ROHM AND HAAS ELECTRONIC MATERIALS
MICROELECTRONIC TECHNOLOGIES

ALD of High-κ $LaErO_3$ and $LaYO_3$ Using Metal Amidinate Sources

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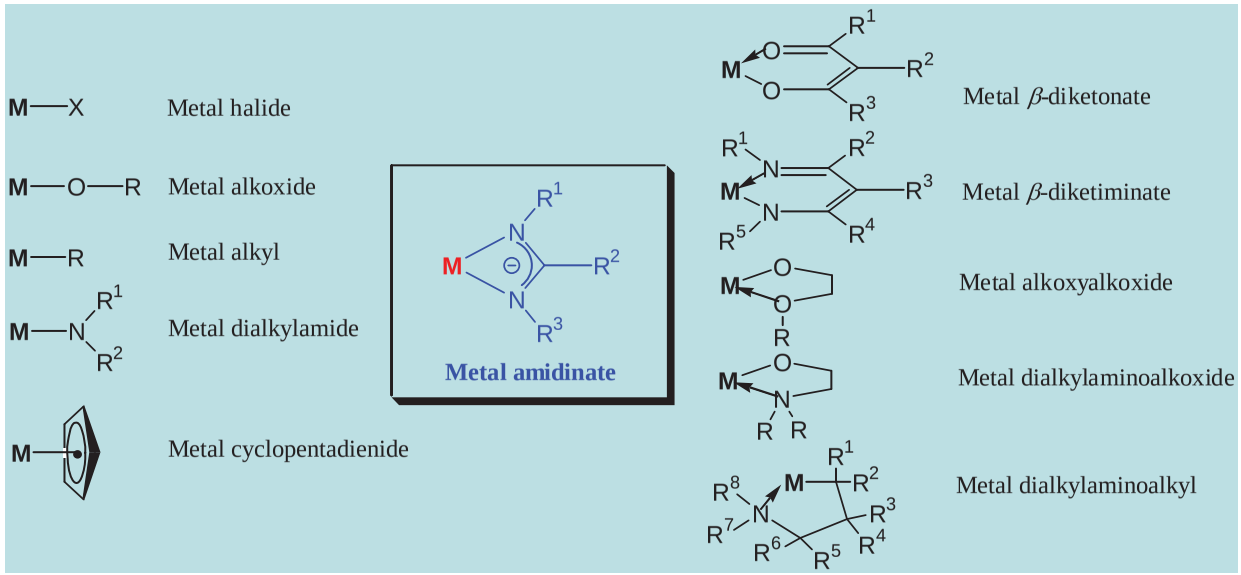
Selection of Suitable Platforms for ALD



Metal Amidinates

- **Bidentate "chelating" effects** ⇨ Improved thermal stability than amides
- **$R^{1,2,3}$ tuning in amidinate** ⇨ Volatility and reactivity control
- **No direct M-C bonds** ⇨ Less carbon incorporation in films

Stable Amorphous High-k Dielectrics

$LaMO_3$ (M = Lu, Y, Er, Yb) are alternative candidates to achieve higher k (30 – 40), and <1.0E-8A/cm² current leakage, with <10nm film thickness

Dielectric	*k*	*Conduction Band offset*	*Valance Band offset*
SiO_2	3.9	3.5	4.4
Al_2O_3	8	2.8	4.9
$HfSiO_4$	12	1.5	3.4
$LaAlO_3$	**18**	1.9	3.2
$LaHfO_x$	**20**	2.0	2.6
$GdScO_3$	**22**	2.0	2.5
$DyScO_3$	**22**	2.0	2.5
$LaLuO_3$	**32**	2.1	2.1

