

Microwave Plasma Synthesis of Lanthanide Zirconates From Microwave Transparent Oxides

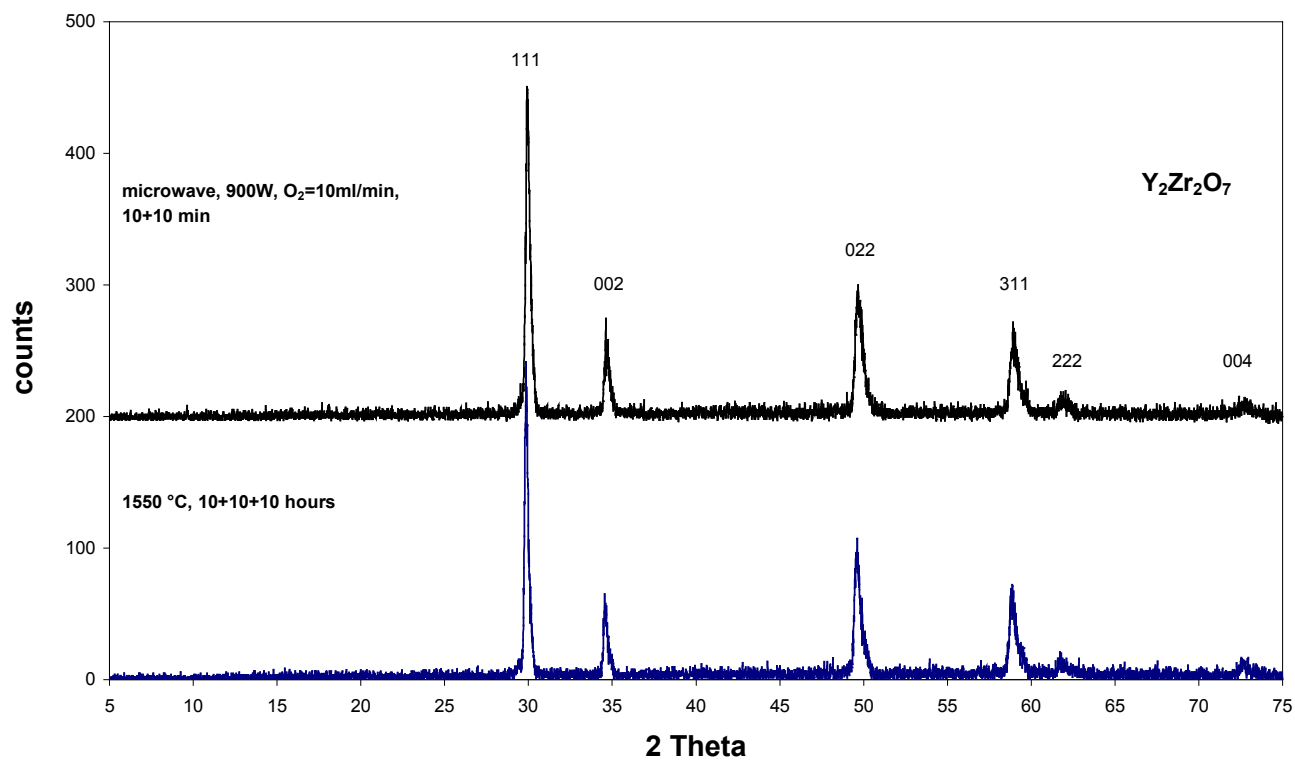
Yi-Hsin Chou^a, Nicole Hondow^b, Chris I. Thomas^a, Robert Mitchell^a, Rik Brydson^b and Richard E Douthwaite^a

^aDepartment of Chemistry, University of York, Heslington, York, YO10 5DD, UK

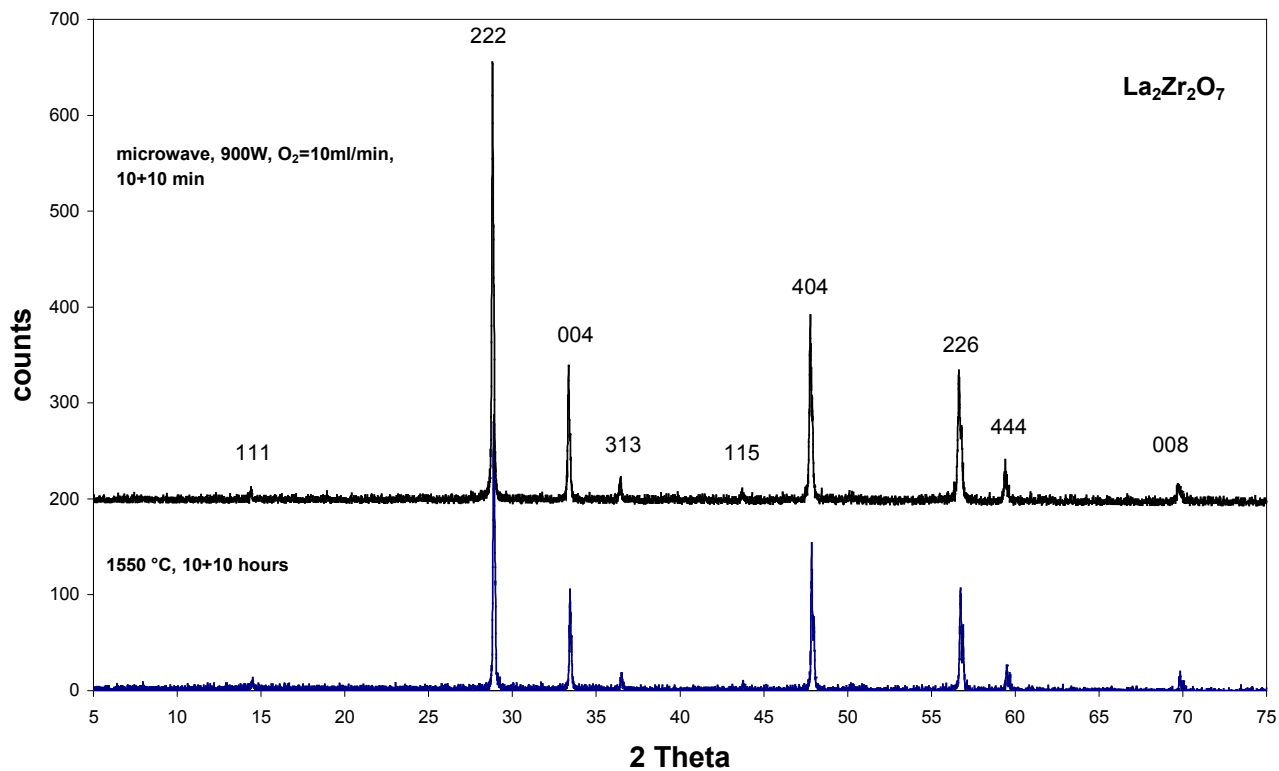
^bLeeds Electron Microscopy and Spectroscopy (LEMAS) Centre, Institute of Materials Research , University of Leeds, Leeds LS2 9JT, UK

Supplementary Information

	Pages
PXRD comparison of microwave and furnace prepared $\text{Ln}_2\text{Zr}_2\text{O}_7$ and $\text{Ln}_4\text{Zr}_3\text{O}_{12}$	2-11
SEM comparison of microwave and furnace prepared $\text{Ln}_2\text{Zr}_2\text{O}_7$ and $\text{Ln}_4\text{Zr}_3\text{O}_{12}$	11-13
Microwave apparatus diagrams	14
Heating profiles of microwave prepared $\text{Ln}_2\text{Zr}_2\text{O}_7$ and $\text{Ln}_4\text{Zr}_3\text{O}_{12}$	15-20

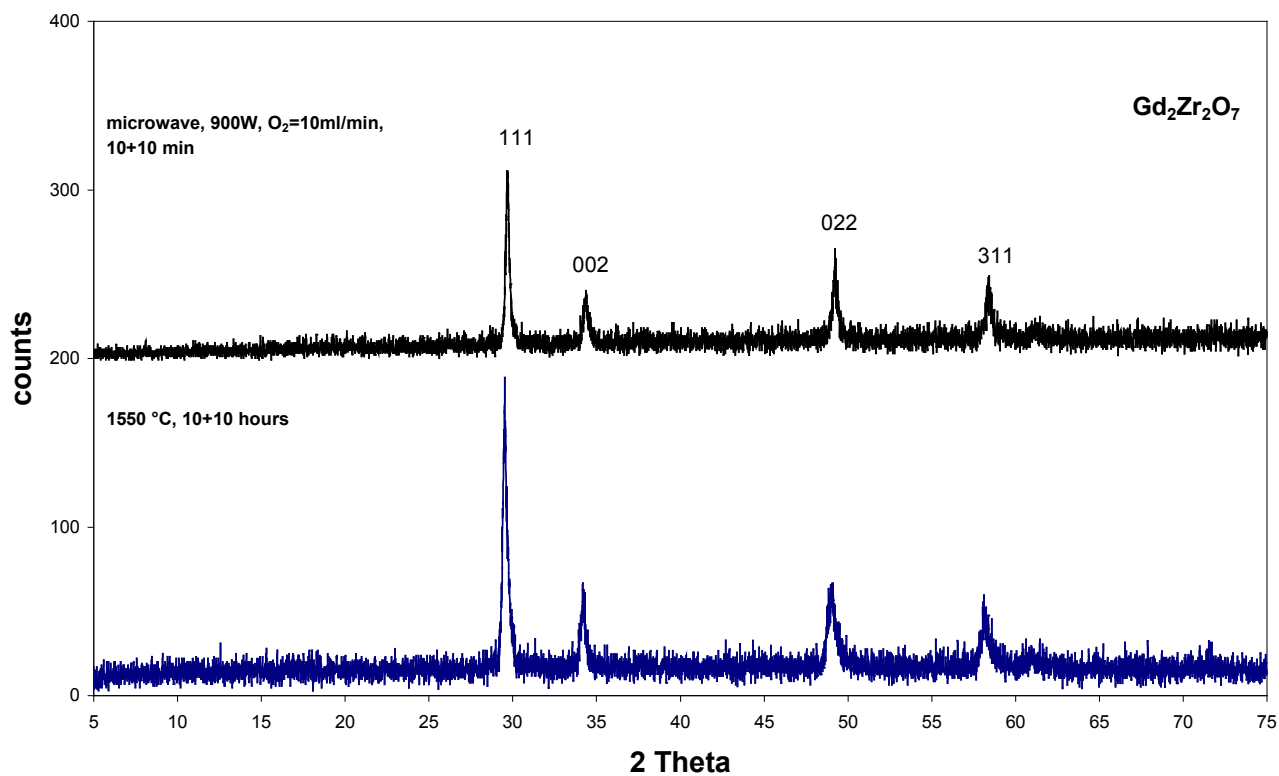


	Furnace	Microwave	Reference ^[9a]
Space Group	Fm $\bar{3}$ m	Fm $\bar{3}$ m	Fm $\bar{3}$ m
Lattice Parameter a	5.201(8) Å	5.175(9)Å	5.211 Å

