Inorganic Chemistry

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Alkaline-Earth Metal Hydrides as Novel Host Lattices for Eu^{II} Luminescence

Nathalie Kunkel, Holger Kohlmann,* Adlane Sayede,† and Michael Springborg

FR 8.1 Fachrichtung Chemie, Universität des Saarlandes, Postfach 151150, 66041 Saarbrücken, Germany

Supporting Information

ABSTRACT: Luminescence of divalent europium has been investigated for the first time in metal hydrides. A complete solid-solution series was found for the pseudobinary system $Eu_xSr_{1-x}H_2$ [$a = 637.6(1)$ pm $-12.1(3)x$ pm, $b = 387.0(1)-6.5(2)x$ pm, $c = 732.2(2)-10.1(4)x$ pm]. Europium-doped alkaline-earth hydrides $Eu_xM_{1-x}H_2$ (M = Ca, Sr, Ba) with a small europium concentration ($x = 0.005$) exhibit luminescence with maximum emission wavelengths of 764 nm (M = Ca), 728 nm (M = Sr), and 750 nm (M = Ba); i.e., the emission energy of divalent europium shows an extremely large red shift compared to the emission energies of fluorides or oxides. Theoretical calculations (LDA+*U*) confirm decreasing band gaps with increasing europium content of the solid solutions.

Because of their application as hydrogen storage materials,[1] metal hydrides have been the subject of various studies lately. They provide a way of safely storing hydrogen as an efficient and environmentally friendly energy carrier. Divalent europium is of great interest for applications such as light-emitting diodes or lasers because the d → f emission is parity-allowed, resulting in high emission intensities. Furthermore, the emission energy shows a strong dependence on the coordination sphere, allowing the design of phosphors emitting radiation of any desired color.[2] Yet, mainly oxides, fluorides, or chlorides have been used as host lattices. Even though several europium hydrides have been characterized so far,[3] luminescence of divalent europium in a hydridic matrix has never been observed before. However, a hydridic matrix could serve as an interesting host lattice because the hydride ligand possesses a strong influence on the energetic position of the d levels because of its softness and its strong ligand field. Using a hydride host lattice, a red shift in the emission energy compared to known emission energies of divalent europium as a dopant in compounds such as oxides can be expected. Furthermore, because many metal hydrides possess isotypic fluoride compounds, it might be possible to partially substitute hydride by fluoride in order to obtain different strengths of the ligand field and thus design phosphors with radiation of variable colors. To investigate Eu^{II} luminescence in a hydridic matrix, we have chosen the systems $Eu_xM_{1-x}H_2$ (M = Ca, Sr, Ba) because of their low complexity. Because of its very similar ionic radius, strontium can be easily substituted by divalent europium and vice versa.[4]

The mixed-crystal compounds $Eu_xM_{1-x}H_2$ (M = Ca, Sr, Ba) were synthesized (see the Supporting Information) and characterized by powder X-ray diffraction. As expected, on the basis of the similar ionic radii of divalent europium and strontium and the isotypy of the binary hydrides EuH_2 and SrH_2, a complete solid-solution series was found. The compounds $Eu_xSr_{1-x}H_2$ with $x = 0.0-1.0$ crystallize in the orthorhombic $PbCl_2$ structure in the space group *Pnma*. Europium and strontium are coordinated by nine hydrogen atoms, forming a tricapped trigonal prism. The lattice parameters show approximately linear behavior as a function of x (Figure 1). A color transition from white SrH_2 over yellow $Eu_{0.01}Sr_{0.99}H_2$, orange $Eu_{0.05}Sr_{0.95}H_2$, and red $Eu_{0.2}Sr_{0.8}H_2$ to dark purple EuH_2 could be observed. Additionally, differential scanning calorimetry measurements under H_2 pressure of about 50 bar were carried out, showing strongly exothermal signals from 320 to 430 K typical for the formation of salt-like hydrides. The corresponding calcium and barium compounds doped with divalent europium, $CaH_2:Eu^{2+}$ and $BaH_2:Eu^{2+}$, were prepared in a similar manner.

Samples with small europium concentrations (0.2 and 0.5 mol %) exhibit red luminescence; excitation at 390 nm resulted in emission wavelengths of 764 nm for M = Ca, 728 nm for M = Sr, and 750 nm for M = Ba in $M_{0.995}Eu_{0.005}H_2$ (Figure 2), representing the widest red shift in the emission energy of divalent europium in calcium, strontium, or barium containing host lattices, respectively, to the best of our knowledge, so far known. The broad band in the emission spectrum can be assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{II}. Because the emission of divalent lanthanide ions originates mainly from transitions of the lowest 5d levels to the $4f^n$ ground state, a shift of the energetic position of the 5d states consequently causes a shift of the emission energy. Even though only few investigations on host lattices other than oxides and fluorides have been conducted, the shift can apparently be large for different kinds of anions and coordination spheres. Nevertheless, to the best of our knowledge, no Eu^{II} luminescence in a hydridic crystal field has ever been observed before. However, because of the expected softness of the crystal field and the high polarizability of the hydride ligand, hydrides are an extremely interesting new type of host lattice. Anyhow, the ligand field strength of hydrogen is still a controversial matter. In the spectrochemical series, hydride is generally assigned a position near cyanide, even though, on the basis of the electronic spectra of rhodium ammine complexes, its ligand field strength was estimated to be similar to that of NH_3. Recently, its position in the spectrochemical series of low-spin Fe^{2+} was determined to be below cyanide but far ahead of *o*-phenanthroline.[5] The red shift of divalent europium observed in a hydridic matrix strongly supports this classification. The soft hydride ligand shifts the lowest excited 5d states to lower energy, resulting in a large red shift of the emission energy compared to

