REACTIVE FIELD ASSISTED SINTERING (FAST/SPS) OF VARIOUS GARNETS FOR PLASMA ETCHING APPLICATIONS

XVIII ECerS LYON I 6/29/2023

CHRISTIAN STERN, MORITZ KINDELMANN, CHRISTIAN SCHWAB, INHEE PARK, MARTIN BRAM, OLIVIER GUILLON

MOTIVATION - PLASMA ETCHING

YAG ($Y_3Al_5O_{12}$) is an advanced material used in **plasma etching chambers**

Continuous improvement of the etching process over the last decades puts higher demands on etching conditions:

- High cleanliness
- Wafer to wafer reproducibility

For further miniaturization of transistors: need for materials with higher plasma resistance and advanced etching devices

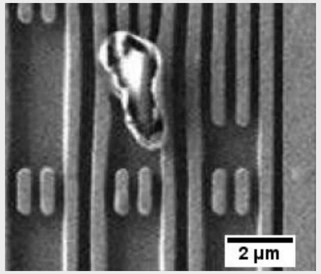
Hypothesis: Plasma resistance of YAG can be improved by **replacement of Y by rare earth ions** (Er, Yb, Lu)

Etching chamber

[1]

Producer® Selectra® Etch

"Killer defect" on wafer



[2]

1. https://www.appliedmaterials.com/us/en/product-library/producer-selectra-etch.html#carousel-94c4c76187-item-f3e253bb6e-tabpanel
2. Hong Shih. *"A Systematic Study and Characterization of Advanced Corrosion Resistance […]."* Corrosion Resistance. DOI: 10.5772/31992

OBJECTIVES

- Substitution of Y in YAG with rare earth elements
- Synthesis of various garnets by reactive FAST/SPS
- Systematic etching study in fluorine based etching plasma
- Investigation of plasma erosion by AFM, SIMS and TEM

Produced samples:

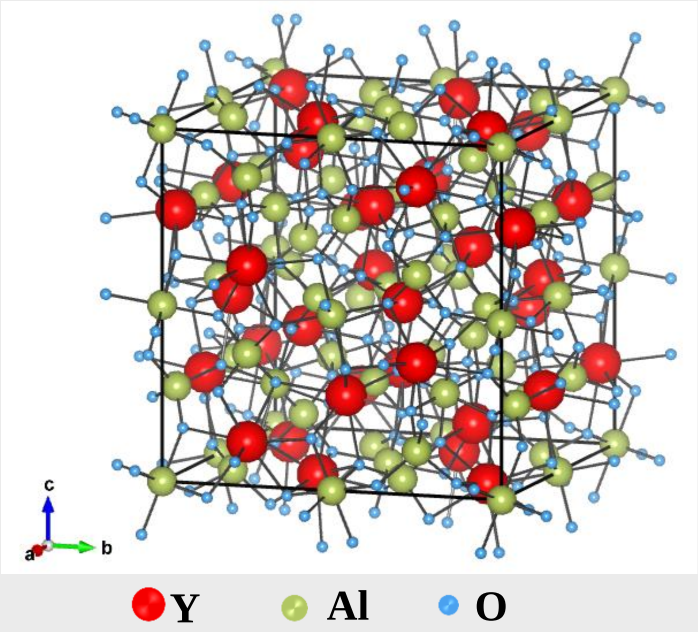
Sample	Composition
YAG	$Y_3Al_5O_{12}$
YbAG	$Yb_3Al_5O_{12}$
LuAG	$Lu_3Al_5O_{12}$
ErAG	$Er_3Al_5O_{12}$

Relevant ions:

Ion	Atomic mass [u]	Effective ionic radius [Å]
Y^{3+}	88.906	1.019
Er^{3+}	167.26	1.004
Yb^{3+}	173.05	0.985
Lu^{3+}	174.97	0.977

[3]

YAG: crystal structure



Generated from ICSD No. 67102 with VESTA3.
Representation not true to scale.

