Valence Changes in Dicarbide Solid Solutions

S. Busch and U. Ruschewitz

Department für Chemie, Universität zu Köln, 50939 Köln, Germany

The crystal structures of the solid solutions Yb<sub>x</sub>Sr<sub>1-x</sub>C<sub>2</sub> and Eu<sub>x</sub>Ba<sub>1-x</sub>C<sub>2</sub> as well as their low and high temperature structural behavior were investigated by means of synchrotron powder diffraction at beamline P02.1 using an image plate detector. Due to the high sensitivity of these compounds to moisture, the samples were measured in glass capillaries in an inert atmosphere. These capillaries were spun during the diffraction experiments. Silicon was chosen as a standard for high temperature calibration.

YbC<sub>2</sub> is a mixed-valence compound with an average valence of 2.81, which is temperature independent between 15 K and 1123 K, as revealed by XANES investigations.<sup>[1]</sup> Solid solutions containing Yb show several unusual effects that point to a change of Yb valence stimulated by different crystal structures, composition and temperature. Structural investigations at room temperature revealed a complete solid solution series Yb<sub>x</sub>Sr<sub>1-x</sub>C<sub>2</sub> (0 < x < 1) with three different modifications depending upon x: for x ≤ 0.4 a ThC<sub>2</sub> type structure (C2/c, Z = 4) is observed, whereas for x = 0.9 the CaC<sub>2</sub> type structure (I4/mmm, Z = 2) is found. In the composition range 0.4 < x < 0.9 the high temperature modification CaC<sub>2</sub> IV is stable already at room temperature. We recorded XANES spectra of three selected compounds with x = 0.90, 0.80 and 0.60 that show temperature dependent changes of the Yb valence. For x = 0.9 a decrease from 2.68 (RT) to 2.58 (723 K) was observed, and for x = 0.8 the Yb valence decreases from 2.62 (RT) to 2.56 (673 K). The effect is particularly obvious for Yb<sub>0.6</sub>Sr<sub>0.4</sub>C<sub>2</sub> (Figure 1a), for which an Yb valence of 2.0 is observed at 673 K.<sup>[2]</sup>

After data reduction (FIT2D<sup>[3]</sup>) powder diffraction data recorded on Yb<sub>0.6</sub>Sr<sub>0.4</sub>C<sub>2</sub> at P02.1 were analyzed by Rietveld refinements (GSAS<sup>[4]</sup>). The compound shows a non-linear volume expansion below 680 K and a linear behavior above 680 K (Figure 1b). These results are in a good agreement with those obtained from XANES spectroscopy, as from 10 K to 680 K a decrease of the Yb valence to 2.0 was observed. Above 680 K a constant Yb valence of 2.0 occurs, which leads to a linear volume expansion.

We also measured the compound Yb<sub>0.4</sub>Sr<sub>0.6</sub>C<sub>2</sub>. XANES data resulted in an Yb valence of 2.0 already at room temperature. We obtained a linear volume expansion between 100 K and 300 K (Figure 2a). For Yb<sub>0.5</sub>Sr<sub>0.5</sub>C<sub>2</sub> we also investigated the unit cell volume as a function of temperature (Figure 2b). The low temperature data (black dots) were obtained at P02.1, whereas the high temperature data (red dots) are older results obtained at the PDIFF beamline at ANKA.<sup>[2]</sup> A linear volume expansion is found in the range 100 – 230 K and 550 – 900 K. XANES data of this compound have also been recorded (at DELTA). But the analysis has not been finished yet.
Previous investigations have shown that the solid solution Eu$_x$Sr$_{1-x}$C$_2$ is a perfect example of a strain free system following Vegard’s law, as both cations (Eu$^{2+}$, Sr$^{2+}$) have similar radii. Eu$_x$Ba$_{1-x}$C$_2$ seems to be another promising solid solution. However, due to the larger difference of the respective ionic radii (r(Ba$^{2+}$) $>$ r(Eu$^{2+}$)) a higher lattice strain is expected. The solid solution Eu$_x$Ba$_{1-x}$C$_2$ was measured at P02.1, reduced (FIT2D) and analyzed by Rietveld refinements (GSAS). Three different modifications were found depending on x: for x = 0.7 - 0.9 the ThC$_2$ type structure was observed, whereas for x = 0.1 - 0.2 the CaC$_2$ type structure was found. These phases follow Vegard’s law. We focused our investigations on the range between x = 0.2 and 0.7. These compounds crystallize in the cubic CaC$_2$ IV type structure already at room temperature, which usually only occurs at higher temperatures. But a similar behavior was found in former investigations by McColm and Adachi for various solid solutions with different lanthanide cations, if the relative difference of the ionic radii of the cations exceeds a value of 10-14% (18% for Eu$_x$Ba$_{1-x}$C$_2$). We also investigated the temperature dependent phase behavior of the Eu rich and Ba rich compounds Eu$_0.9$Ba$_{0.1}$C$_2$ and Eu$_0.1$Ba$_{0.9}$C$_2$. In the temperature range 300 – 820 K no phase transition to the cubic CaC$_2$ IV type was observed for Eu$_0.1$Ba$_{0.9}$C$_2$. For Eu$_0.2$Ba$_{0.8}$C$_2$ however, the temperature dependent measurements showed a reversible phase transition to the cubic high temperature modification (Fm-3m, Z = 4, CaC$_2$ IV type structure, Figure 3a).

For Eu$_0.2$Ba$_{0.8}$C$_2$ we observed a phase transition from CaC$_2$ type structure (I4/mmm, Z = 2) to the ThC$_2$ type structure (C2/c, Z = 4) in the temperature range 175 – 250 K (Figure 3b). It should be mentioned that a similar behavior was found for pure BaC$_2$.

References


P02.1-Publications U. Ruschewitz