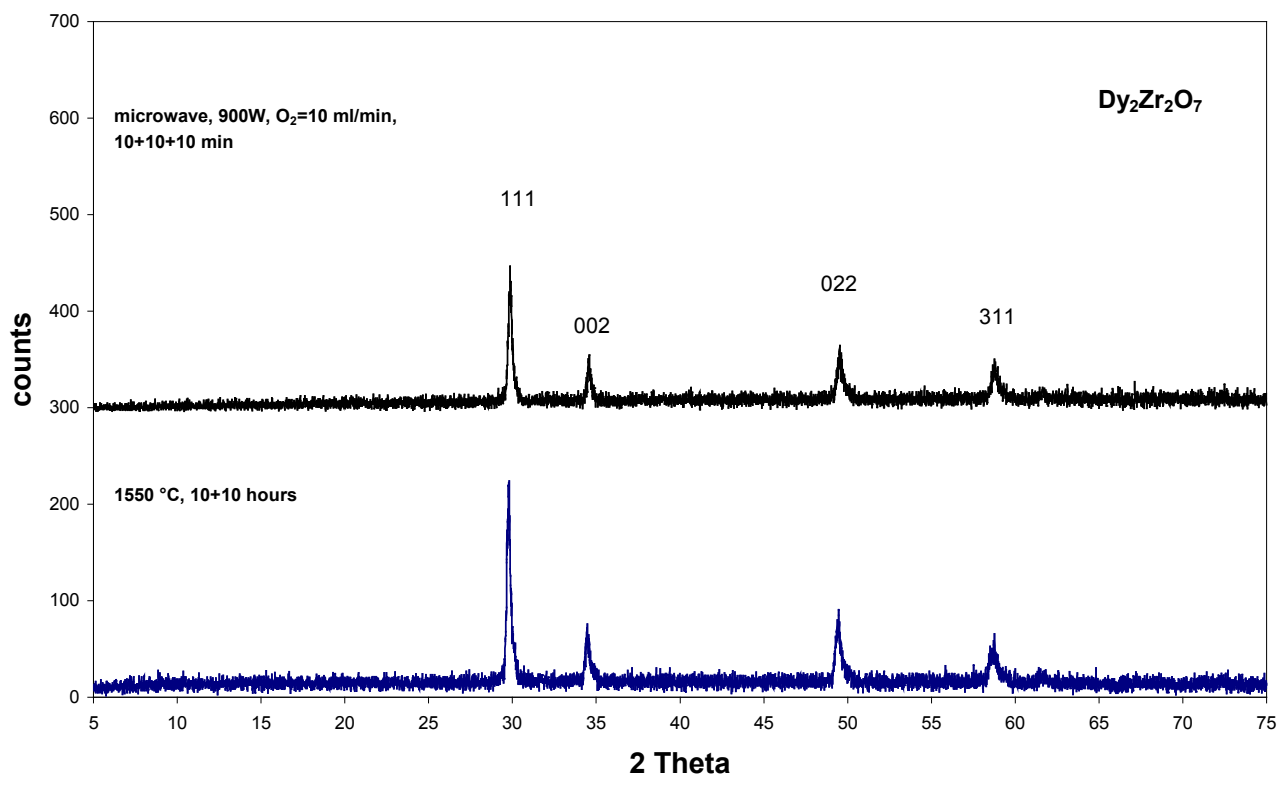


	Furnace	Microwave	Reference ^[&]
Space Group	$\text{Fd } \bar{3}\text{m}$	$\text{Fd } \bar{3}\text{m}$	$\text{Fd } \bar{3}\text{m}$
Lattice Parameter a	10.73(2) Å	10.77(2)Å	10.882 Å

[&] M. E. Björketuna, C. S. Knee, B. J. Nymana and G. Wahnströma, *Solid State Ionics*, 2008, **178**, 1642-1647.

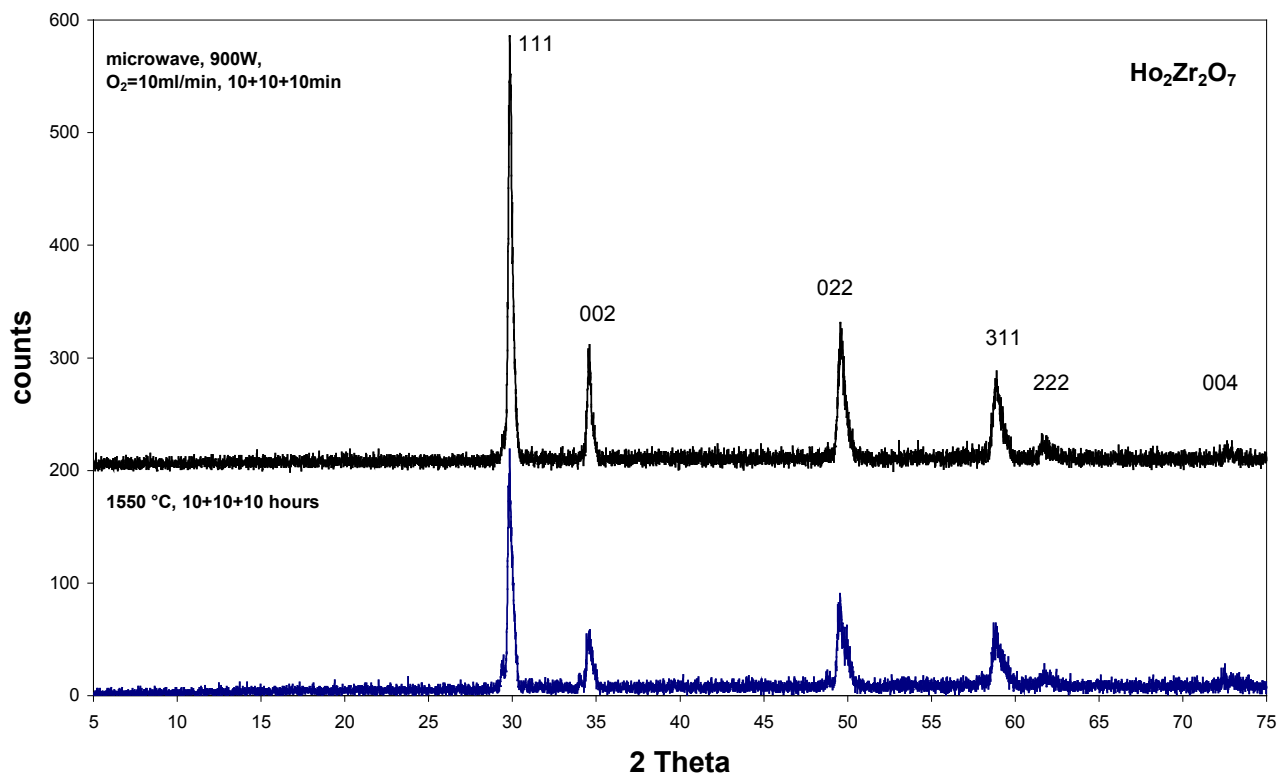


	Furnace	Microwave	Reference ^[9a]
Space Group	Fm $\bar{3}m$	Fm $\bar{3}m$	Fm $\bar{3}m$
Lattice Parameter a	5.24(2) Å	5.22 (4)Å	5.280 Å