3. Shannon, R.D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A, 1976. 32(5): p. 751-767.

FAST/SPS: Field assisted sintering technology/ Spark plasma sintering. **AFM**: Atomic force microscopy.
SIMS: Secondary ion mass spectrometry. **TEM**: Transmission electron microscopy

SYNTHESIS

Processing

Raw materials:

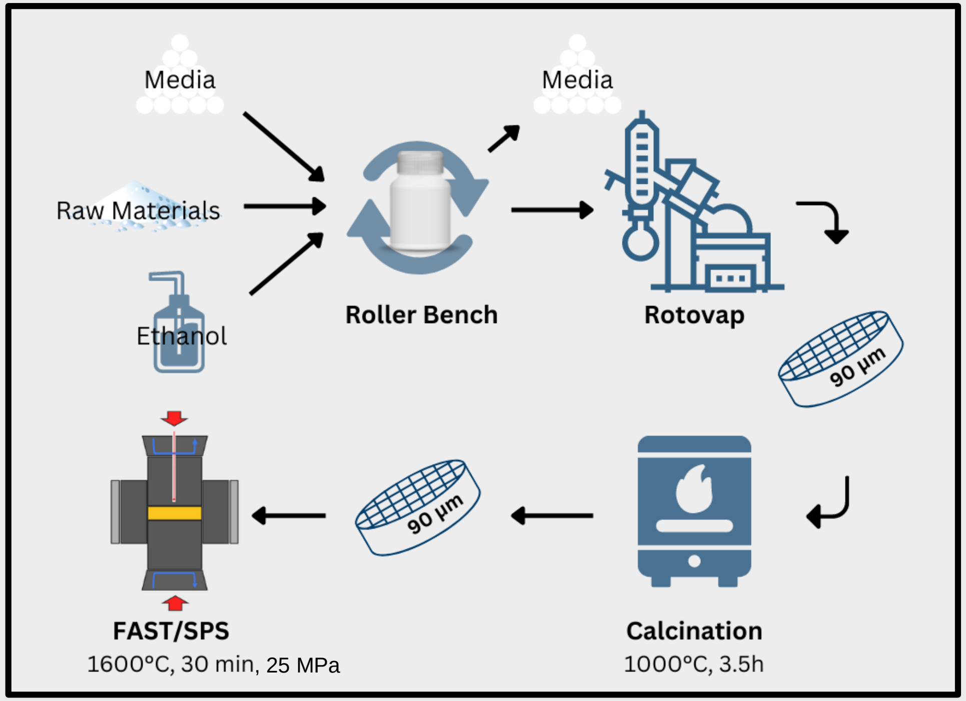
- **Alumina:** 99.999% purity; Heraeus CONAMIC NA
- **Yttria:** 99.999% purity; Neo Performance Materials
- **Lu_2O_3, Yb_2O_3, Yb_2O_3:** 99.999% purity; Neo Performance Materials

Homogenization: 24h on roller bench

Drying: Rotovap

Calcination: 1000°C, 3.5h

Overview



SYNTHESIS

Reactive Field Assisted Sintering Technology/ Spark Plasma Sintering (Reactive FAST/SPS)

Overall chemical reaction:

$3\,Y_2O_3 + 5\,Al_2O_3 \rightarrow 2\,Y_3Al_5O_{12}$ (YAG)

$2\,Y_2O_3 + Al_2O_3 \rightarrow Y_4Al_2O_9$ (YAM)

$Y_4Al_2O_9 + Al_2O_3 \rightarrow 4\,YAlO_3$ (YAP)

