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The Influence of Fe Valency on Microstructural Evolution of Alumina

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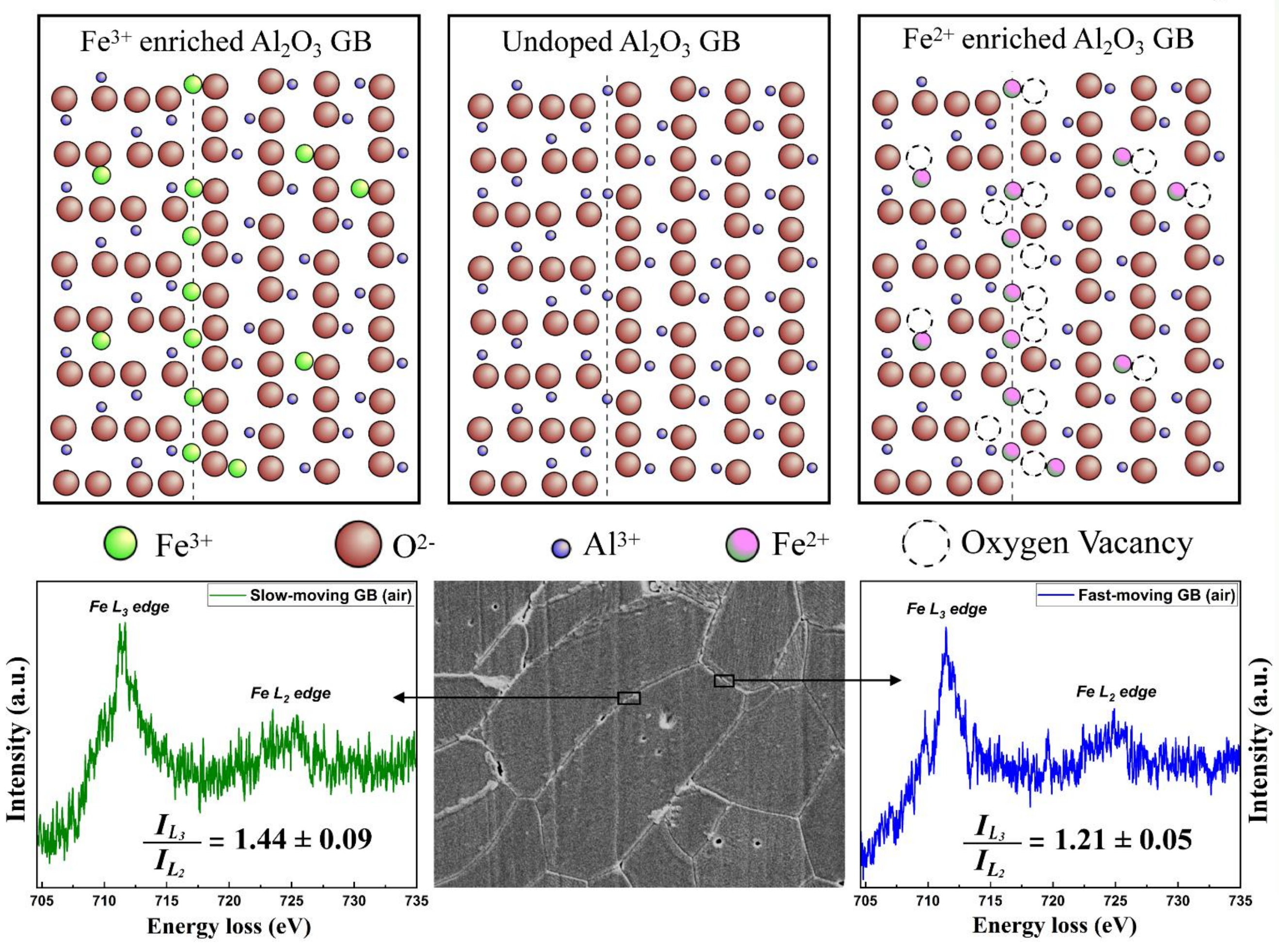
Graphical Abstract



Introduction & Motivation

I. Materials' properties and applications are usually determined by their microstructure, which in polycrystalline materials is controlled by grain boundary (GB) migration, which depends on GB energy and mobility.

II. Adjusting annealing atmospheres and powder composition via doping are two main routes of controlling the microstructural evolution

III. Doping at a concentration above the solubility limit can result in the precipitation of secondary phases, which may manifest as solid or liquid particles. Solid particles can reduce the GB mobility by the Zener drag effect.