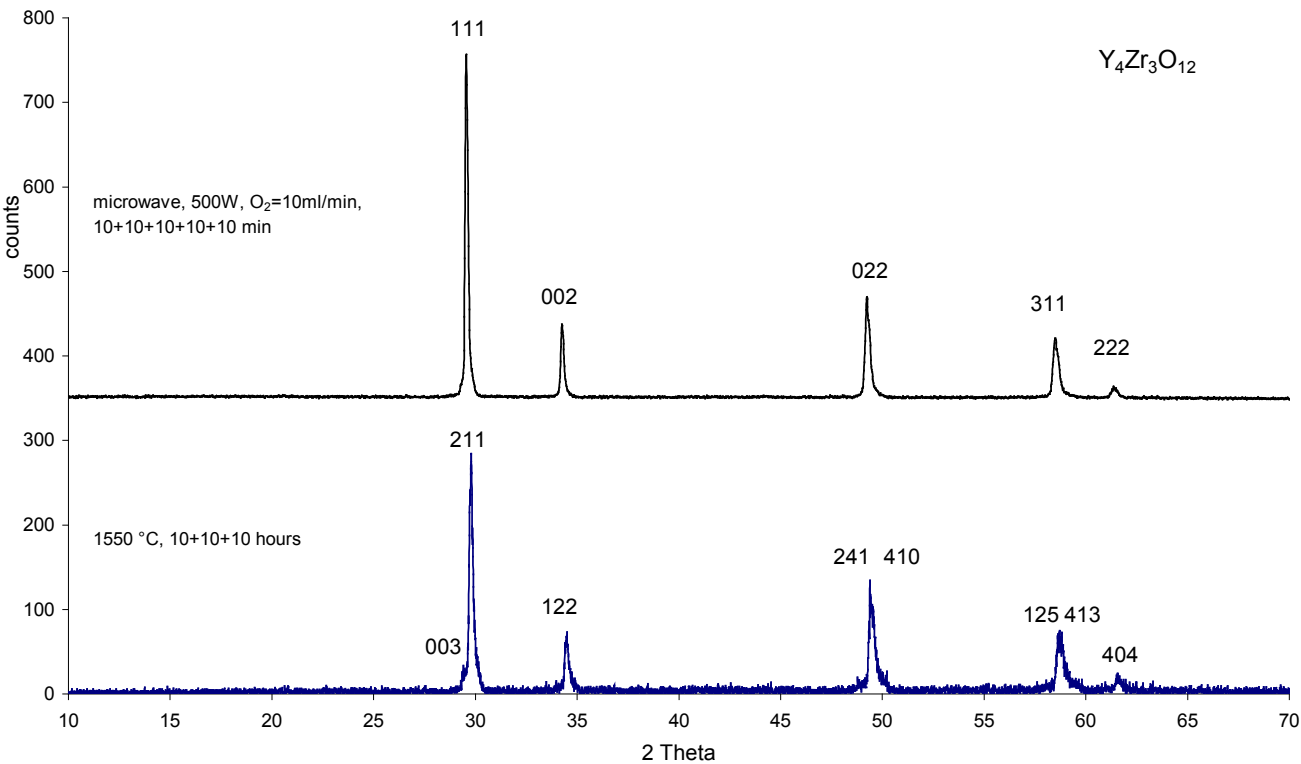
	Furnace	Microwave	Reference ^[†]
Space Group	Fm $\bar{3}$ m	Fm $\bar{3}$ m	Fm $\bar{3}$ m
Lattice Parameter a	5.210(6) Å	5.20 (5)Å	5.21Å

[†] data from ICSD ref Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser (1967) **35**, 1-37



	Furnace	Microwave	Reference ^[†]
Space Group	Fm $\bar{3}$ m	Fm $\bar{3}$ m	Fm $\bar{3}$ m
Lattice Parameter a	5.19(4) Å	5.19 (2) Å	5.2 Å

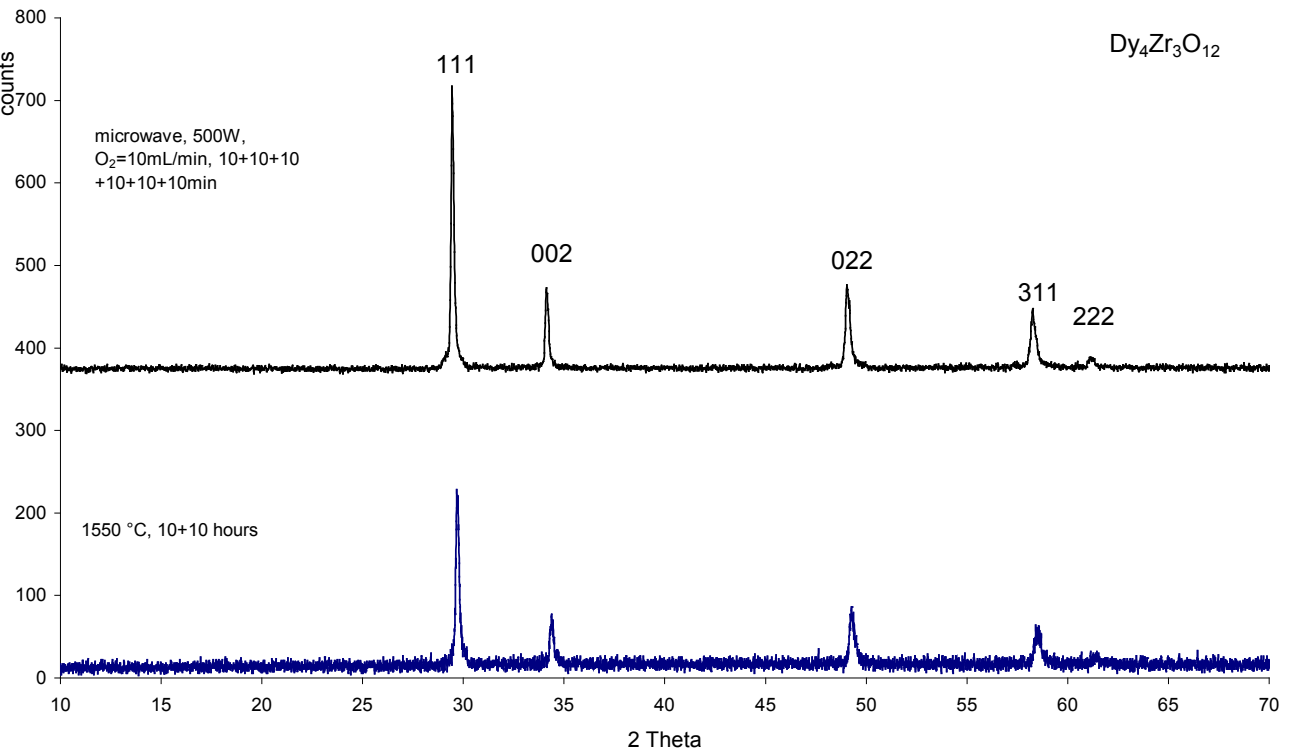
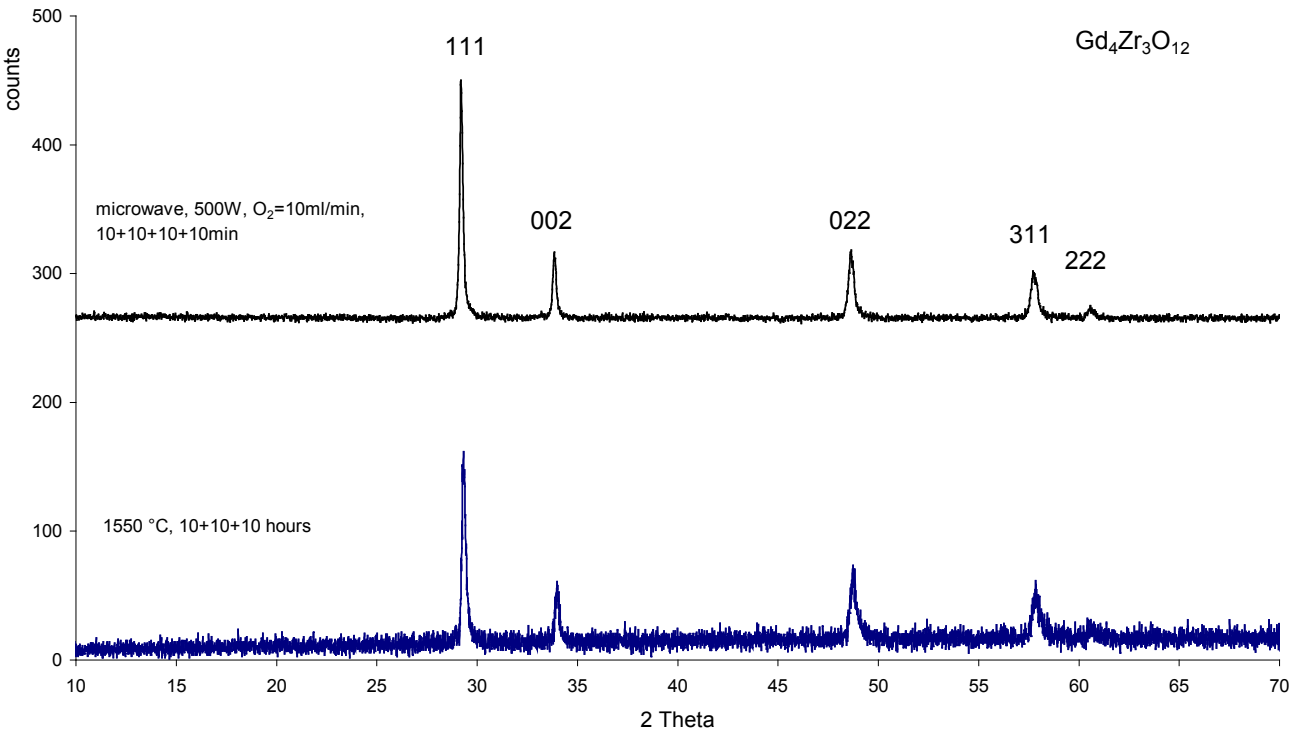
[†] data from ICSD ref Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser (1967) **35**, 1-37



	Furnace	Microwave	Reference ^[*]
Space Group	$R\bar{3}$ (hex)	$Fm\bar{3}m$	$R\bar{3}$ (hex)
Lattice Parameter a	9.74(2) Å	5.232(3)Å	9.729(1) - 9.738(2) Å
c	9.06(1) Å	5.232(3)Å	9.103(2) - 9.115(3) Å