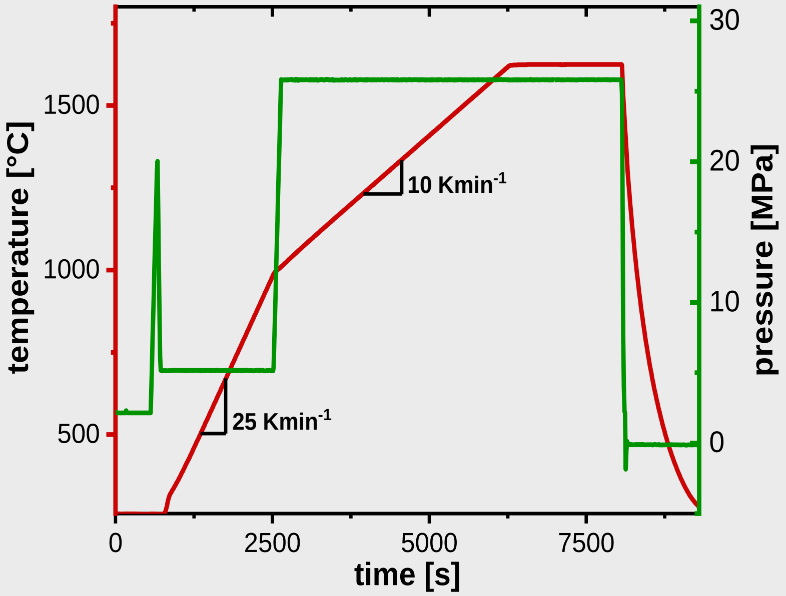
$3\,YAlO_3 + Al_2O_3 \rightarrow Y_3Al_5O_{12}$ (YAG)

(T = 1000 – 1600 °C)

FAST/SPS Parameters:

Heating: 25 $Kmin^{-1}$, 5 MPa, RT-1000°C
10 $Kmin^{-1}$, 25 MPa, to 1600°C
Dwell: 30 min, 25 MPa, 1600°C
Cooling: switch off power source

