On the Thermal Decomposition of CeO_2, Pr_6O_{11}, Eu_2O_3, and Tb_4O_7

Fachhochschule Münster University of Applied Sciences

Julian Plewa and Thomas Jüstel

University of Applied Sciences Münster, Stegerwaldstraße 39, D- 48565 Steinfurt, Germany

RARE EARTH REEC ELEMENTS + COMPOUNDS

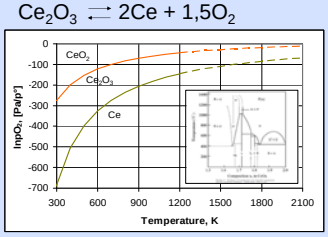
Rare earth activated luminescent compositions are essential to the light generation process in fluorescent light sources, such as LEDs and gas discharge lamps, in emissive displays such as CRTs and PDPs, in many kind of scintillators, and in gain media for solid state lasers. Amongst the chemical stable rare earth (RE) ions, Ce^{3+}, Pr^{3+}, Eu^{2+}, Eu^{3+}, and Tb^{3+} are the most important ones for the activation of presently applied materials. These activator ions are homogenously incorporated into the respective solid state compound by diffusion processes at a sufficiently high temperature, whereby the oxygen partial pressure is essential to obtain the respective activator ion in the desired oxidation state. In this work, we thus studied the thermal decomposition of commonly used sources for the activator ions, viz. the oxides CeO_2, Pr_6O_{11}, Eu_2O_3, and Tb_4O_7 in the temperature range between RT and 1400 °C

Thermodynamic Analysis – Calculated Stability Diagram of the RE - O Systems

Ce-O System

$2CeO_2 \rightleftarrows Ce_2O_3 + 0{,}5O_2$

$Ce_2O_3 \rightleftarrows 2Ce + 1{,}5O_2$

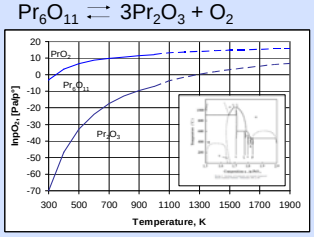


Cer-Oxide: CeO_2, $CeO_{1.651\text{-}1.91}$, Ce_2O_3

Pr-O System

$6PrO_2 \rightleftarrows Pr_6O_{11} + 0{,}5O_2$

$Pr_6O_{11} \rightleftarrows 3Pr_2O_3 + O_2$

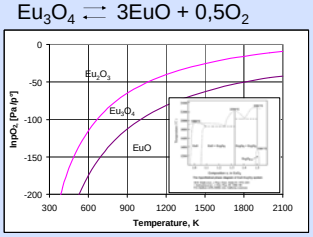


Praseodymium Oxides: PrO_2, Pr_6O_{11} $P_{1.818\text{-}1.555}$, and Pr_2O_3

Eu-O System

$3Eu_2O_3 \rightleftarrows 2Eu_3O_4 + 0{,}5O_2$

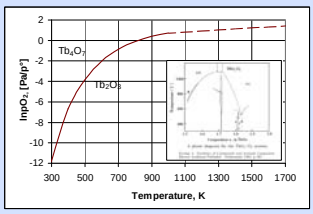
$Eu_3O_4 \rightleftarrows 3EuO + 0{,}5O_2$



Europium Oxides: Eu_2O_3, Eu_3O_4 and EuO

Tb-O System

$Tb_4O_7 \rightleftarrows 2Tb_2O_3 + 0{,}5O_2$

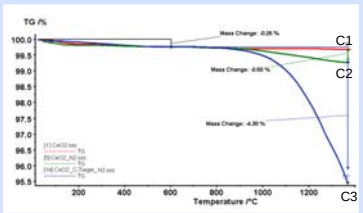


Terbium oxides: Tb_2O_3, $TbO_{1.61\text{-}1.74}$, Tb_4O_7 and TbO_2

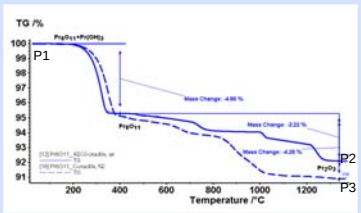
Thermal Analysis –TG curves and Simultaneous DTA/TG Curves of Pure RE Oxides

Thermogravimetric Curves of Pure RE-Oxide at Nitrogen (Al_2O_3- and Carbon-Crucible)