⇨ **$LaMO_3$ has potential to replace current high-k material**

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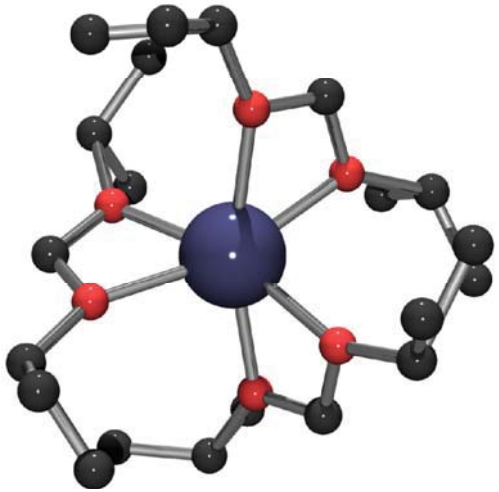
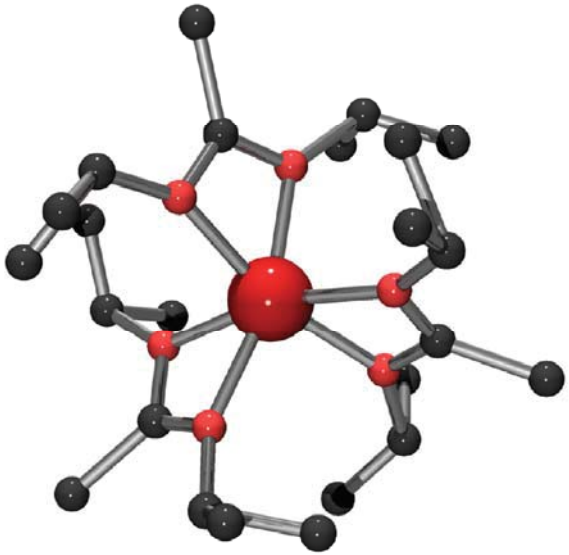
La, Y, and Er Amidinate Sources from Rohm and Haas



La-FAMD
La(*i*Pr$_2$-famd)$_3$

Y-AMD
Y(*i*Pr$_2$-amd)$_3$



Er-AMD
Er(*i*Pr$_2$-amd)$_3$

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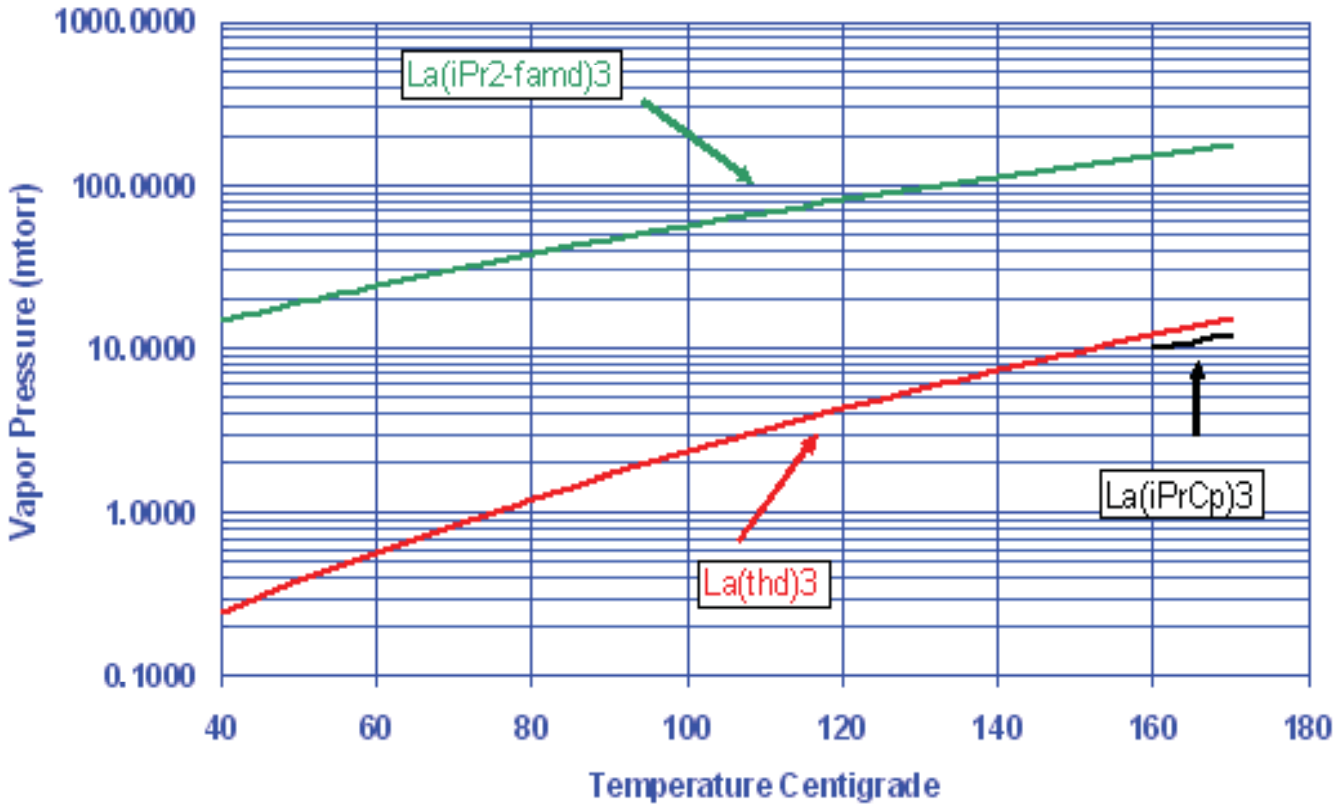
Properties of Lanthanoid Amidinate Precursors