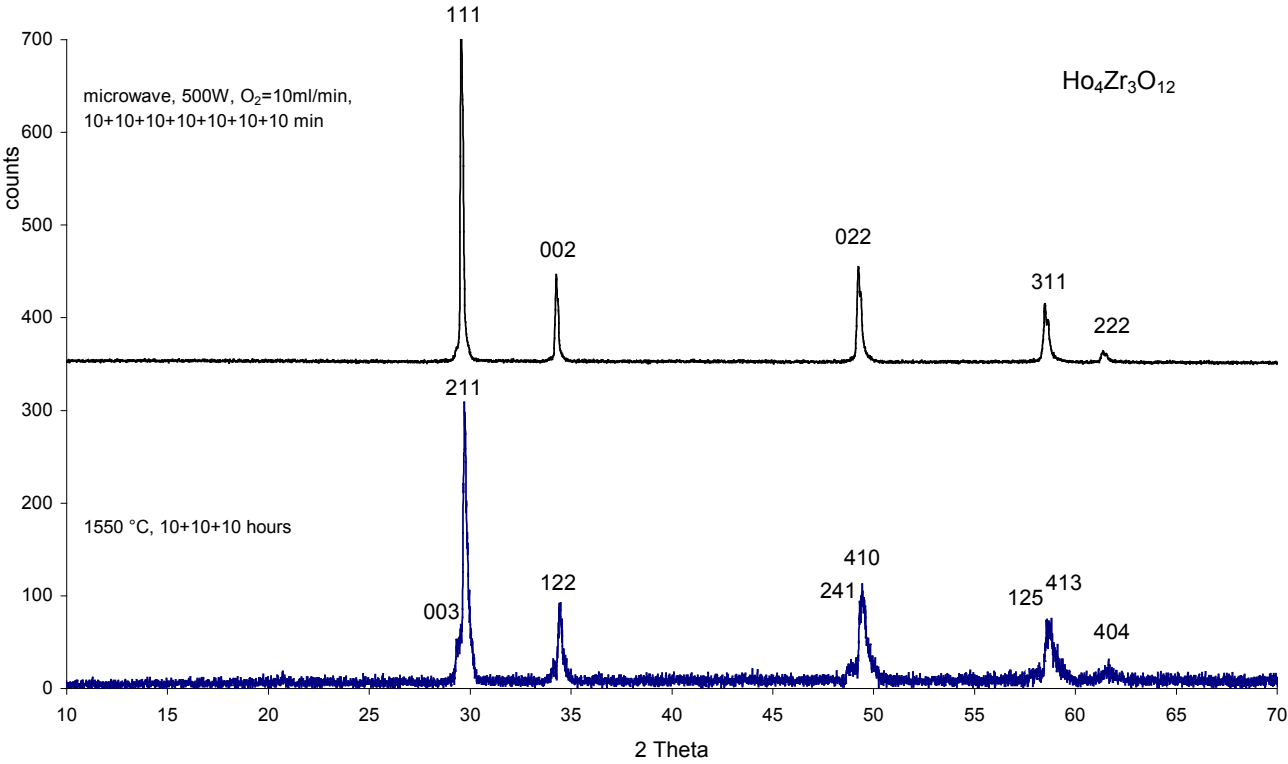
[*] V. P. Redko and L. M. Lopato, *Inorg. Mater.*, 1991, **27**, 1609-1614.

Space Group	Fm $\bar{3}m$	Fm $\bar{3}m$
Lattice Parameter	5.275(8) Å	5.295(1)Å



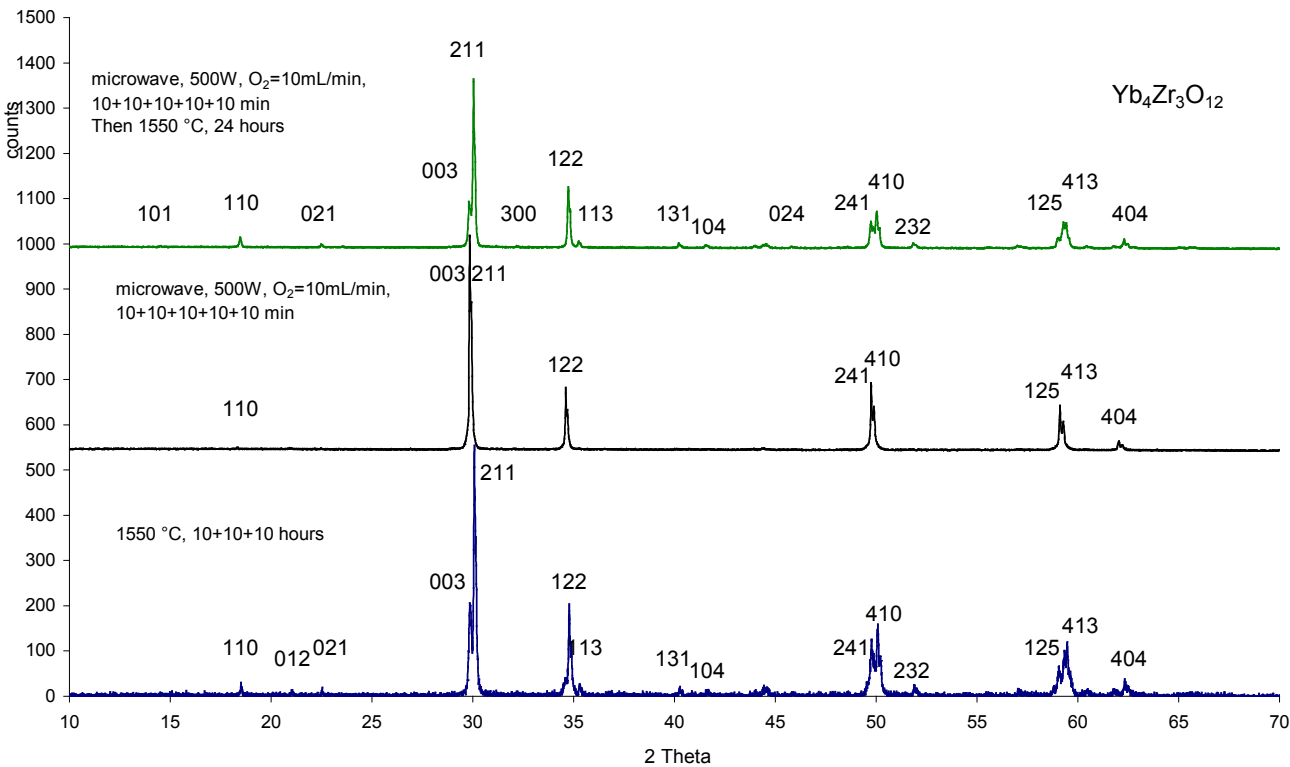
Furnace Microwave

Space Group	Fm $\bar{3}$ m	Fm $\bar{3}$ m
Lattice Parameter	5.22(4)Å	5.250(3)Å



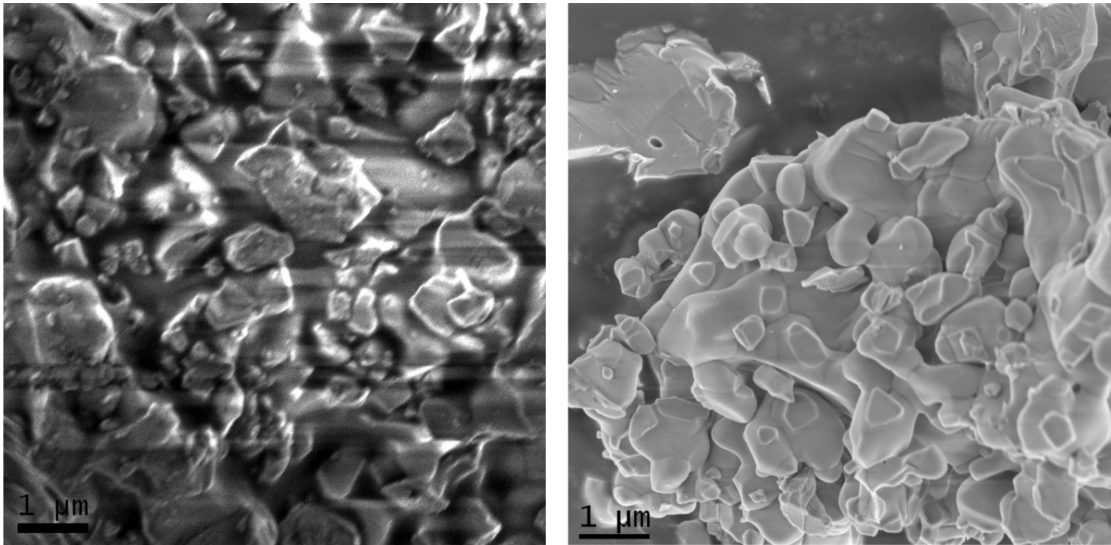
	Furnace	Microwave	Reference ^[*]
Space Group	R $\bar{3}$ (hex)	Fm $\bar{3}m$	R $\bar{3}$ (hex)
Lattice Parameter a	9.78(4) Å	5.233(2)Å	9.732(2) Å
c	8.94(8) Å	5.233(2)Å	9.109(3) Å

[*] V. P. Redko and L. M. Lopato, *Inorg. Mater.*, 1991, **27**, 1609-1614.