Received: April 19, 2011
Published: June 02, 2011

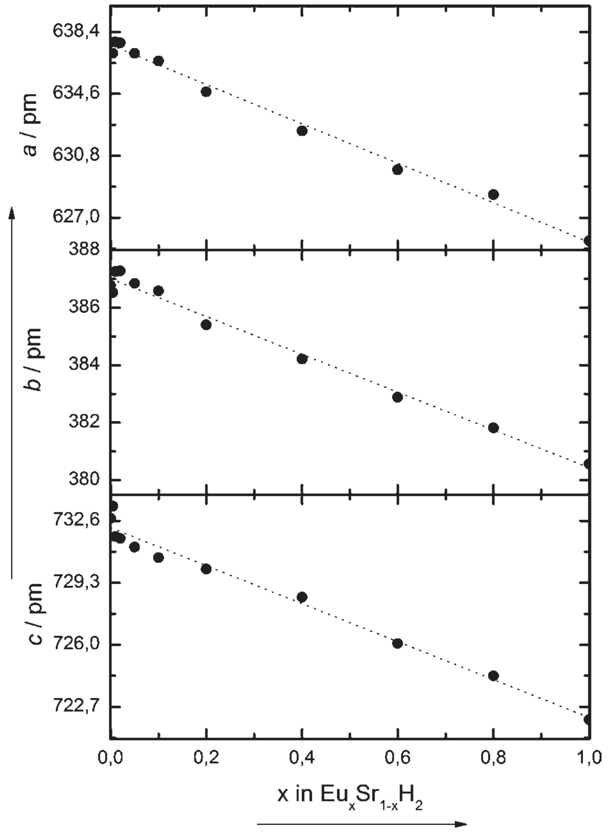

Figure 1. Lattice parameters of $Eu_xSr_{1-x}H_2$ obtained from Rietveld analysis. Linear regression results in a = 637.6(1)−12.1(3)x pm, b = 387.0(1)−6.5(2)x pm, and c = 732.2(2)−10.1(4)x pm.

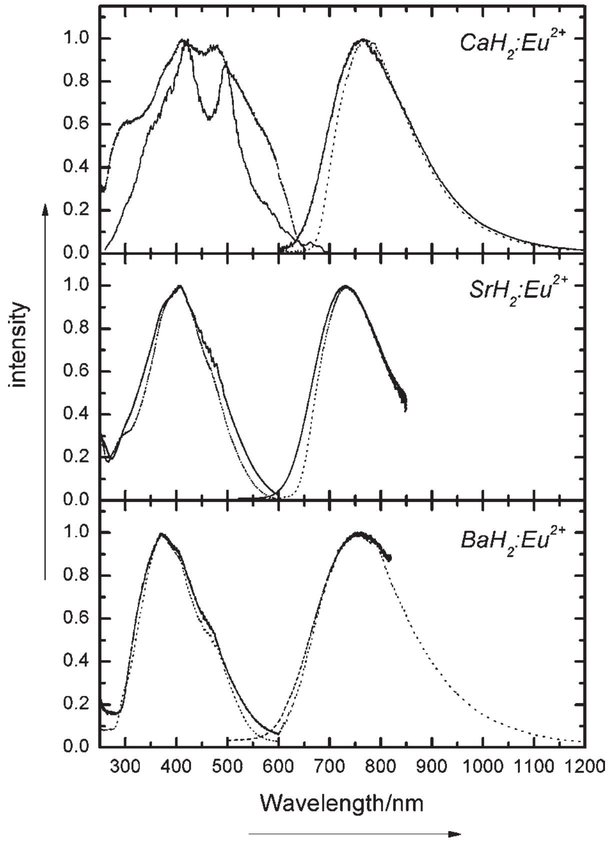

Figure 2. Luminescence spectra of MH_2:Eu^{2+} (M = Ca, Sr, Ba; 0.5 mol % Eu^{2+}). Solid lines correspond to spectra measured at room temperature and dotted lines to those at 10 K. Bands below 600 nm belong to excitation, and emission bands are above 600 nm. Intensity values are in arbitrary units.