IV. A dopant concentration below the solubility limit can result in solute segregation at GBs without precipitation of a secondary phase, if the GB solute excess reduces the excess GB energy.

V. Using alumina (α-Al_2O_3) as a model system, we investigated how Fe dopants in two valence states, Fe^{3+} and Fe^{2+}, affect GB mobility.

Material & Methodology

Powder Processing → **Sintering (air, 1600°C)** → **Grain Growth (air or Ar, 1600°C)** → **GB Mobility Measurement** → **Fe Excess at GBs** → **Fe valency**

Green bodies

Undoped Al_2O_3

Varying Fe-doped Al_2O_3

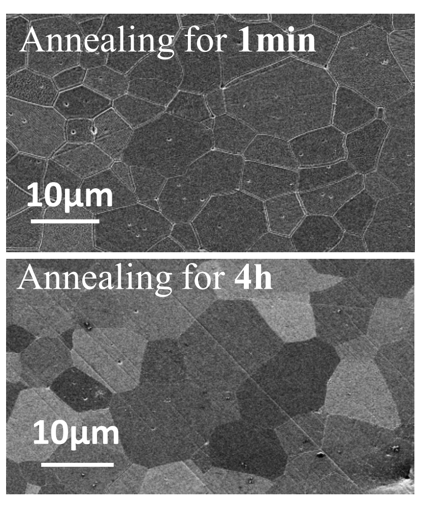
Fe content by WDS

undoped

0.18wt%Fe

0.71wt%Fe

1.26wt%Fe



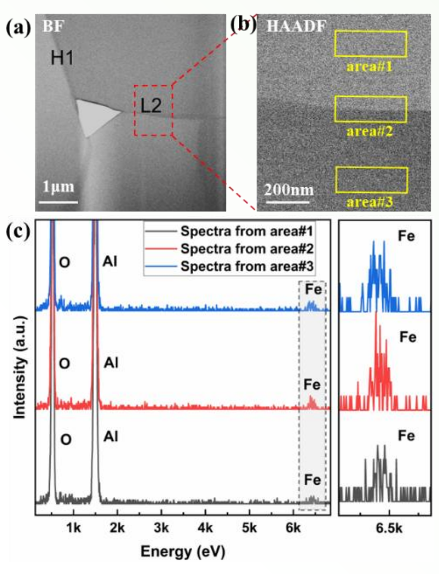
Extracting from grain size

$$\bar{G}_t^2 - \bar{G}_0^2 = 4 \cdot M_{GB}\gamma_{GB} \cdot t$$

$\bar{G}_t^2$ - average squared grain size at t

$\bar{G}_0^2$- average squared grain size at t=0

$M_{GB}\gamma_{GB}$- effective GB mobility.