FAST/SPS data



FCT HP-D 5

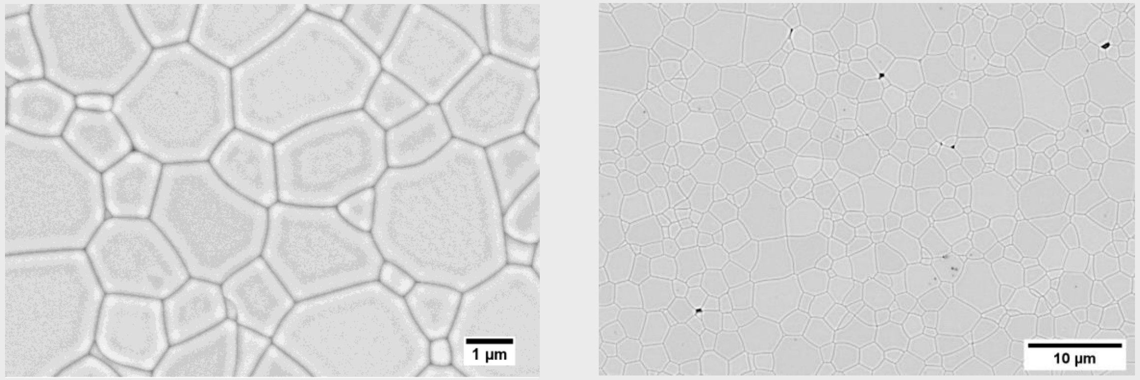
JÜLICH Forschungszentrum

CHARACTERIZATION

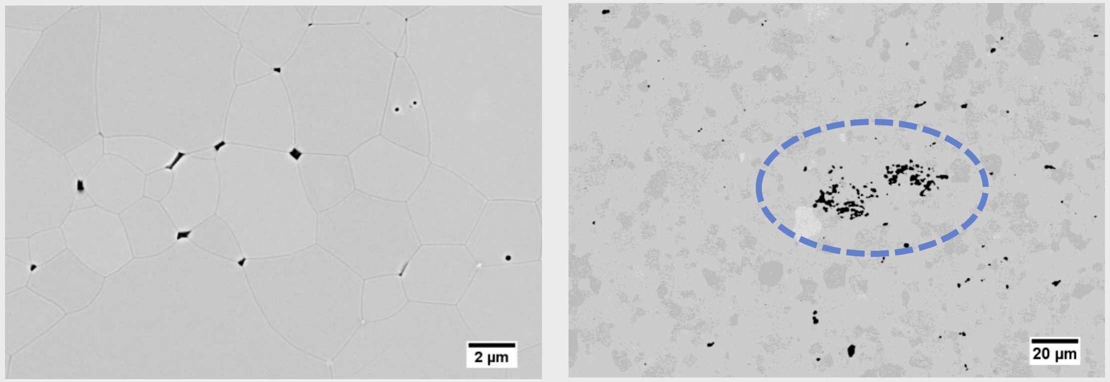
Scanning electron microscopy (SEM)

Microstructure:

- homogenous, dense (ρ~99.9%)
- Grain size: d_{50} = 2-3 µm
- Small amounts of residual alumina (~1 %)



YAG (thermally etched)



LuAG (thermally etched) with residual alumina

Microscope: Ultra 55 (Carl Zeiss AG, Oberkochen, Germany)

JÜLICH Forschungszentrum

CHARACTERIZATION

X-Ray diffraction (XRD)

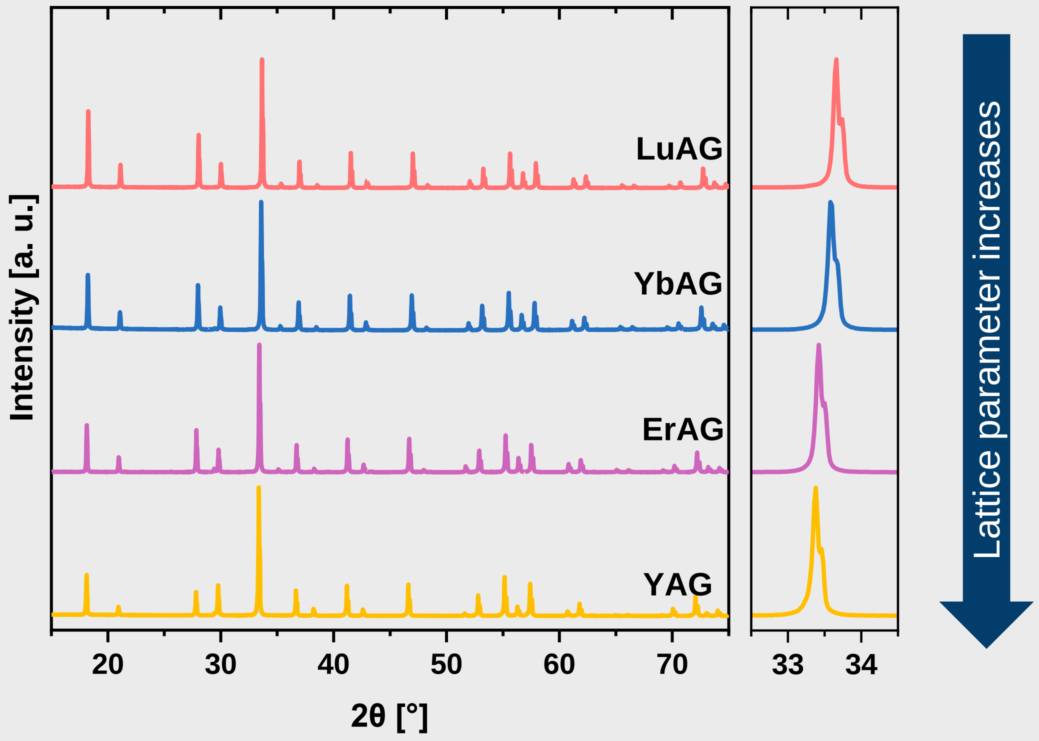
- Crystal structure: garnet (cubic)
- Space group: Ia-3d
- Lattice parameters:

YAG: a = 12.0163 Å
ErAG: a = 11.9827 Å
YbAG: a = 11.9182 Å
LuAG: a = 11.9064 Å

➡ Possible impact on induced chemical gradient

- Residual alumina not detectable
- No intermediates (YAM, YAP etc.)