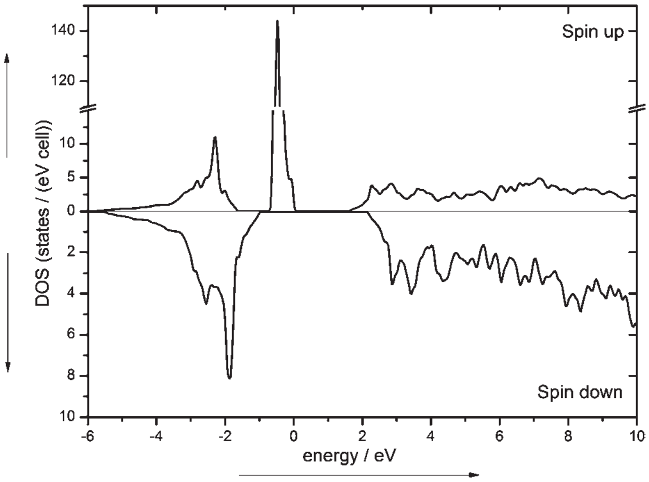

Figure 3. Density of states of EuH_2 from a GGA+U calculation. The energy zero is at the top of the valence band.

those of compounds such as fluorides and oxides. In a comparison of the emission bands of the three Eu^{II}-doped alkaline-earth hydrides (Figure 2), those for M = Ca and Sr show very similar shape, with a 36 nm shift to longer wavelengths for the calcium compound compared to the strontium compound. This might be explained by the smaller unit cell volumes of the calcium compound, in which then the hydride anion exerts an even stronger ligand field effect on Eu^{II}. For M = Ba, however, the emission band is of different shape and in between those of M = Ca and Sr. This might be due to the fact that the Ba position in BaH_2 is too large for a Eu^{2+} ion,[6] thus realizing an environment different from Ba either by a local relaxation of the structure or by the occupation of different lattice sites. This feature is also consistent with the frequent observation of the so-called anomalous emission, resulting in a large Stokes shift in europium-doped barium compounds.[2]

Additionally, electronic structures were calculated using (L)APW.[7] It turned out that the density functional theory calculations with a local density approximation (LDA) or a generalized gradient approximation (GGA) were not able to give an accurate description of the Eu 4f orbitals. Therefore, we used the so-called LDA+U method, for which U = 7 eV, which is typical for europium,[8] was used. We have considered the compounds $Eu_xSr_{1-x}H_2$ with x = 0.0, 0.33, 0.66, and 1.0 (for details, see the Supporting Information). For EuH_2, a band gap of 1.7 eV was found to be in good accordance with the experimental value of 1.85 eV[9] (see Figure 3).

The calculated values for the band gaps of the compounds with x = 0.0, 0.33, and 0.66 can be found in Figure 4. As expected, the size of the band gap increases with decreasing europium concentration. Knowledge of the size of the band gaps could in the future be helpful for predicting luminescence properties.

In conclusion, we have shown that the complete solid-solution series $Eu_xSr_{1-x}H_2$ exists and that compounds $Eu_xM_{1-x}H_2$ (M =

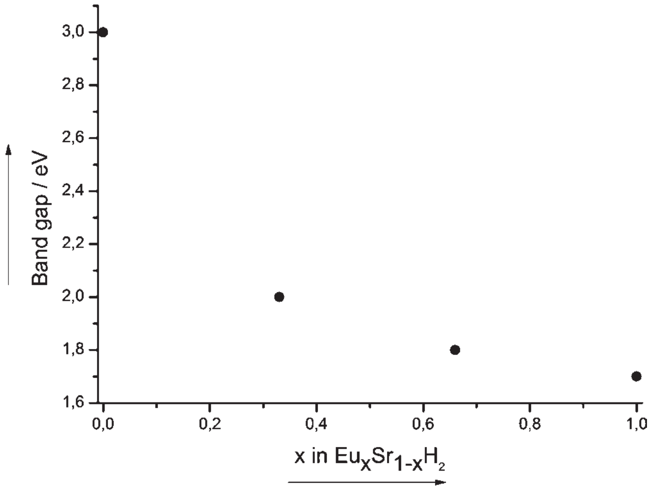

Figure 4. Calculated band gaps for $Eu_xSr_{1-x}H_2$.

Ca, Sr, Ba) with a small europium concentration exhibit luminescence with maximum emission wavelengths of 764 nm (M = Ca), 728 nm (M = Sr), and 750 nm (M = Ba). Even though the position of hydride in the spectrochemical series is still under debate, the large red shift in the emission energy of Eu^{II} strongly suggests it to be near cyanide. For future studies, hydride could be partially substituted by fluoride. Because of the hydride fluoride analogy,[10] mixed crystals of ternary alkaline-earth hydrides and fluorides might in some cases form complete solid-solution series, thus allowing a continuously variable substitution of hydride by fluoride and consequently also the design of a continuously variable emission wavelength of almost any desired color.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, characterization data, and information about theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: h.kohlmann@mx.uni-saarland.de.

Present Addresses
† Université Lille Nord de France, F-59000 Lille, France, UArtois, UCCS, F-62300 Lens, France, and CNRS, UMR, 8181, F-59650 Villeneuve d'Ascq, France.

■ ACKNOWLEDGMENT

The authors are grateful to Dr. Matthias Adlung and Prof. Dr. Claudia Wickleder, University of Siegen, for help with spectroscopic measurements, CINES and Lille1 University for allocation of computer resources, and the Deutsche Forschungsgemeinschaft for financial support (SPP 1166 and Ko1803/3).

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