Name	La-FAMD	Y-AMD	Er-AMD
M. W. (g/mol)	520.53	512.61	590.96
Appearance	White solid	White solid	Pink solid
M.P. (ºC)	193 -195	not observed below 250 ºC	not observed below 250 ºC
Density (g/mL)	0.55	0.51	0.53
Vapor Pressure	log P(Torr) = 1.8408 – 1151/T(K) **> 0.1 Torr @ 130 ºC**	log P(Torr) = 1.941 – 1117/T(K) **> 0.1 Torr @ 130 ºC**	log P(Torr) = 5.867 – 2377/T(K) **> 0.1 Torr @ 130 ºC**
Thermal Stability	**Stable to 300 ºC by ARC**	**Stable to 250 ºC by ARC**	**Stable to 250 ºC by ARC**
^{1}H NMR	organic impurity N.D.	organic impurity N.D.	organic impurity N.D.
ICP Purity	**>99.9999%**	**>99.99999%**	**>99.99999%**
Shelf life	Stable over 9 months	Stable over 9 months	Stable over 9 months
TGA	Clean evaporation with negligible residue	Clean evaporation with negligible residue	Clean evaporation with negligible residue

Vapor Pressure Curves for La Sources



- ***La-FAMD offers higher vapor pressure than other platforms.***

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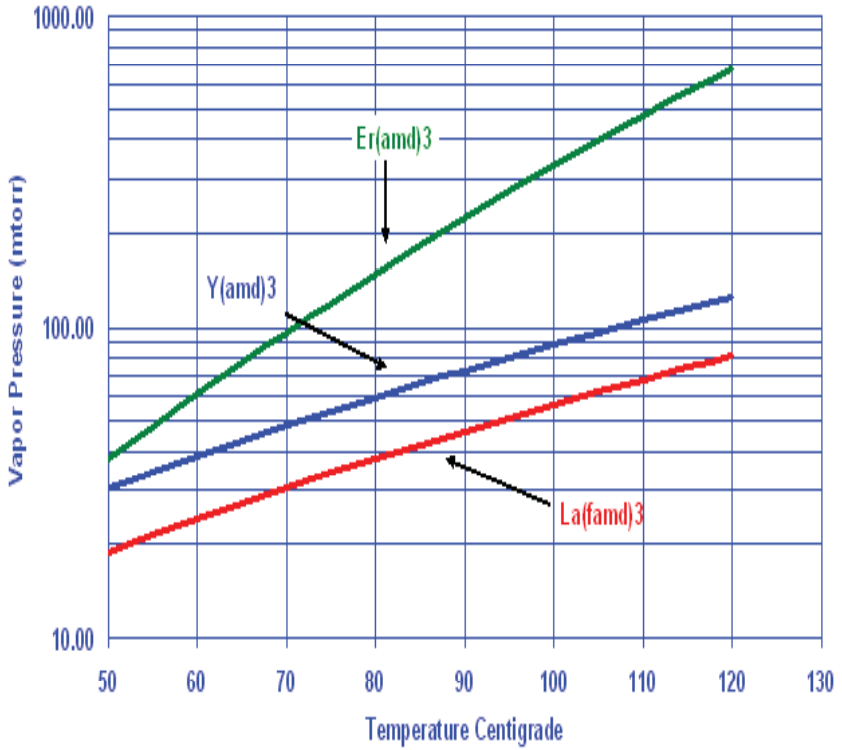
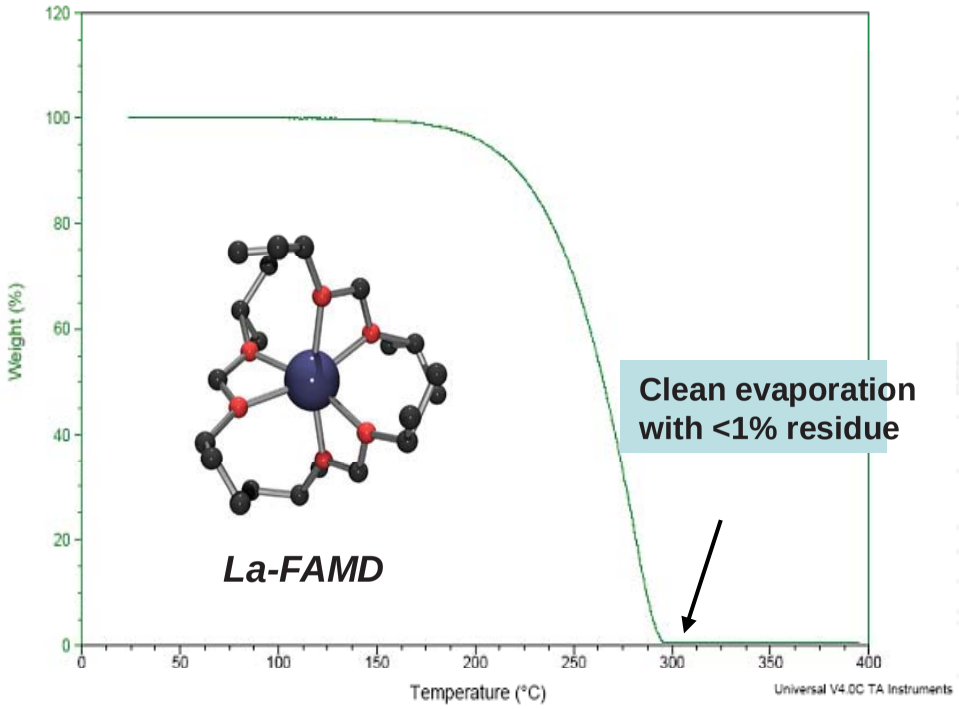
Vapor Pressure and TGA of La, Y, Er Amidinates