Diffractogram



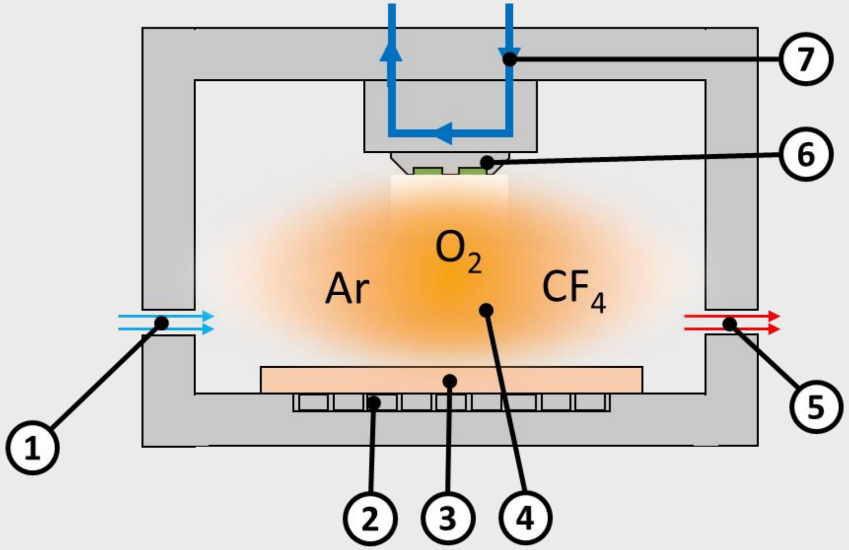
XRD: Bruker D4 ENDEAVOR

ICSD: YAG: col. code 67102. ErAG: col. code 170147. YbAG: col. Code 170159. LuAG: col code 23846.

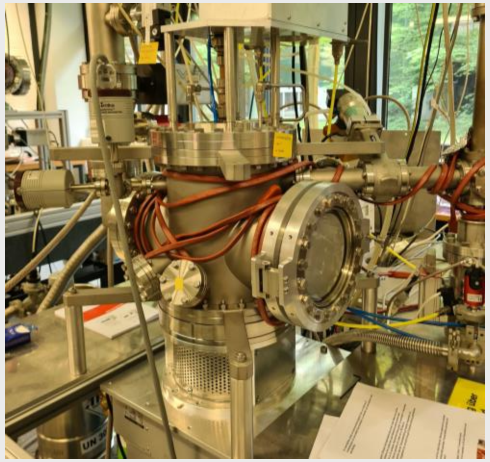
PLASMA ETCHING

Experimental setup and plasma parameters

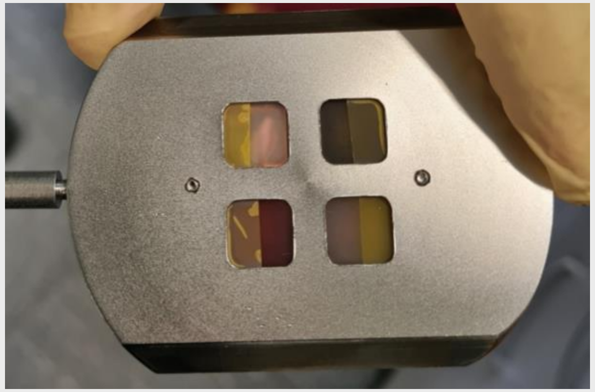
ICP-etching chamber



(1) Gas inlet (2) ICP generator (3) Protective window (4) Plasma (5) Vacuum pump (6) Sample holder (7) Water cooling system