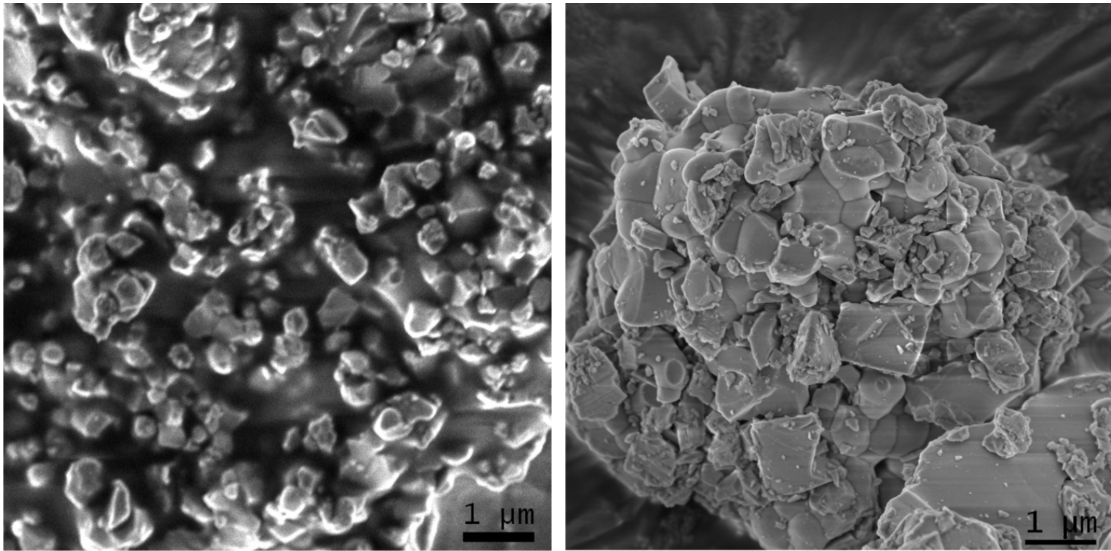


	Furnace	Microwave	Anneal	Low T ref ^[*]	High T ref ^[11]
Space Group	R $\bar{3}$ (hex)	R $\bar{3}$ (hex)	R $\bar{3}$ (hex)	R $\bar{3}$ (hex)	R $\bar{3}$ (hex)
Lattice a	9.64(3) Å	9.659(10) Å	9.641(6) Å	9.654(1) Å	9.68(3) Å
c	9.01(7) Å	8.987(1) Å	9.009(7) Å	9.021(1) Å	8.96(7) Å

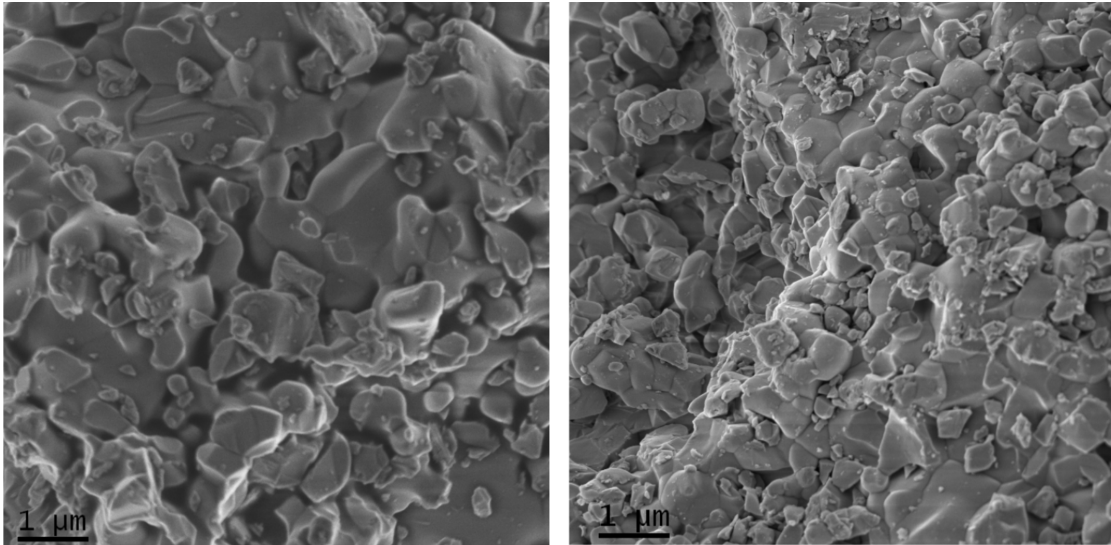
[*] V. P. Redko and L. M. Lopato, *Inorg. Mater.*, 1991, **27**, 1609-1614.



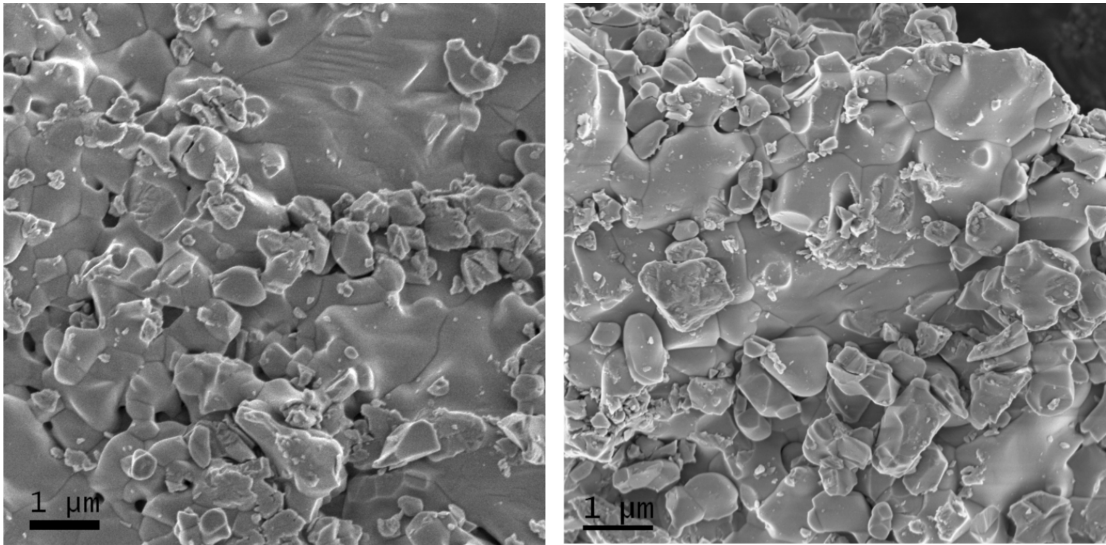
$\text{Y}_2\text{Zr}_2\text{O}_7$ microwave synthesis (left); furnace synthesis (right)



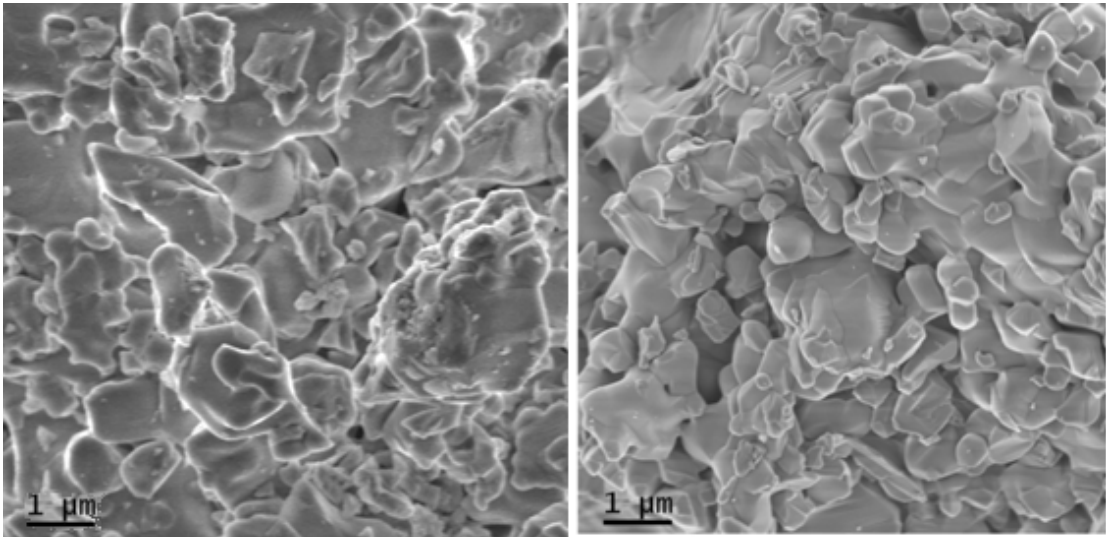
$\text{La}_2\text{Zr}_2\text{O}_7$ microwave synthesis (left); furnace synthesis (right)



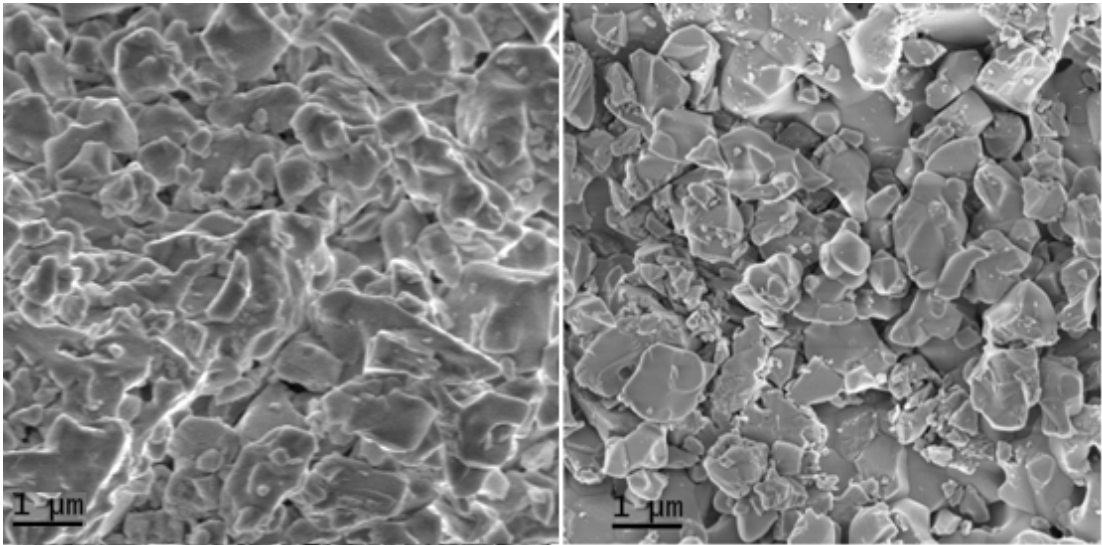
$\text{Gd}_2\text{Zr}_2\text{O}_7$ microwave synthesis (left); furnace synthesis (right)