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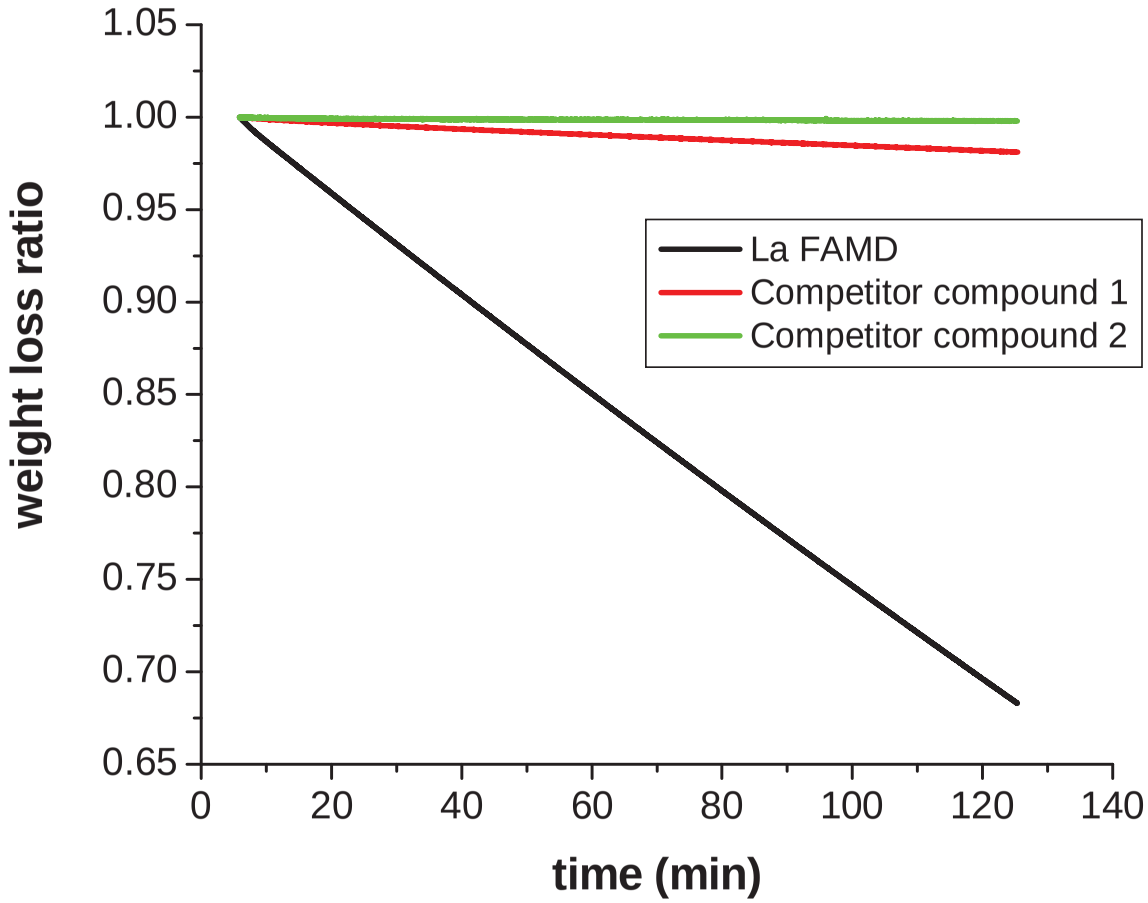
Evaporation Behavior of La Precursors by Isothermal TGA at 120 ºC