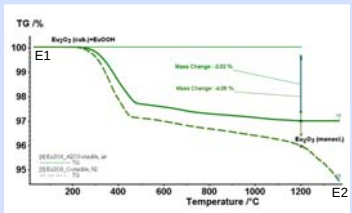
$CeO_2 \rightarrow CeO_{2-x}$



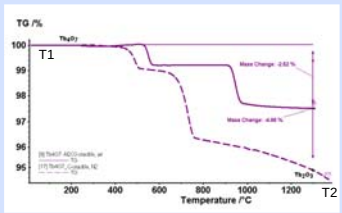
Pr_6O_{11} $(Pr(OH)_3) \rightarrow Pr_6O_{11} \rightarrow Pr_5O_9 \rightarrow Pr_7O_{12} \rightarrow Pr_8O_{13} \rightarrow Pr_2O_3$

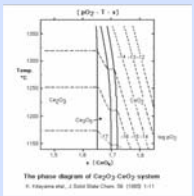


Eu_2O_3 $(EuOOH) \rightarrow Eu_2O_3$



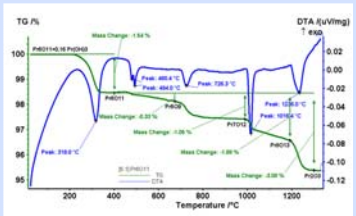
$Tb_4O_7 \rightarrow Tb_7O_{12} \rightarrow Tb_2O_3$

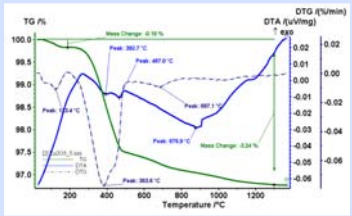


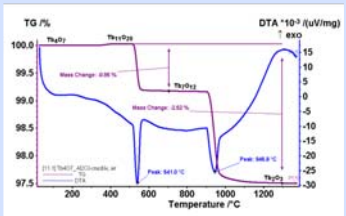


The relationship between the oxygen partial pressure and the composition of cerium oxide CeO_x (dotted lines)

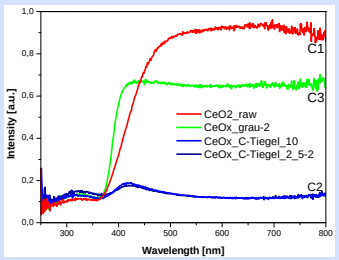
Simultaneous DTA/TG Curves of Pure Pr_6O_{11}, Eu_2O_3 and Tb_4O_7 at air

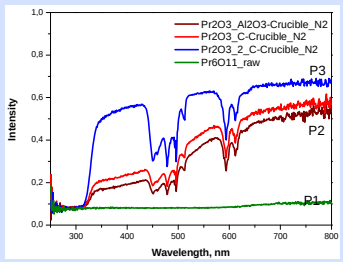


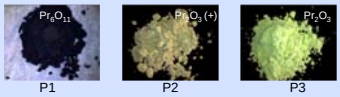


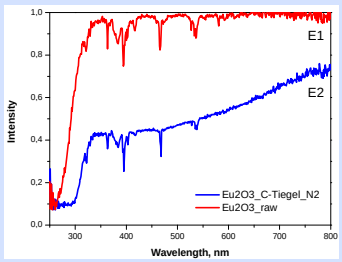


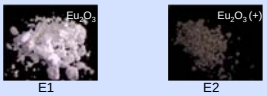
Optical Characterisation – Reflexion Spectra and Photographs of Powders

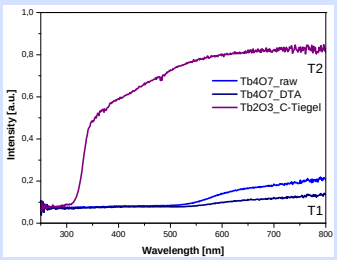












It turned out that the oxides Pr_6O_{11} and Eu_2O_3 easily absorb water at the surface, which results in the formation of $Pr(OH)_3$ and EuOOH at the surface of Pr_6O_{11} and Eu_2O_3 particles, respectively. Dehydration takes place in the temperature range from 350 to 450 °C. In contrast Pr_6O_{11} and Tb_4O_7 do not tend to take up water and decompose by annealing in air step wisely to the sesquioxides. This decomposition process is completely reversible and during cooling in air Pr_6O_{11} and Tb_4O_7 is recovered again. CeO_2 and Eu_2O_3 will remain stable in air at least until 1400 °C. A reducing CO atmosphere during the temperature increase will lead to the elimination of oxygen (at 1200 °C for Eu_2O_3 and at 900 °C for CeO_2). At temperatures higher than 1200 °C $Eu_2O_{3\text{-}x}$ is present, while its complete conversion into EuO requires a temperature higher than 1600 °C or a hydrogen comprising atmosphere to sufficiently reduce the oxygen partial pressure. The formation of pure Ce_2O_3 is already achieved by annealing at about 1500 °C.

September 4-6, 2012, Münster, Germany