Dy₂Zr₂O₇ microwave synthesis (left); furnace synthesis (right)

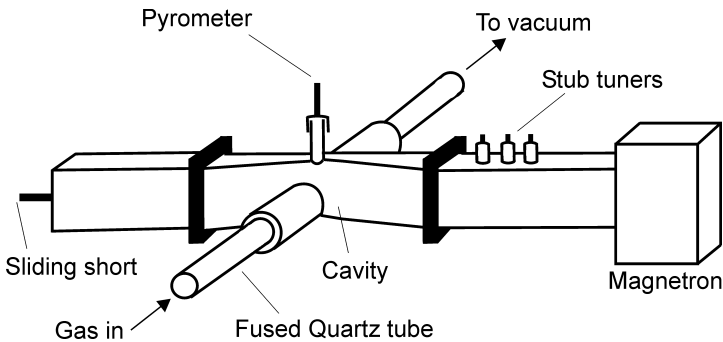
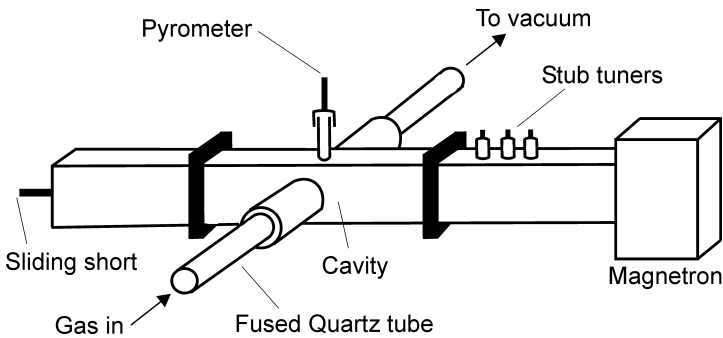


Gd₄Zr₃O₁₂ microwave synthesis (left); furnace synthesis (right)

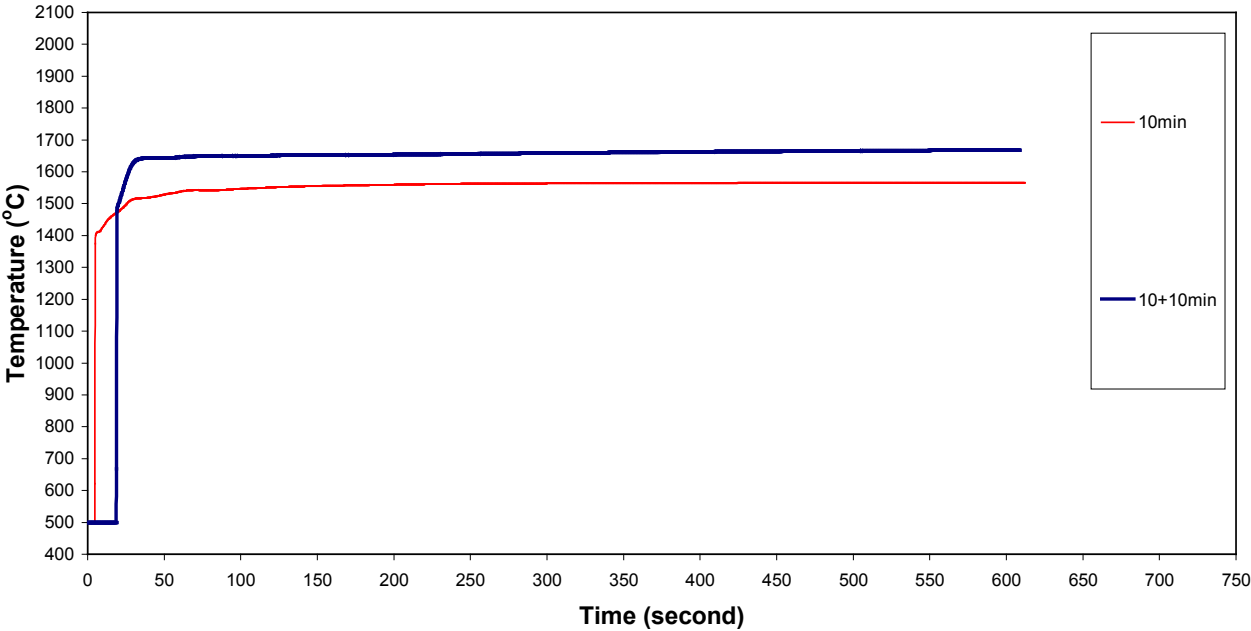


Dy₄Zr₃O₁₂ microwave synthesis (left); furnace synthesis (right)

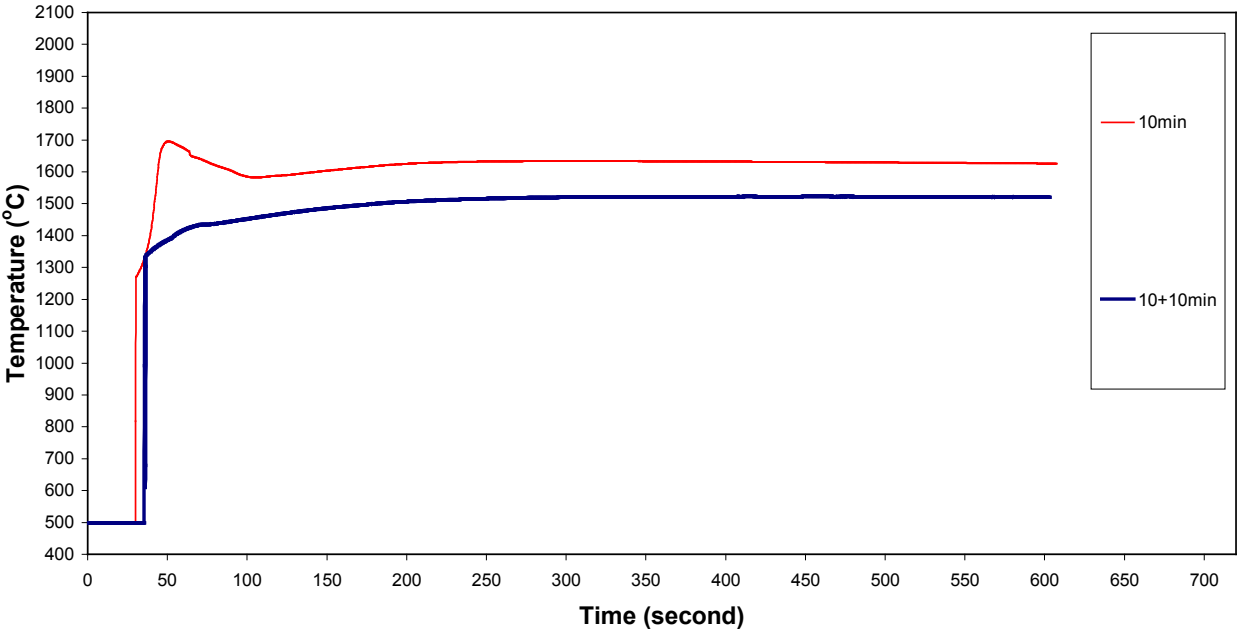
Microwave apparatus used for temperature measurements and synthetic reactions. The unfocussed cavity (top) was used for the $\text{Ln}_2\text{Zr}_2\text{O}_7$ systems and the focussed cavity (bottom) was used for the $\text{Ln}_4\text{Zr}_3\text{O}_{12}$ systems.



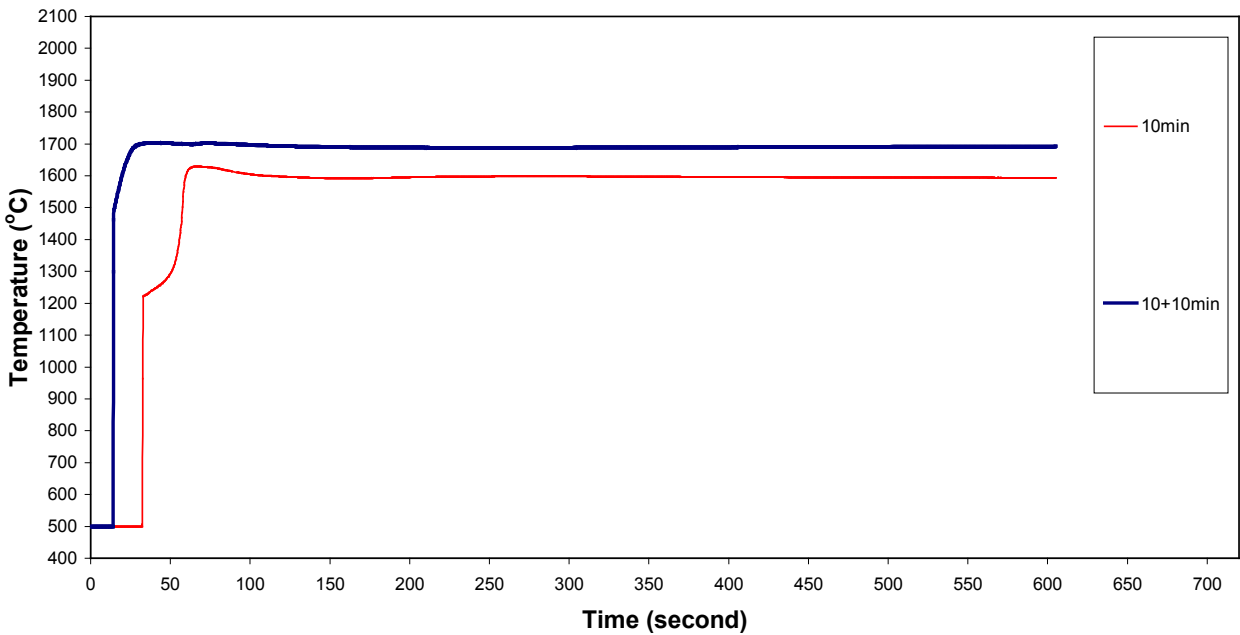
Y₂Zr₂O₇ heating profile at O₂=10ml/min, 900W



