

Direct Calorimetric Measurement of Enthalpies of Phase Transitions at 2000°C–2400°C in Yttria and Zirconia

Reference: Direct Calorimetric Measurement of Enthalpies of Phase Transitions at 2000°C–2400°C in Yttria and Zirconia. Alexandra Navrotsky, Luc Benoist and Herve Lefebvre. J. Am. Ceram. Soc., 88 [10] 2942–2944 (2005)

Introduction

High-temperature differential thermal analysis provided data on phase transitions in zirconia and yttria. The tetragonal form of ZrO₂ transforms to the cubic fluorite structure at 2311±15°C with an enthalpy of 3.4±2 kJ/mol. Cubic C-type Y₂O₃ transforms, probably to the fluorite structure, at 2308±15°C with $\Delta H=47.7\pm 3.0$ kJ/mol. This high-temperature polymorph melts at 2382±15°C with an enthalpy of fusion of 35.6±3.0 kJ/mol.

Experimental

Crucibles made of tungsten are used. Temperature and sensitivity were calibrated before each experiment by performing the melting of α -alumina in a tungsten crucible at a heating rate of 10°C/min under helium (melting temperature of 2052°C and enthalpy of fusion of 1092 J/g). For zirconia analysis, a calibration was also performed afterwards. It was then observed that the temperature correction increased by 50°C. This variation is mainly because of the aging of the thermocouple during the heating at 2400°C. Each sample was scanned upwards in temperature from 1600° to 2400°C at a rate of 10°C/min (heating run), and then the scanning direction was reversed (cooling run).



Instrument :
SETSYS Evolution DTA 24
(Ambient to 2400°C)

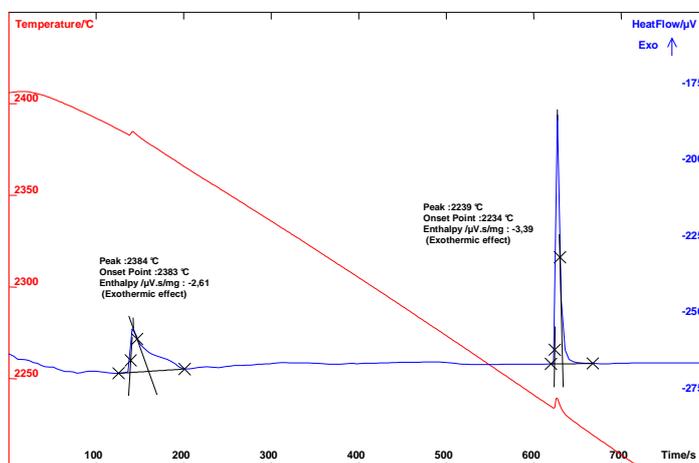


Fig. 1: Cooling curve for Y₂O₃

Results

In general, the cooling runs gave clearer signals than the initial heating runs, probably because the sample, after heating, made better thermal contact with the pan. As an example, Fig. 1 shows a cooling scan for yttria. For zirconia, one transition, namely that of the tetragonal to the cubic phase, could be clearly seen, three runs showing peaks at 2265°C, 2278°C and 2311°C.

Recommended Values of Thermodynamic parameters for Transitions in ZrO₂ and Y₂O₃

Material	Transition	T (°C)	ΔH (kJ/mol)	ΔS (J/mol/K)
ZrO ₂	m-t	1199	5.43 ± 0.31	3.69 ± 0.21
ZrO ₂	t-c	2311	3.4 ± 2.1	1.3 ± 0.8
Y ₂ O ₃	c-c	2308	47.7 ± 3.0	18.5 ± 1.2
Y ₂ O ₃	c-m	2382	35.6 ± 3.2	13.9 ± 1.2

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