Reversible Thermal Decomposition of Pr_6O_{11} and Tb_4O_7 in Air

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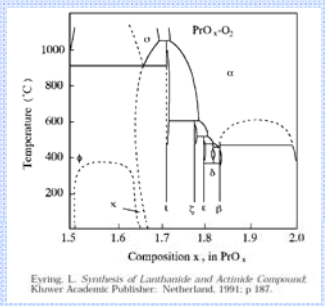
RARE EARTH REEC ELEMENTS + COMPOUNDS

Sesquioxides RE_2O_3 of the rare earth metals are important starting compounds for the synthesis of optical materials such as luminescent pigments and laser gain media. Some of the rare earth metals also form oxides, wherein the metal is in the divalent, trivalent, or in a mixed valent state, as e.g. in Tb_4O_7 or Pr_6O_{11}. In those cases, where the rare earth metal can attain different oxidation states, i.e. the metals Ce, Pr, Nd, Sm, Eu, Tb, Tm, and Yb, the type of oxide obtained is a sensitive function of the oxygen partial pressure, whereby the different oxides can be described by the general formula RE_nO_{2n-m}. Praseodymium, for instance, forms with increasing oxygen partial pressure the oxides Pr_2O_3, Pr_6O_{11}, or PrO_2, whereby the latter one is a very strong oxidizer. For the proper synthesis of optical materials it is of substantial interest to know the thermal decomposition of the commercially available oxides, such as Pr_6O_{11} and Tb_4O_7. Therefore, we performed thermal analysis of these oxides in the range between room temperature and 1600 K. It turned out, that both oxides decompose to Pr_2O_3 and Tb_2O_3, respectively, whereby the process is completely reversible. That means independent of the cooling rate, we obtained Pr_6O_{11} and Tb_4O_7 after a thermal cycle in air. In order to maintain the sesquioxides after the thermal decomposition, it is necessary to reduce the oxygen partial pressure, i.e. to work under an inert (N_2, Ar) or under a reducing gas atmosphere (H_2, CO). Our findings are important for the reasonable choice of the annealing conditions during the synthesis of optical materials comprising rare earth metals.

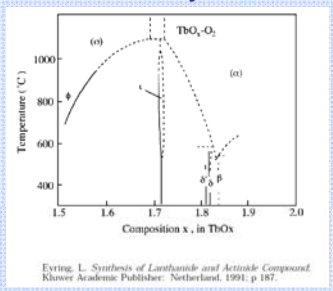
The Intermediate Ordered Oxides between Re_2O_3 and ReO_2

Compound	PrO_x	Hypothetic Mixture	Δm, %	Color
Pr_2O_3 (ϕ)	$PrO_{1.5}$	$0*PrO_2+0.5*Pr_2O_3$	-3,133	green
Pr_9O_{14}	$PrO_{1.555}$	$1*PrO_2+4*Pr_2O_3$	-2,611	black brown
Pr_7O_{11}	$PrO_{1.571}$	$1*PrO_2+3*Pr_2O_3$	-2,461	
Pr_6O_{13} (σ)	$PrO_{1.625}$	$2*PrO_2+3*Pr_2O_3$	-1,958	
Pr_3O_5 (κ)	$PrO_{1.666}$	$1*PrO_2+1*Pr_2O_3$	-1,566	
Pr_7O_{12} (ι)	$PrO_{1.714}$	$3*PrO_2+2*Pr_2O_3$	-1,119	
Pr_4O_7	$PrO_{1.75}$	$2*PrO_2+1*Pr_2O_3$	-0,783	
Pr_9O_{16} (ζ)	$PrO_{1.778}$	$5*PrO_2+2*Pr_2O_3$	-0,522	
Pr_5O_9 (ε)	$PrO_{1.8}$	$3*PrO_2+1*Pr_2O_3$	-0,313	
$Pr_{11}O_{20}$ (δ)	$PrO_{1.818}$	$7*PrO_2+2*Pr_2O_3$	-0,142	
$Pr_{17}O_{31}$ (π)	$PrO_{1.823}$	$11*PrO_2+3*Pr_2O_3$	-0,092	
Pr_6O_{11} (β)	$PrO_{1.83}$	$4*PrO_2+1*Pr_2O_3$	0	black
PrO_2 (α)	PrO_2	$1*PrO_2+0*Pr_2O_3$	+1,566	white