La FAMD Improved volatility than other commercial La precursors

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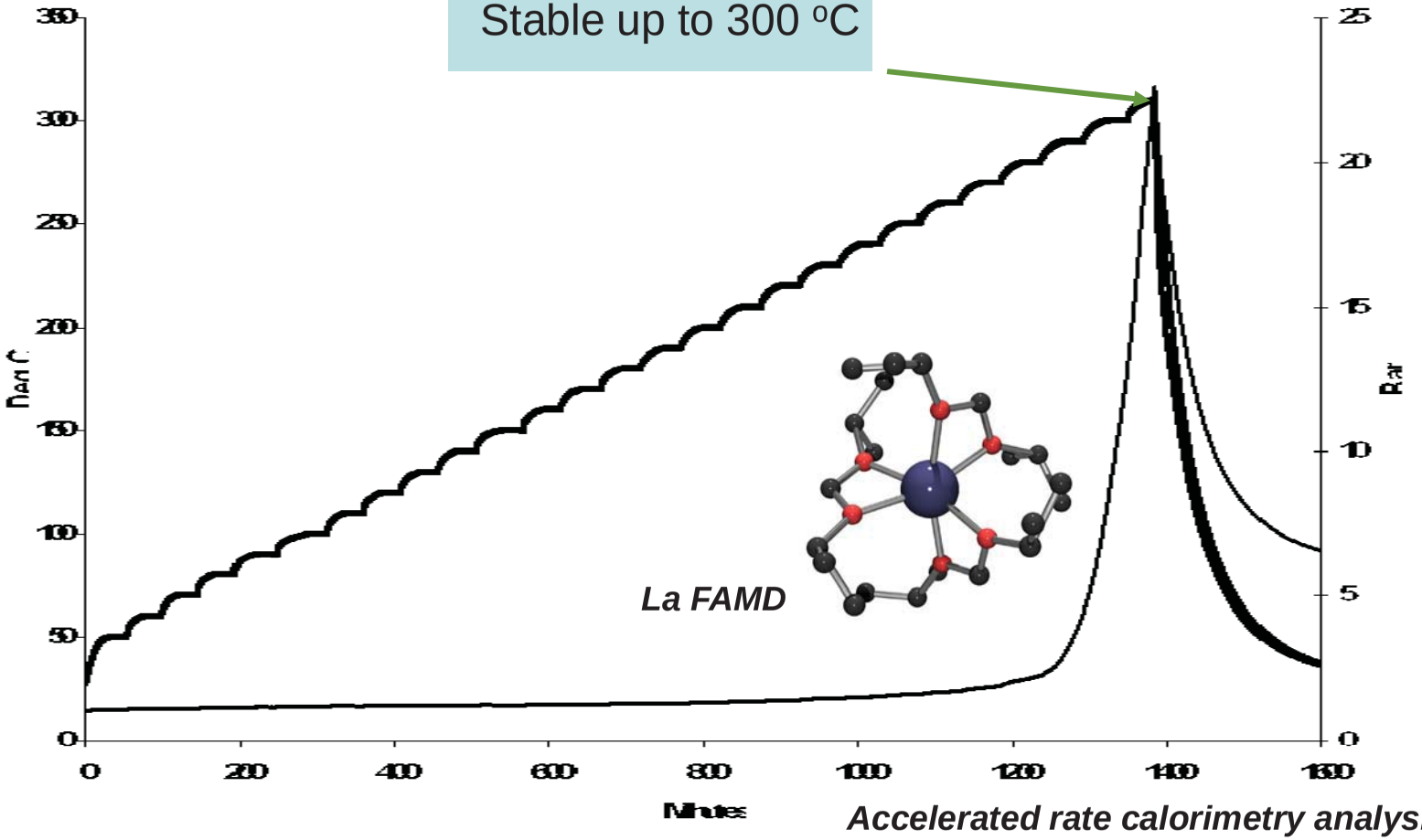
High Thermal Stability of Lanthanoid Amidinates

