An origin of excess vibrational entropies at grain boundaries in Al, Si and MgO: A first-principles analysis with lattice dynamics

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S1. Grain boundary energy and excess volume at 0 K

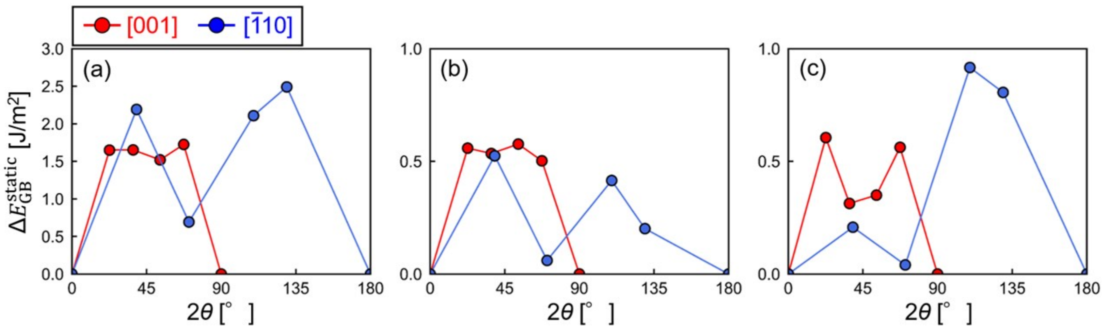

Fig. S1. Zero-temperature grain boundary (GB) energy (ΔE_{GB}^{static}) as a function of misorientation angle of two grains (2θ) for (a) MgO, (b) Al and (c) Si. The red and blue lines correspond to the GBs with the [001] and [$\bar{1}$10] tilt axes, respectively. ΔE_{GB}^{static} was calculated from DFT total energies.

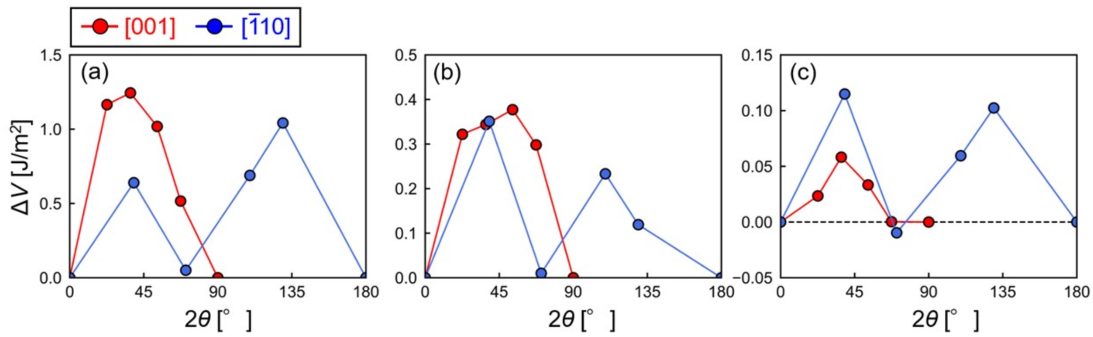

Fig. S2. Excess volume (ΔV) as a function of misorientation angle of two grains (2θ) for (a) MgO, (b) Al and (c) Si. The red and blue lines correspond to the GBs with the [001] and [$\bar{1}$10] tilt axes, respectively. ΔV was calculated using the lowest-energy structures at 0 K.