Samples masked with Kapton® tape



Plasma parameters:

P_{ICP} [W]	t_{etch} [min]	p [mbar]	U_B [V]	CF_4 [sccm]	Ar [sccm]	O_2 [sccm]
600	120	0.02	-150	1.0	5.0	0.3

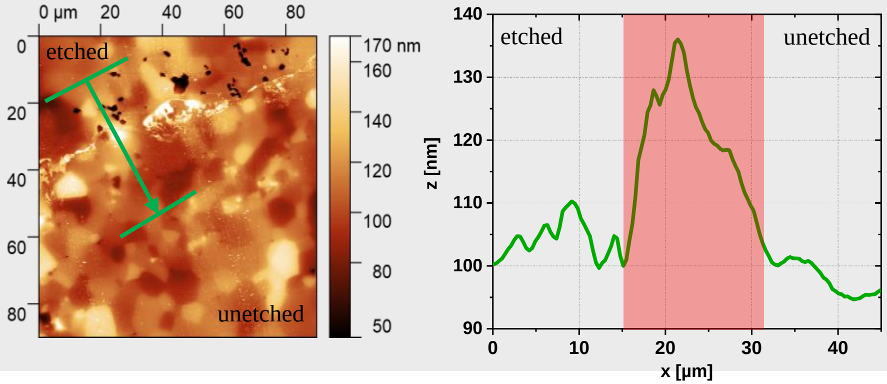
JÜLICH Forschungszentrum

CHARACTERIZATION

Characterization of plasma etched samples – AFM + SEM/EDS

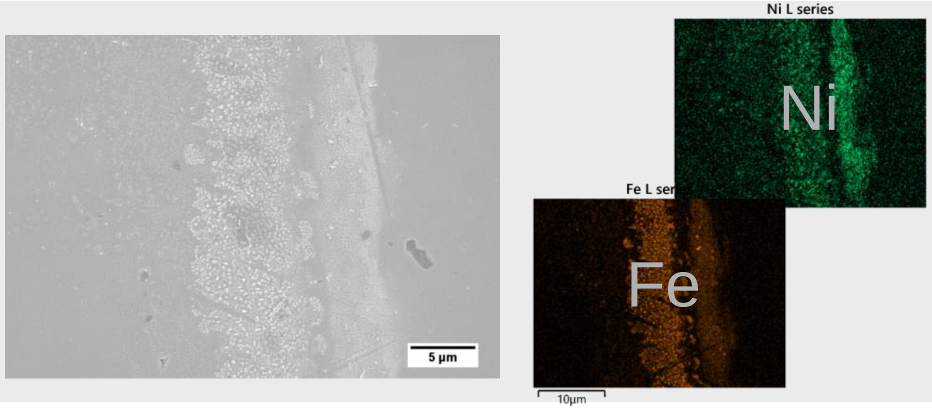
Atomic force microscopy (AFM)

- **Tapping mode**
- **No physical erosion** detected
- **Contamination** covering the etch step
- Black „dots“ in etched part: former alumina phase



Scanning electron microscopy (SEM/EDS)