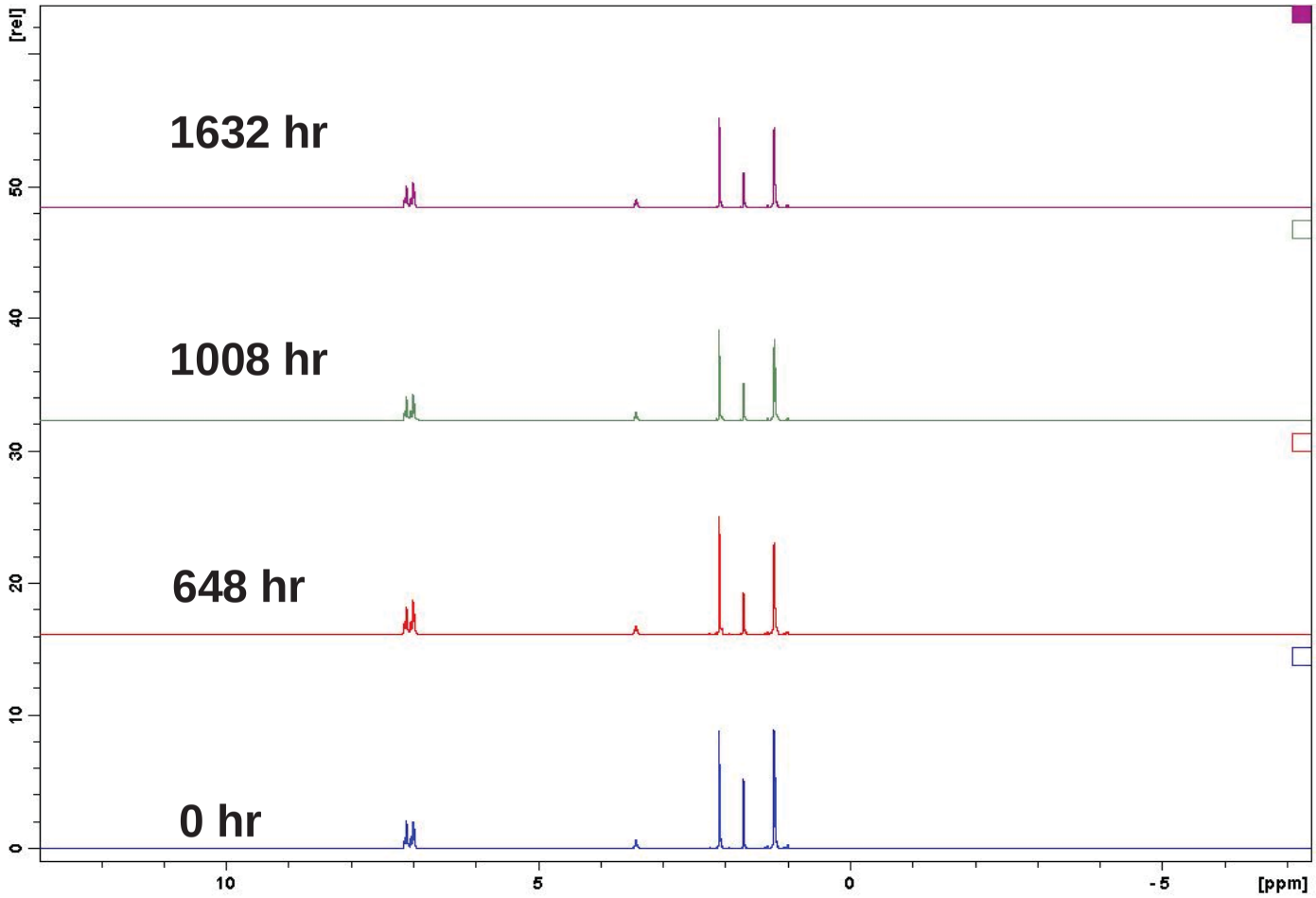
Stable up to 300 °C



La FAMD

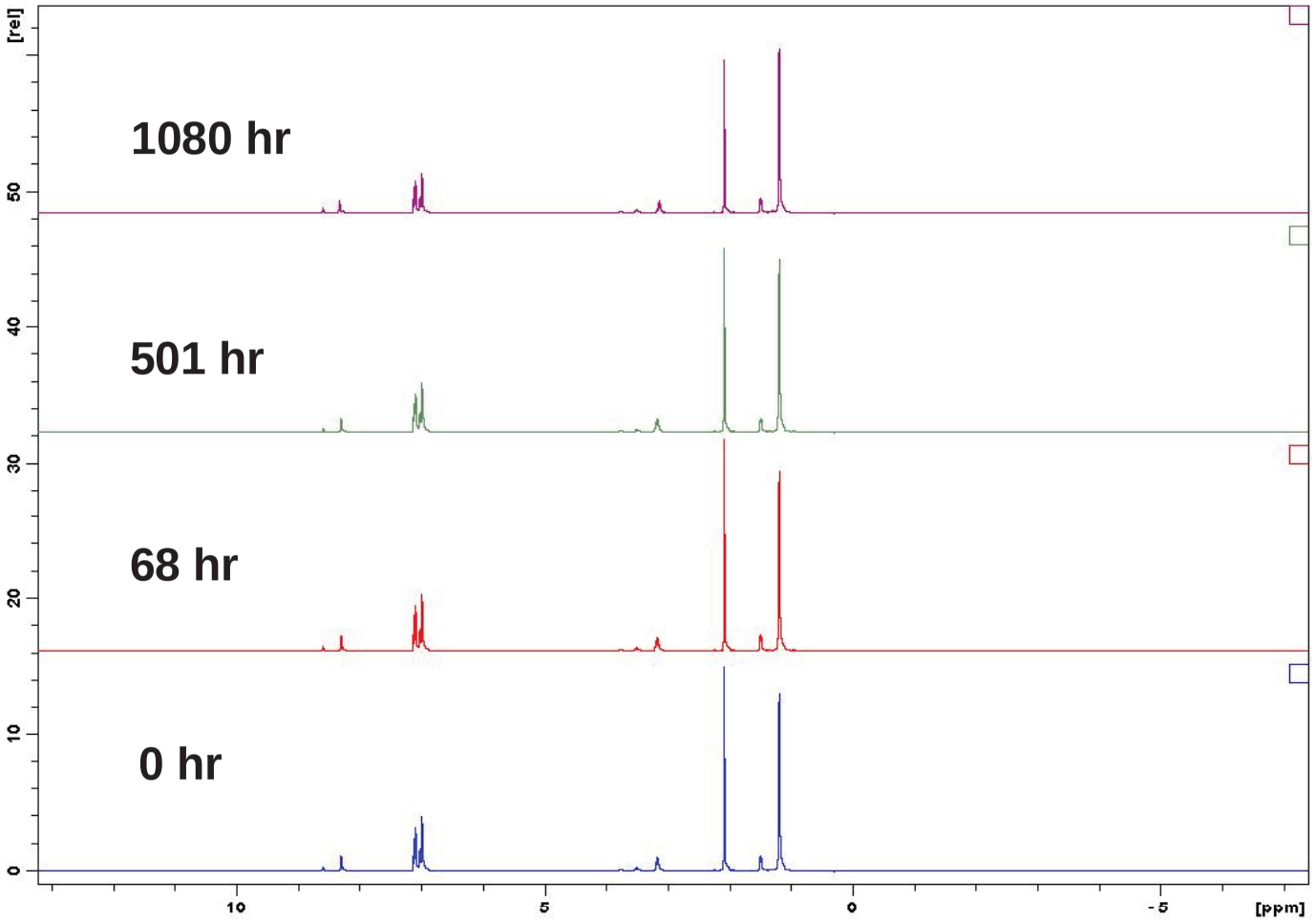
Accelerated rate calorimetry analysis

^{1}H NMR of Y AMD @ 200C



Y AMD High thermal stability demonstrated by NMR Study

^{1}H NMR of La FAMD @ 200C



