ABSTRACT

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Valence changes in dicarbide solid solutions induced by structural changes

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The rare-earth metal carbides (REC_2) EuC_2 and YbC_2 are isostructural to alkaline-earth metal carbides (AEC_2), both containing C_2 dumbbells. Despite their similar crystal structures completely different physical properties are observed, i.e. metallic (REC_2) versus insulating (AEC_2) behaviour. In this context, semiconducting properties with divalent Eu(II) under ambient conditions are found for EuC_2 ^[1], but under pressure metallic EuC_2 with trivalent Eu(III) is observed.^[2] However, for YbC_2 an intermediate valence of approx. 2.8 was determined.^[3] As confirmed by XRPD data at RT we were able to synthesize several solid solutions by reaction of the elements, e.g. $\text{Yb}_x\text{Sr}_{1-x}\text{C}_2$ ^[4], $\text{Eu}_x\text{Ca}_{1-x}\text{C}_2$, $\text{Eu}_x\text{Ba}_{1-x}\text{C}_2$ and $\text{Yb}_x\text{Ca}_{1-x}\text{C}_2$ ^[4] ($0 < x < 1$). As a result, all solid solutions crystallize in different modifications depending on x . In addition, solid solutions containing Eu show a clear tendency towards a perfect Vegard behaviour as reported for $\text{Eu}_x\text{Sr}_{1-x}\text{C}_2$ ^[5], whereas solutions containing Yb show unusual effects that point to a change of Yb valence stimulated by composition, temperature and different crystal structures. .

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