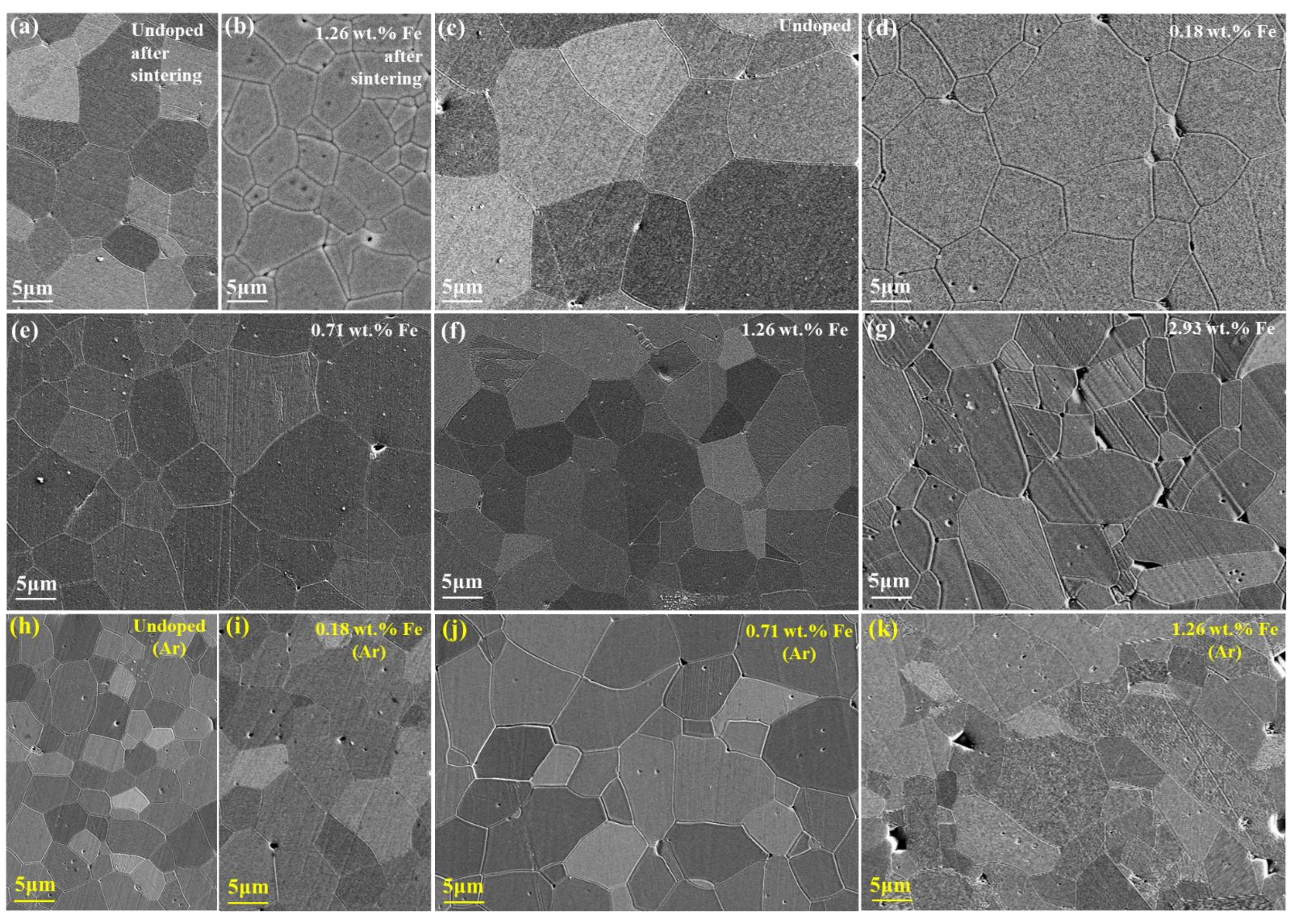
+2 +3

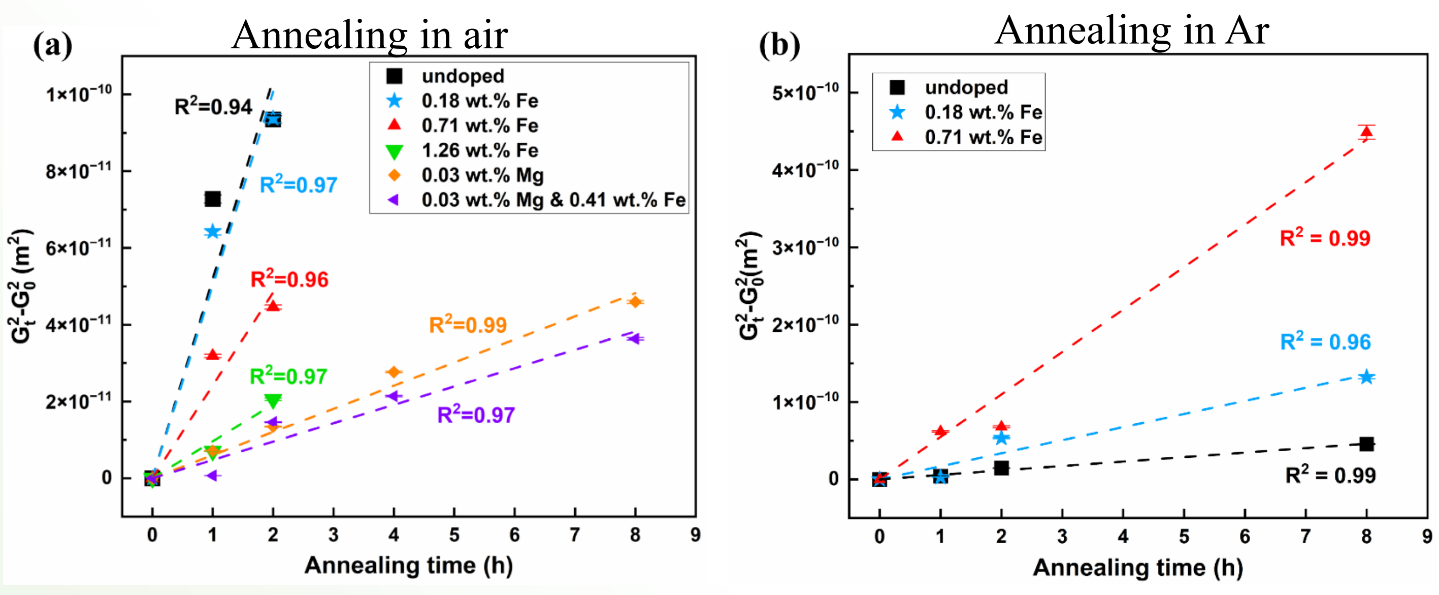
Fe valency → Bulk region → By XPS

Fe valency → GB region → by EELS