La FAMD improved thermal stability demonstrated by NMR Study

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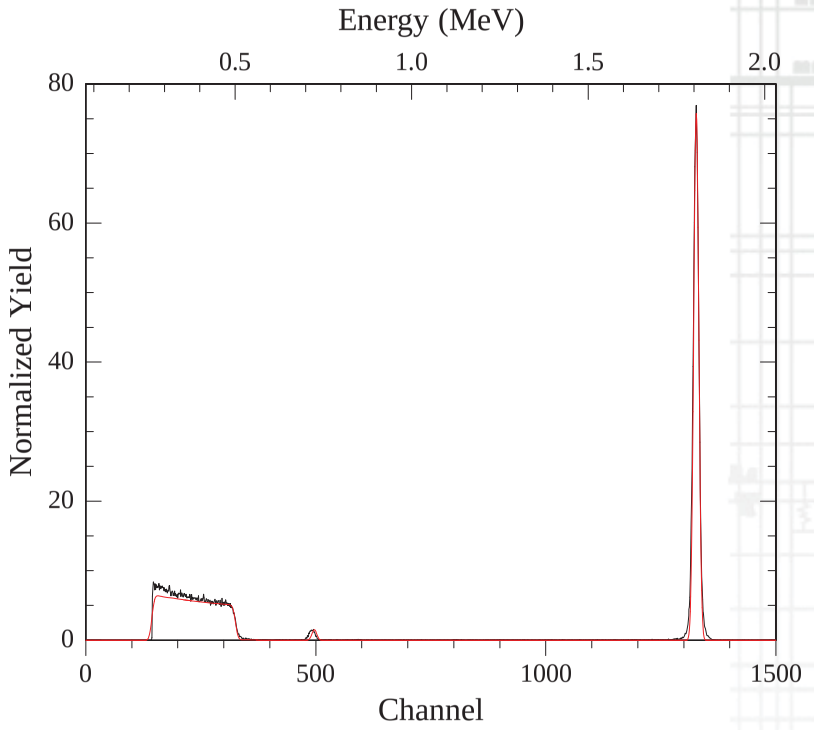
ALD Er_2O_3

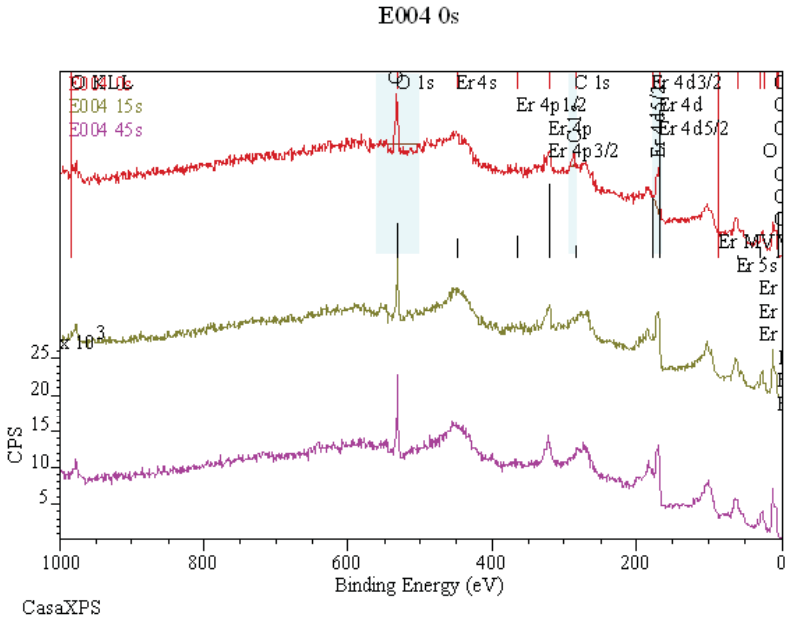
Er source temperature 140 °C

ALD with H_2O at 300 °C substrate temperature
=> Er_2O_3 @ 0.83 Angstrom/cycle

No impurities in film by RBS on C substrate

Film density 6.8 g cm^{-3}, ~80 % of bulk density





with surface C contamination

No C after sputtering

No carbon in film by XPS

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ALD Er_2O_3

Cubic crystal structure