Eu²⁺ [3, 7, 12] is actually from samples that
 284 contain small quantities of a CaS:Eu²⁺ impurity phase. CaZnOS:Eu²⁺ samples that are
 285 washed with nitric acid solution have no longer any XRD lines characteristic for CaS nor
 286 have any red emission at 650 nm. Also the diffuse reflection spectrum of a washed and
 287 phase pure CaZnOS:Eu²⁺ sample does not have the characteristic absorption bands of
 288 Eu²⁺ in CaS between 400 and 600 nm but instead it has a band at much shorter
 289 wavelength peaking at 380nm (3.3 eV).
 290

291 Based on the collected spectroscopic data presented above, the vacuum referred binding
 292 energy diagram for CaZnOS can be constructed. The energy-values used to construct the
 293 diagram in Figure 6 are indicated by the vertical arrows 1, 2, 3 and 4 that represent the
 294 host exciton creation energy of 4.5 eV, the 4f⁷→4f⁶[⁷F₀]5d¹ energy of 2.6 eV, the Eu³⁺ and
 295 Yb³⁺ CT energies respectively. The energy difference between the Eu²⁺ ground state and
 296 Eu³⁺ ground state, the so-called U-value in the chemical shift model, [17, 18] was taken
 297 as 6.4 eV which is the average of the values that pertain to CaO, ZnO, CaS, and ZnS
 298 presented below. The electron-hole binding energy in the host exciton is assumed to be
 299 about 4% of the exciton creation energy. It is evident that the lowest 5d state of Eu²⁺ in
 300 CaZnOS is well above the bottom of the conduction band, which implies that upon
 301 excitation of the 5d state, the electron will immediately delocalise into the conduction
 302 without Eu²⁺ 5d→4f emission even at 10 K.
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320 **Figure 6. VRBE diagram for CaZnOS. The vertical arrows indicate the experimentally determined**
 321 **energies that were used to construct this diagram.**

322 It is instructive to compare the VRBE-diagrams of the related compounds CaO, CaS, ZnO,
323 ZnS and CaZnOS.

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325 The VRBE-diagrams of CaS and ZnO were published earlier [19, 20]. In electrochemistry
326 the top of the valence band for ZnS is at about 2.36 eV below the H⁺/H₂ redox potential
327 [21] which brings it at -6.8 eV on the VRBE scale. We further used the 3.86 eV for the
328 host exciton creation energy with an exciton binding energy of 40 meV from Hoshina *et*
329 *al.* [22]. In CaO the exciton creation peak is at 6.94 eV [23] and the VB→Eu³⁺ charge
330 transfer band near 250nm (4.96 eV)[24-26]. For the U-parameter a value of 6.3 eV was
331 assumed and the 4f⁷→4f⁶[⁷F₀]5d¹ energy is 1.85 eV[24].

332

333 In figure 8 we present the VRBE diagrams stacked next to each other. It shows the top of
334 the valence band, the VRBE in the Eu²⁺ 4f⁷ ground state and when available in the
335 4f⁶[⁷F₀]5d₁ state, the VRBE in the host exciton state and at the bottom of the conduction
336 band. The conduction band bottom for CaZnOS falls in between that for ZnO and CaS.
337 Something similar applies to the top of the valence band. For sulfides it is usually at -6
338 eV and for oxides between -8 eV and -9 eV. The top of the valence band in CaZnOS falls in
339 between that of a CaS and CaO or ZnS and ZnO.

340

341 From a study of Eu in more than 100 different compounds it was found that the VRBE in
342 the lowest 5d state is on average near -1 eV with a tendency to decrease with smaller
343 value for the U-parameter[27]. The level locations for CaO, CaZnOS and CaS in Figure 7
344 agree with that finding. The absence of Eu²⁺ emission in CaZnOS is then caused by a low
345 lying conduction band bottom like in ZnO. On replacing oxygen for sulphur the
346 conduction band moves upward. For ZnS Eu²⁺ emission is still not observed, but
347 interestingly the Eu²⁺ emission starts to appear for nanosized particles where due to
348 band gap widening the conduction band moves to above the the Eu²⁺ 5d-level [28].

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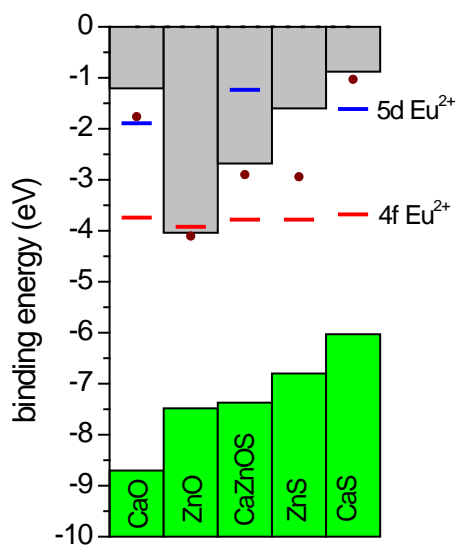
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370 **Figure 7. Energy levels of Eu²⁺ in CaO, ZnO, CaS and ZnS**

371 The low lying conduction band in ZnO as compared to CaO, and in ZnS as compared to
372 CaS means that the electron is stronger bonded in the 4s conduction band orbital of Zn
373 as compared to the 4s CB orbital of Ca. This reflects the atomic properties where the 2nd
374 ionisation potential of Zn (17.96 eV) is much higher than that of Ca (11.57 eV).

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377 **5. Conclusion**

378

379 Based on the presented experimental results it can be concluded that CaZnOS:Eu²⁺ has
380 no luminescence as the Eu²⁺ 5d states are located in the conduction band. The red
381 emission accredited to Eu²⁺ in CaZnOS in literature is in fact emission from Eu²⁺ in a CaS
382 impurity phase that can be washed out using acid water.

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