Results & Discussion

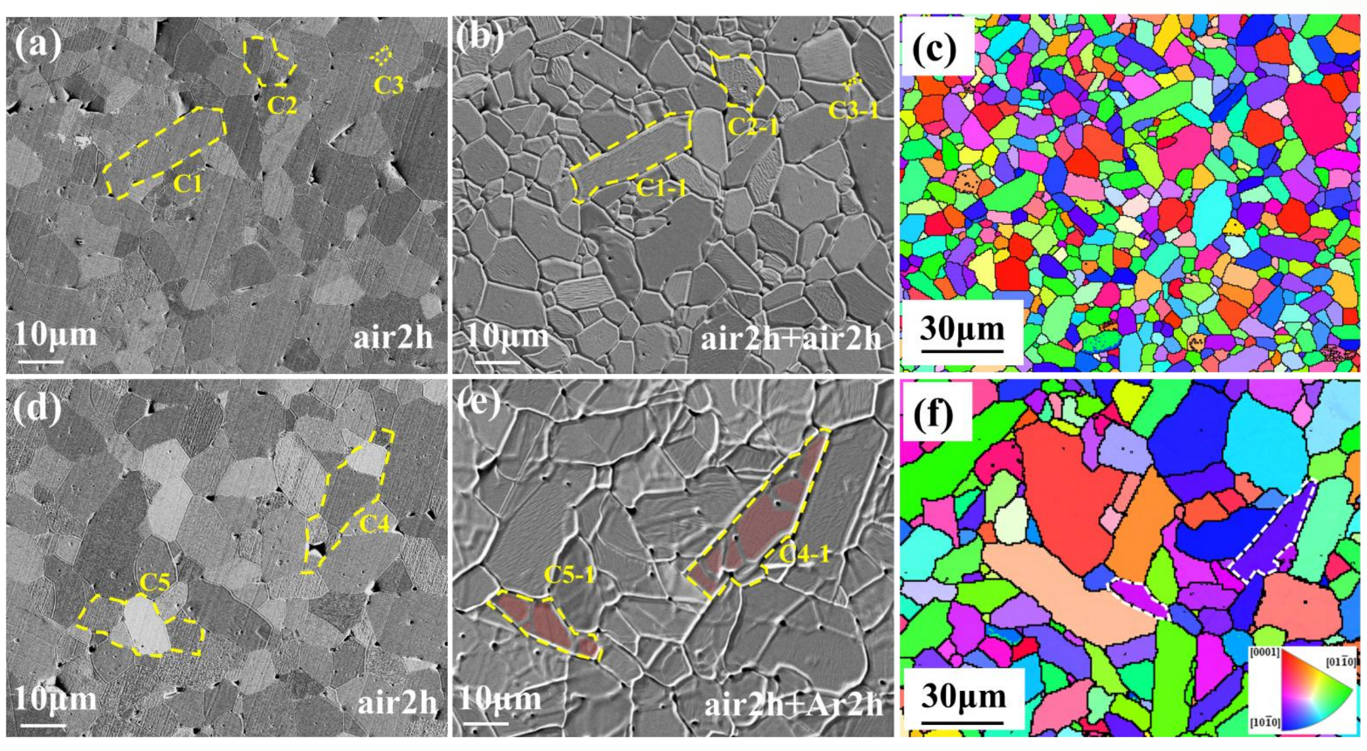
➢ Influence of Fe concentration and annealing atmosphere on Al_2O_3 GB mobility and evolution of grain shape