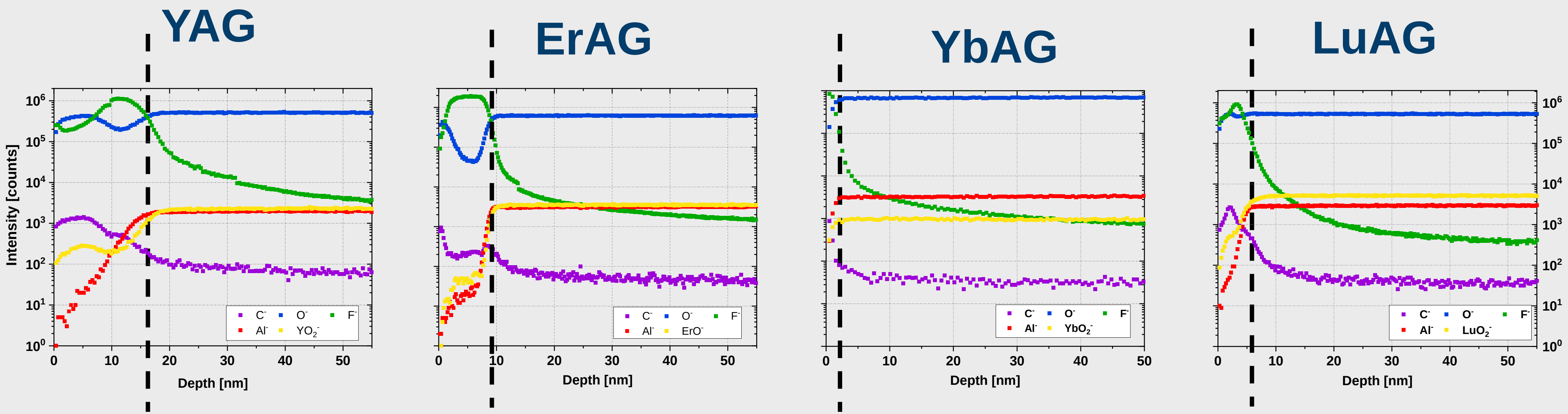
- **Contamination** consists of **metal ions**
- Eroded from sample holder/ chamber



JÜLICH Forschungszentrum

CHARACTERIZATION

Characterization of plasma etched samples – SIMS



- SIMS enables characterisation of induced chemical gradient
- Thickness of reaction layer could be significantly reduced
- Fluorine penetration reduced in rare earth garnets

JÜLICH Forschungszentrum

CHARACTERIZATION: REACTION LAYER IN YAG

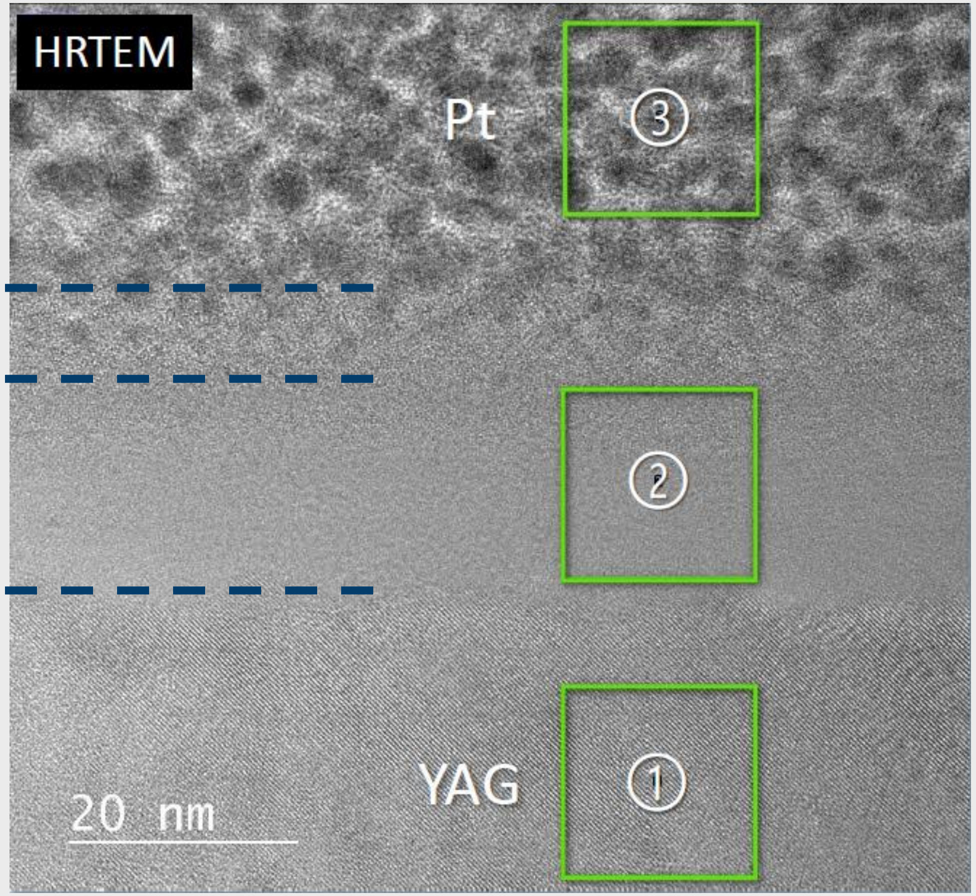
Transmission Electron Microscopy (HRTEM) – In cooperation with GfE Aachen