Pr-O System



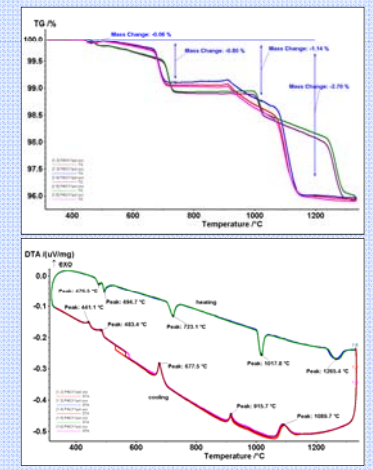
Tb-O System



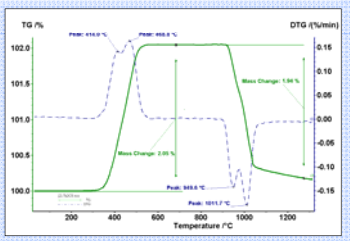
Compound	TbO_x	Hypothetic Mixture	Δm, %	Color
Tb_2O_3	$TbO_{1.5}$	$0*TbO_2+0.5*Tb_2O_3$	-2,140	white
$Tb_{18}O_{29}$ (σ)	$TbO_{1.61}$	$4*TbO_2+7*Tb_2O_3$	-1,189	brown
Tb_7O_{12} (ι)	$TbO_{1.71}$	$3*TbO_2+2*Tb_2O_3$	-0,306	
$Tb_{40}O_{69}$	$TbO_{1.72}$	$18*TbO_2+11Tb_2O_3$	-0,214	
$Tb_{50}O_{87}$	$TbO_{1.74}$	$24*TbO_2+13*Tb_2O_3$	-0,086	
Tb_4O_7	$TbO_{1.75}$	$2*TbO_2+1*Tb_2O_3$	0	
Tb_6O_{16} (ζ)	$TbO_{1.777}$	$5*TbO_2+2*Tb_2O_3$	+0,238	
Tb_7O_9	$TbO_{1.8}$	$3*TbO_2+1*Tb_2O_3$	+0,428	
$Tb_{21}O_{38}$ (δ')	$TbO_{1.809}$	$13*TbO_2+4*Tb_2O_3$	+0,509	dark brown
$Tb_{18}O_{29}$	$TbO_{1.81}$	$10*TbO_2+3*Tb_2O_3$	+0,535	
$Tb_{11}O_{20}$ (δ)	$TbO_{1.82}$	$7*TbO_2+2*Tb_2O_3$	-0,584	
$Tb_{17}O_{31}$	$TbO_{1.823}$	$11*TbO_2+3*Tb_2O_3$	+0,629	
Tb_6O_{11} (β)	$TbO_{1.83}$	$4*TbO_2+1*Tb_2O_3$	+0,713	
Tb_9O_{15} (π)	$TbO_{1.875}$	$6*TbO_2+1*Tb_2O_3$	+1,070	
$Tb_{20}O_{39}$	$TbO_{1.95}$	$18*TbO_2+1*Tb_2O_3$	+1,712	
TbO_2 (α)	TbO_2	$1*TbO_2+0*Tb_2O_3$	+2,140	dark red

Thermal Analysis Curves of the Pr_6O_{11} and Tb_4O_7 Samples during Heating and Cooling

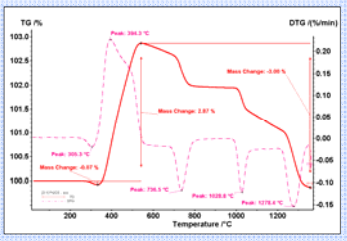
Pr_6O_{11} → Pr_2O_3 → Pr_6O_{11}



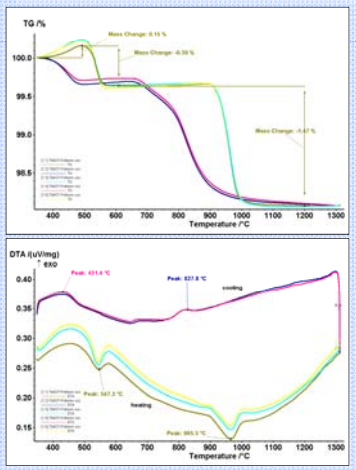
Tb_2O_3 → Tb_4O_7 → Tb_2O_3



Pr_2O_3 → Pr_6O_{11} → Pr_2O_3



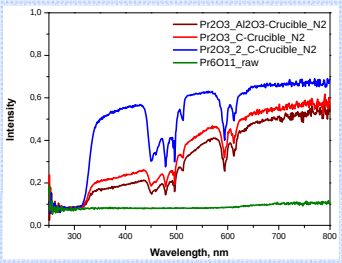
Tb_4O_7 → Tb_2O_3 → Tb_4O_7

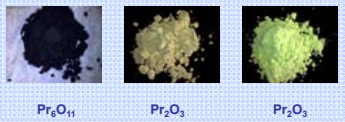


Heating and cooling: Pr_6O_{11} → $Pr_{17}O_{31}$ → $Pr_{11}O_{20}$ → Pr_7O_{12} → Pr_3O_5 → Pr_2O_3

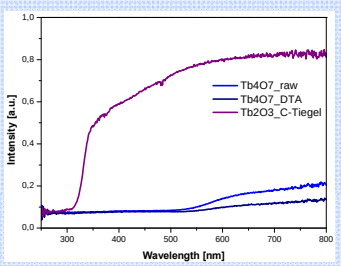
Heating: Tb_4O_7 → $Tb_{11}O_{20}$ → Tb_7O_{12} → Tb_2O_3
Cooling: Tb_2O_3 → Tb_7O_{12} → Tb_4O_7

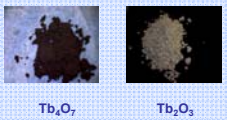
Optical Reflexion Spectra and Photographs of the Powders





Pr_6O_{11} Pr_2O_3 Pr_2O_3





Tb_4O_7 Tb_2O_3

Pr_6O_{11} and Tb_4O_7 decompose by annealing in air step wisely to the sesquioxides Pr_2O_3 and Tb_2O_3. This decomposition process is completely reversible and during cooling in air Pr_6O_{11} and Tb_4O_7 is recovered again. This process is of tremendous interest for the fabrication of phosphors doped with Pr^{3+} or Tb^{3+}.