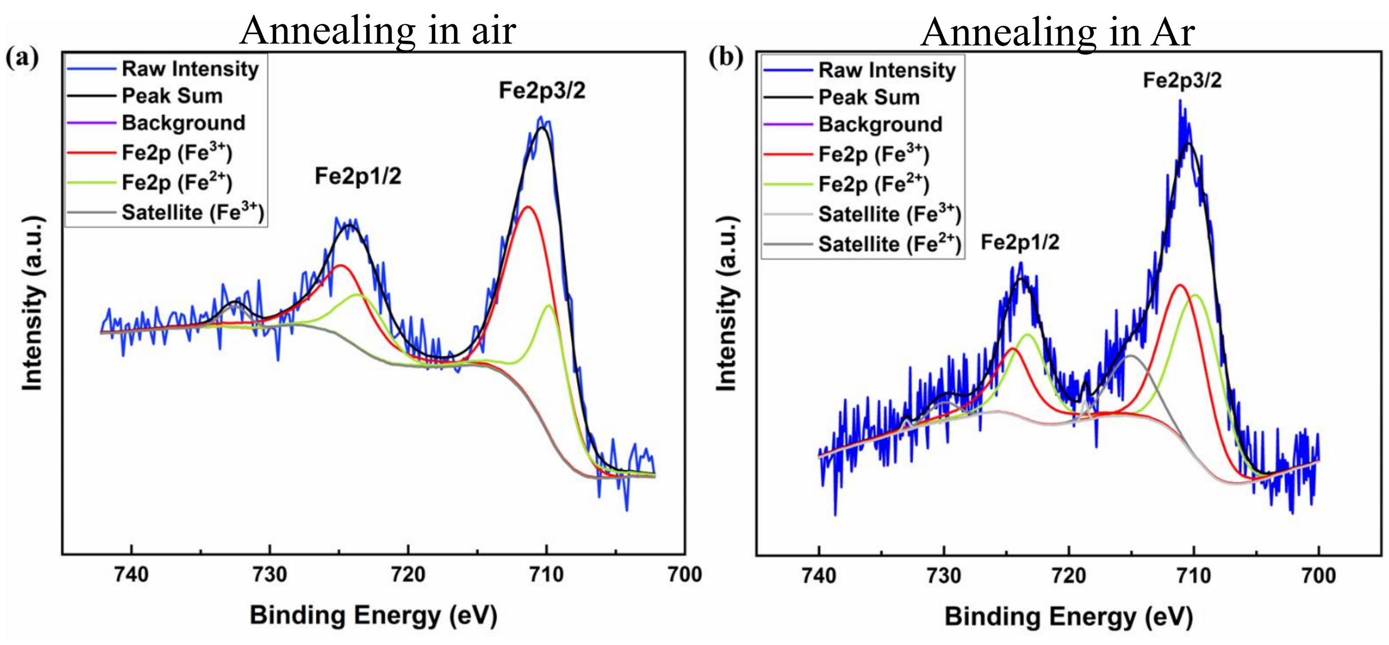
➢ Measurements of Fe excess at Al_2O_3 grain boundaries

Annealing Atmosphere	Sample	GB Type	Fe Segregation (atoms/nm^2)	Detection limit (atoms/nm^2)
Air	1.26 wt. % Fe	Random	3.6 ± 1.4	1.8
	2.93 wt. % Fe	Fast-moving GB	6.6 ± 1.6	3.3
		Slow-moving GB	6.7 ± 0.6	3.3
Ar	1.26 wt. % Fe	Fast-moving GB	3.1 ± 0.2	1.6
		Slow-moving GB	3.0 ± 0.1	1.7
	2.93 wt. % Fe	Fast-moving GB	6.2 ± 0.5	2.6
		Slow-moving GB	6.1 ± 0.3	2.7



(Annealing in Ar results in an anisotropic grain growth)