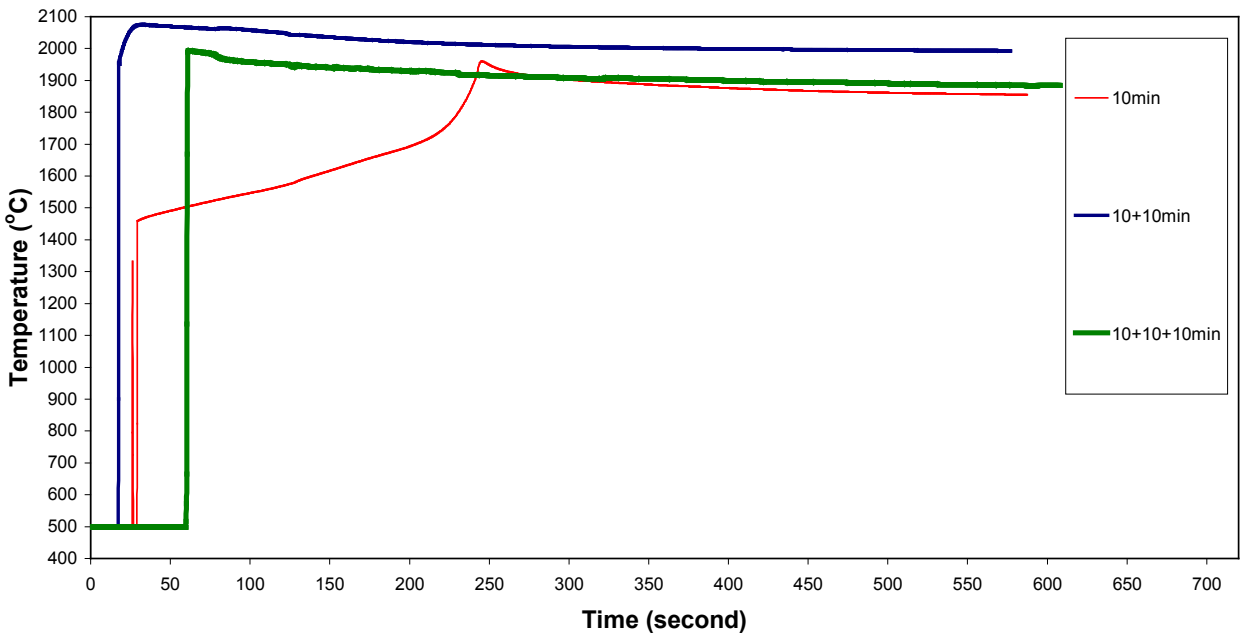
La₂Zr₂O₇ heating profile at O₂=10ml/min, 900W



Gd₂Zr₂O₇ heating profile at O₂=10ml/min, 900W

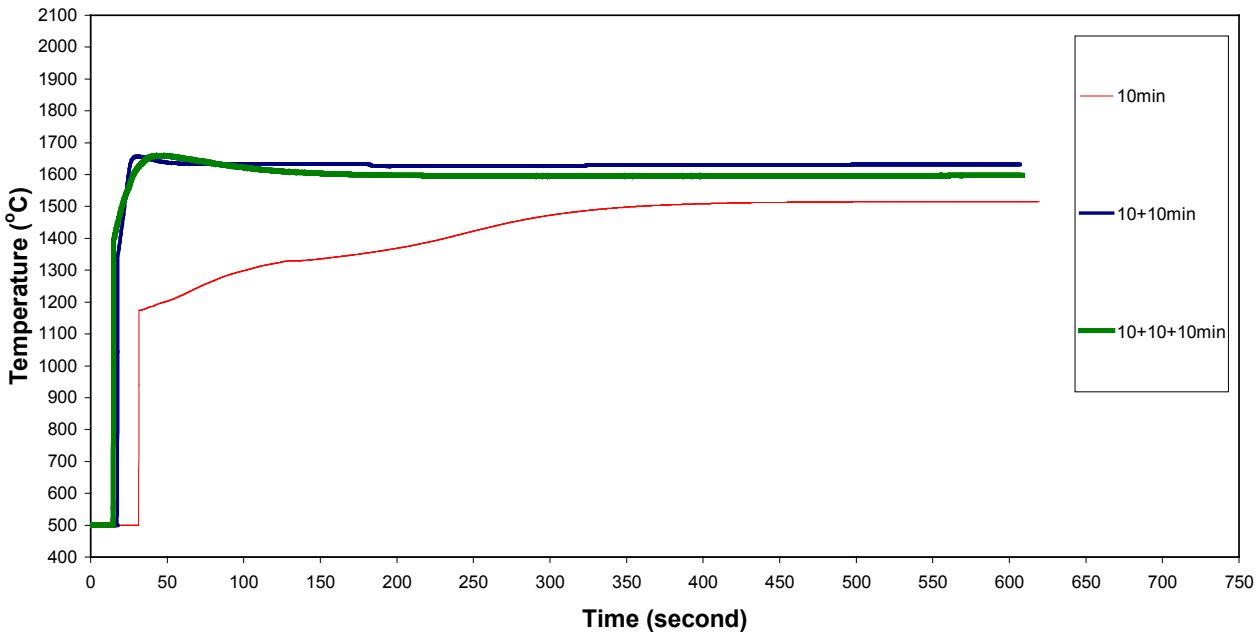


Dy₂Zr₂O₇ heating profile at O₂=10ml/min, 900W

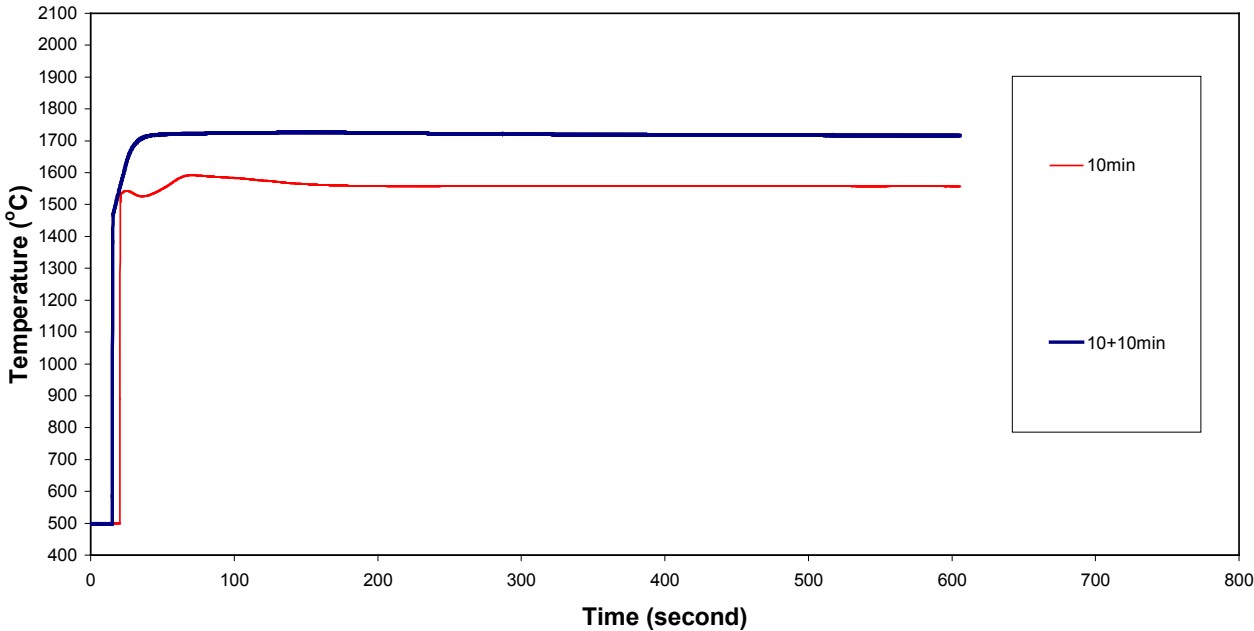


Please note: Sudden drops in the recorded temperature early in the heating process are due to plasma interference, arising from absorption of surface emitted photons by the plasma. Visually, the plasma exhibits some instability early in the experiments but subsequently stabilises, allowing uninterrupted temperature measurement.