Platinum

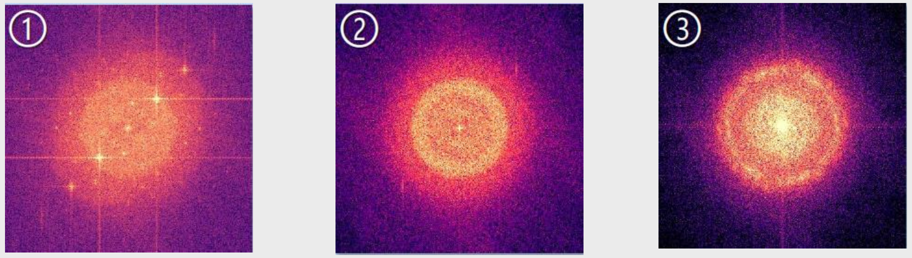
Carbon

Reaction layer

Bulk



SAED



crystallin | amorphous | amorphous

Correlation with SIMS?

Further characterization needed:

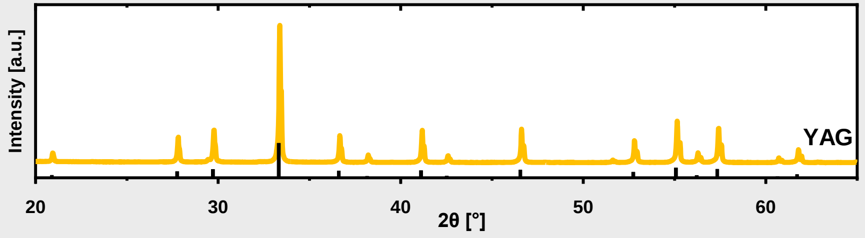
- ➢ **STEM**
- ➢ **Mappings**

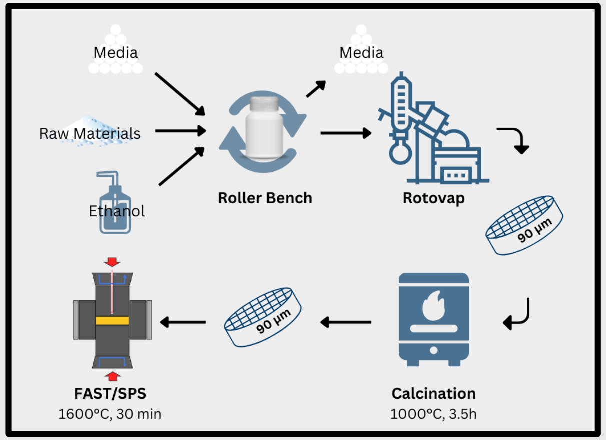
Microscope: JEOL – JEM F200

SUMMARY

Synthesis

- **Succesful synthesis** of different garnets by means of **reactive FAST/SPS**
- **No intermediates** (YAM, YAP) and only **small amounts** of residual **alumina**
- **Close to theoretical density**





Plasma etching

- Samples were **etched in a fluorine based plasma** ($CF_4/Ar/O_2$)
- **No physical erosion** detected in AFM
- **Thickness of reaction layer reduced** in rare earth garnets compared to YAG