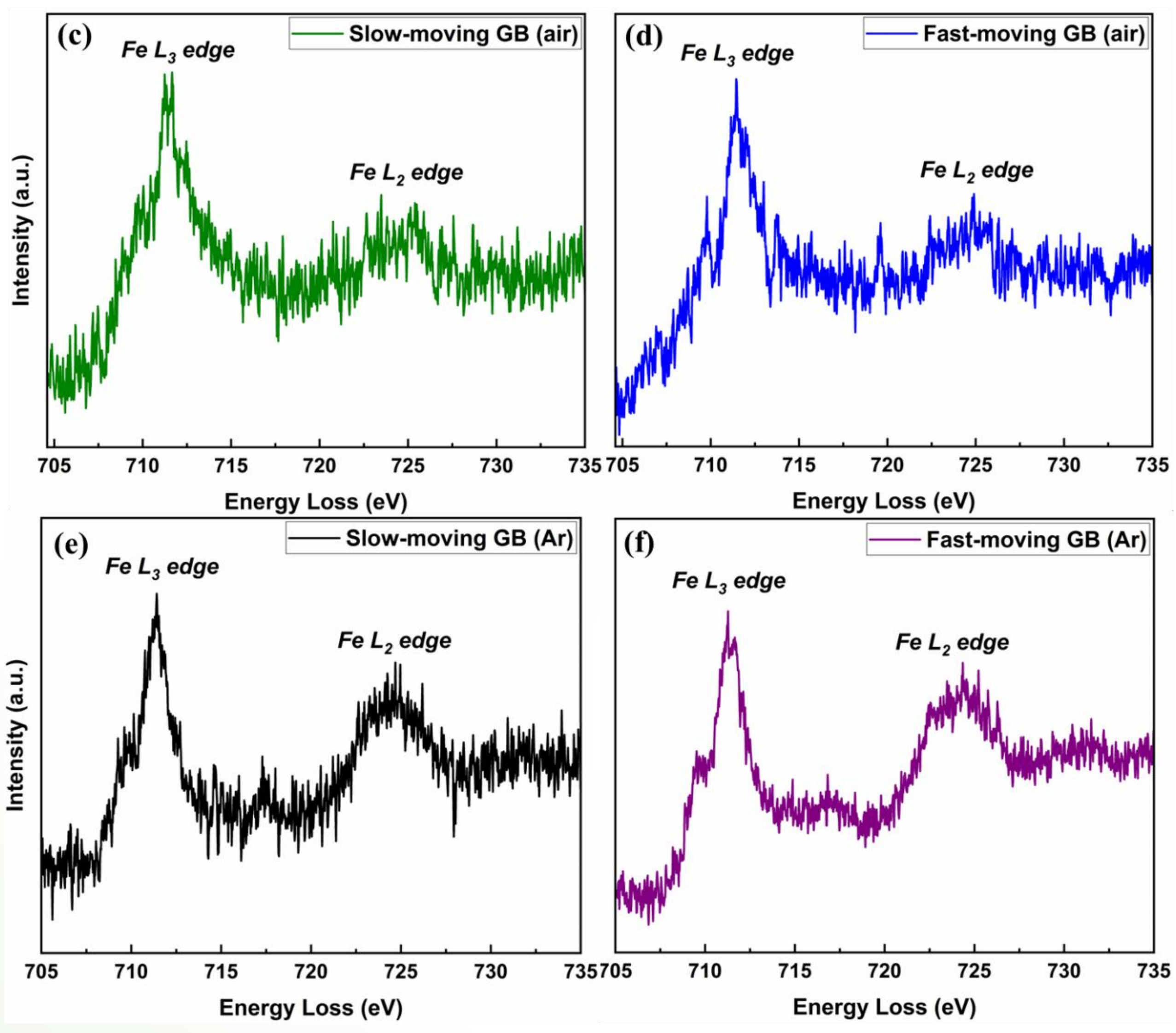
➢ Quantitative analysis of Fe valence state in bulk Al_2O_3



Fe(3+)/Fe(2+) = 1.86

Fe(3+)/Fe(2+) = 0.98

➢ Characterization of valence states of Fe segregated at GBs in an elongated-shaped grain



Annealing Atmosphere	Type of GBs	Repeated Measurements	White Line Ratio [$I(L_3)/I(L_2)$]
air	Slow-moving GB	9	1.44 ± 0.09
	Fast-moving GB	9	1.21 ± 0.05
Ar	Slow-moving GB	12	0.98 ± 0.06
	Fast-moving GB	12	0.84 ± 0.05

Note: a higher integral Fe $L_{2,3}$ white line intensity ratio, and an increased $Fe^{3+}/\Sigma Fe$.

Conclusions

I. In air, grain growth was suppressed by solute drag, as shown by reduced GB mobility with increasing Fe content and by measured Fe segregation at GBs.

II. In Ar, GB mobility increased, and grain growth became anisotropic.

III. We attribute this anisotropy to the lower oxygen partial pressure, which increases the Fe^{2+}/Fe^{3+} ratio and oxygen vacancy concentration.

IV. XPS and EELS confirmed these changes. White-line ratio analysis of the Fe $L_{2,3}$ edges showed that Fe^{2+} preferentially segregates to fast-moving boundaries, promoting elongated grains and altered morphology.

Reference: **Wu, X.**, et al., Acta Mater., 2026. 306: p. 121938-121949.

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