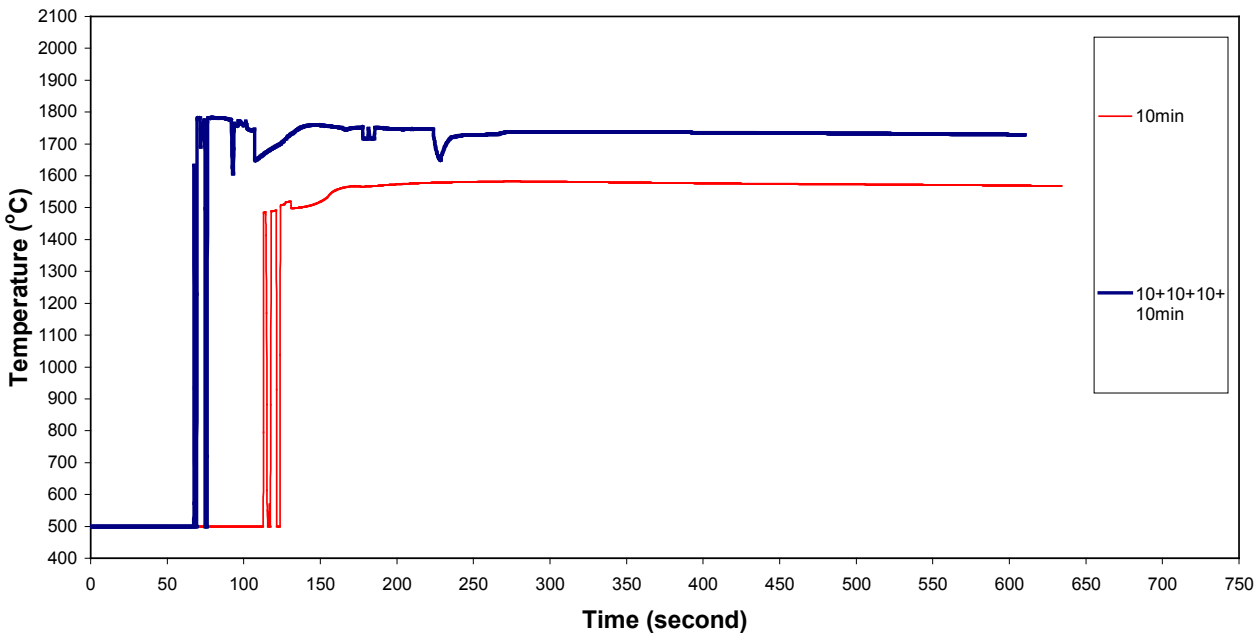
Ho₂Zr₂O₇ heating profile at O₂=10ml/min, 900W



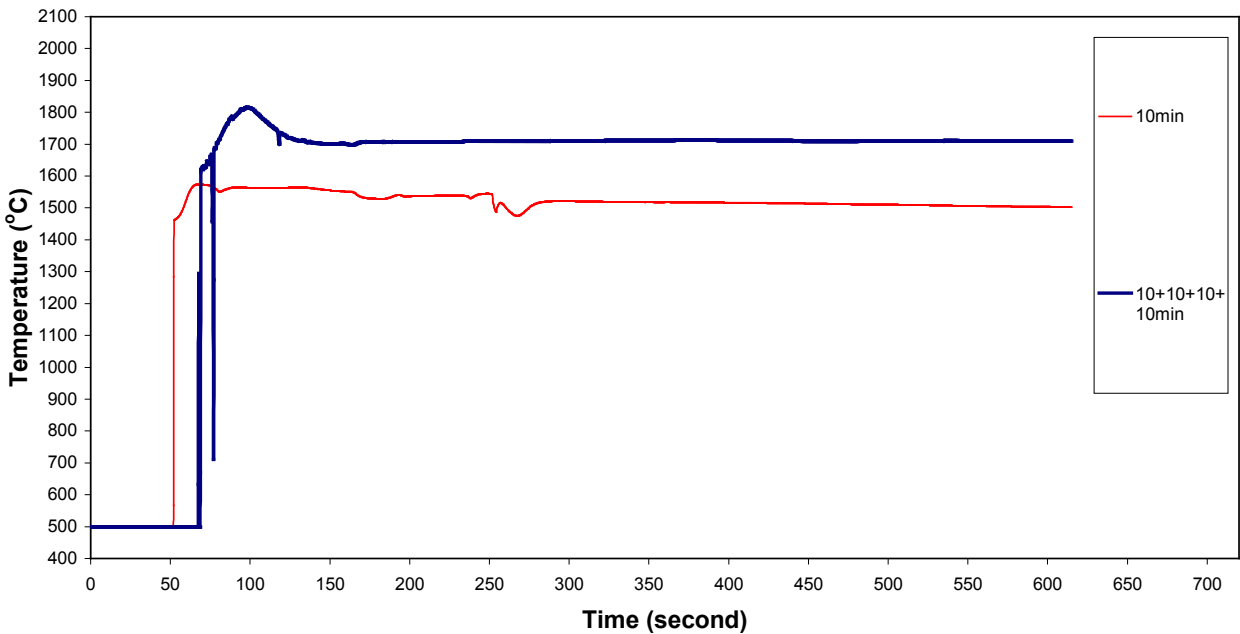
Yb₂Zr₂O₇ heating profile at O₂=10ml/min, 900W



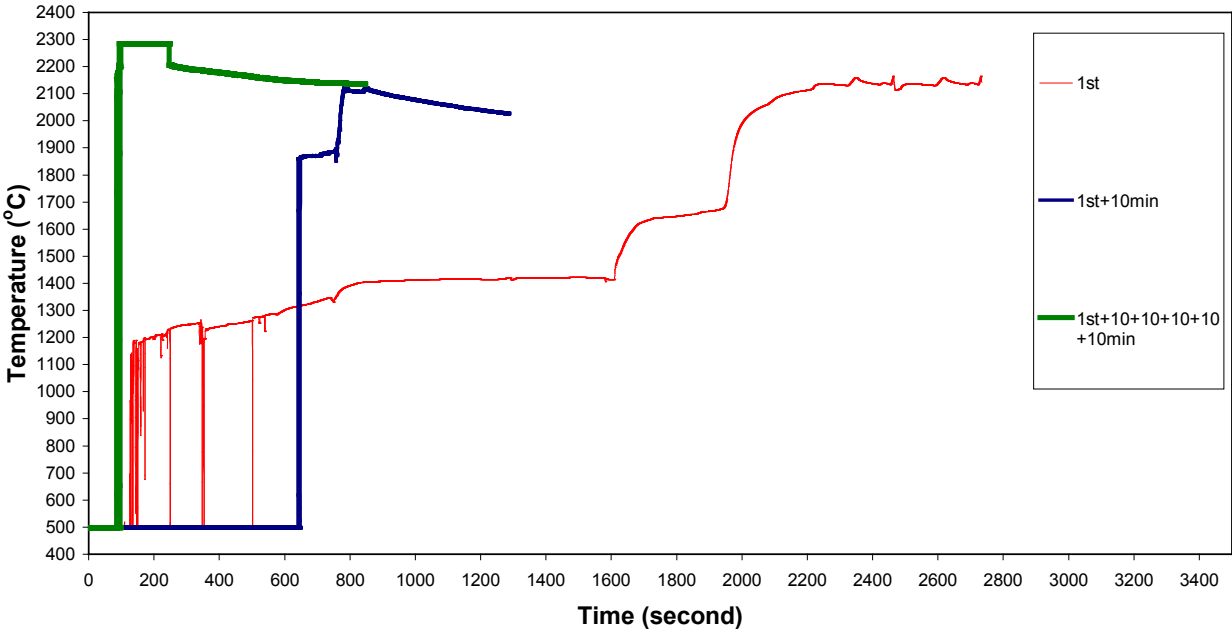
Y₄Zr₃O₁₂ heating profile at O₂=10ml/min, 500W



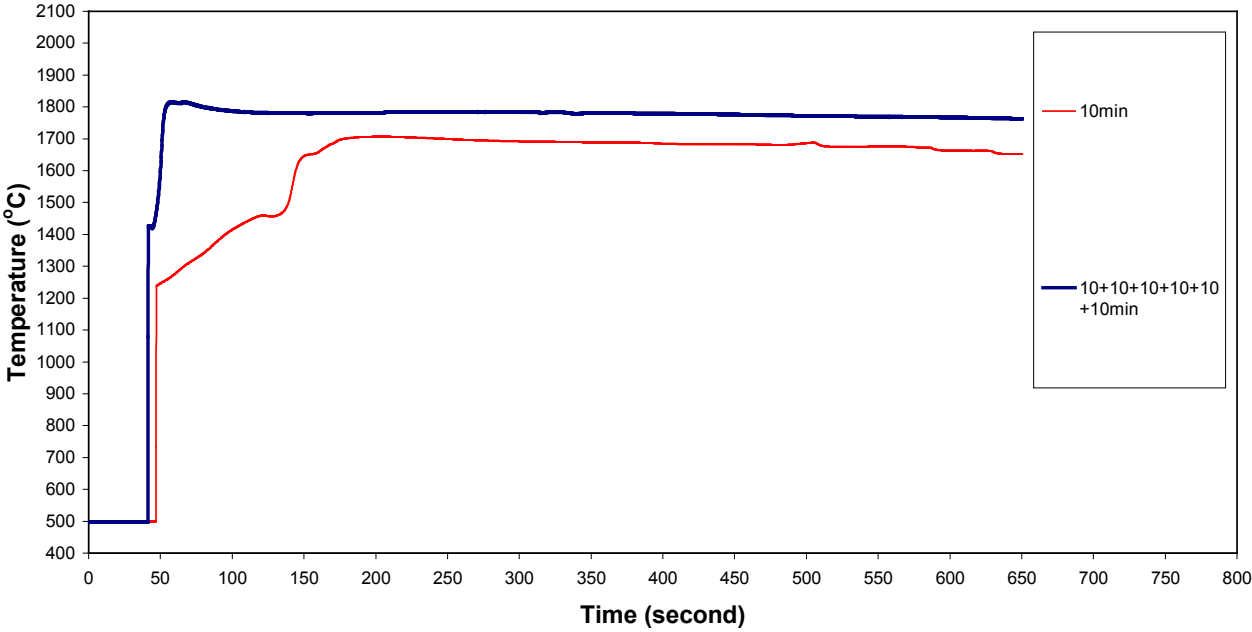
Gd₄Zr₃O₁₂ heating profile at O₂=10ml/min, 500W



Dy₄Zr₃O₁₂ heating profile at O₂=10ml/min, 500W



Ho₄Zr₃O₁₂ heating profile at O₂=10ml/min, 500W



Yb₄Zr₃O₁₂ heating profile at O₂=10ml/min, 500W