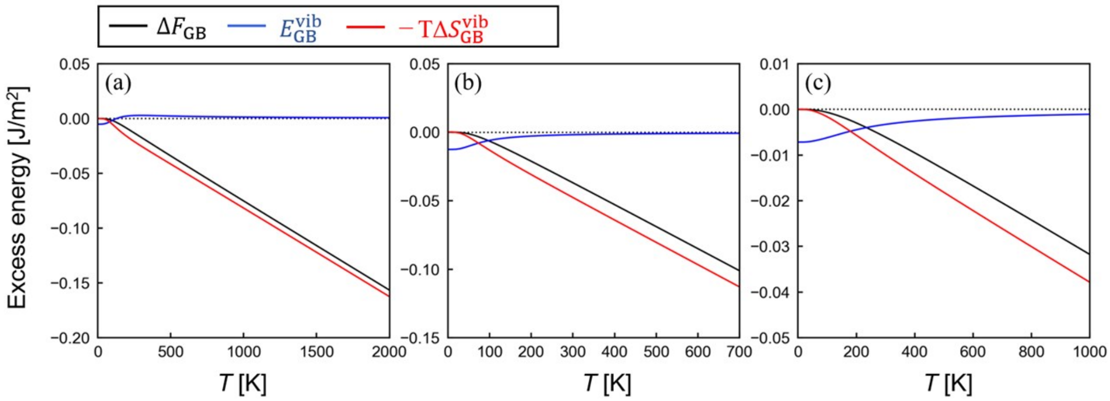

Fig. S3 Temperature dependence of GB free energy (ΔF_{GB}), excess internal energy (ΔE_{GB}^{vib}) and excess vibrational entropy multiplied by temperature ($T\Delta S_{GB}^{vib}$) for the Σ5(310) GB for (a) MgO, (b) Al and (c) Si.

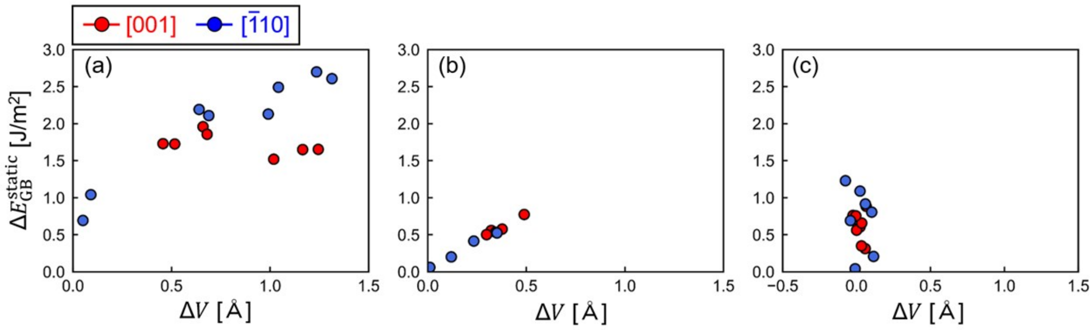

Table S1. Zero-temperature grain boundary (GB) energy (ΔE_{GB}^{static}) for the metastable structures used for lattice dynamics calculations. The value in the parentheses is the increase in ΔE_{GB}^{static} from that of the lowest-energy structure.

Substance	Grain boundary	ΔE_{GB}^{static} [J/m²]
	Σ13(510)/[001]	1.96 (0.31)
MgO	Σ5(310)/[001]	1.86 (0.20)
	Σ13(320)/[001]	1.73 (0.004)

	$\Sigma9(221)/[\bar{1}10]$	2.70 (0.51)
	$\Sigma3(111)/[\bar{1}10]$	1.04 (0.35)
	$\Sigma3(112)/[\bar{1}10]$	2.13 (0.02)
	$\Sigma11(113)/[\bar{1}10]$	2.61 (0.12)
Al	$\Sigma5(310)/[001]$	0.77 (0.24)
	$\Sigma13(510)/[001]$	0.66 (0.05)
	$\Sigma5(310)/[001]$	0.76 (0.45)
	$\Sigma5(210)/[001]$	0.88 (0.53)
Si	$\Sigma13(320)/[001]$	0.76 (0.19)
	$\Sigma9(221)/[\bar{1}10]$	0.69 (0.48)
	$\Sigma3(112)/[\bar{1}10]$	1.23 (0.31)
	$\Sigma11(113)/[\bar{1}10]$	1.09 (0.28)