

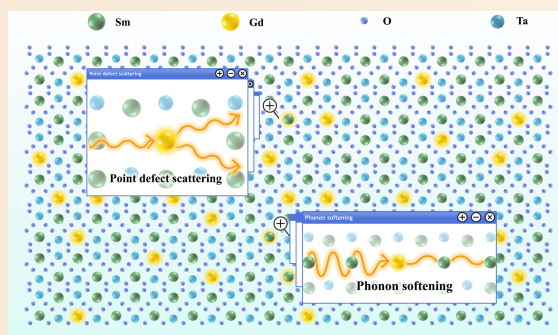
Acoustic softening dominates over Klemens–Abeles disorder in governing the lattice thermal conductivity of $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$ ceramics

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ABSTRACT: Low thermal conductivity oxide ceramics are usually designed around point-defect scattering. Cation mass and ionic-radius mismatch, the Klemens–Abeles descriptors, serve as the primary screening variables. Here, we show that single-phase fergusonite $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$ ceramics ($x = 0-1$) reveal a second, distinct route to low conductivity. This route involves acoustic softening coupled to unit-cell dilation. Replacing Gd with Sm expands the rare-earth (RE)–O coordination shell while leaving the TaO_6 octahedron nearly unchanged. The unit cell grows monotonically with x , and the lattice softens. The mean sound velocity and Debye temperature both drop by approximately 20% from $x = 0$ to $x = 0.8$. The room-temperature lattice thermal conductivity decreases by 32%, from 5.11 to 3.48 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. A Cahill minimum-conductivity estimate is built from sound velocity and atomic number density alone. It reproduces most of this decrease. This result shows that acoustic softening, rather than disorder, sets the baseline trend. Disorder is still active but offset. The Klemens–Abeles scattering parameter peaks at $x = 0.2-0.6$, away from the conductivity minimum at $x = 0.8$. The end member SmTaO_4 provides a decisive test. Its sound velocity matches that of the $x = 0.8$ composition, but its conductivity rebounds. This isolates residual RE-sublattice disorder as the extra channel that deepens the minimum. Acoustic softening and unit-cell volume therefore deserve a place alongside mass and radius mismatch when screening complex oxides for low thermal conductivity.

KEYWORDS: lattice thermal conductivity; rare-earth (RE) tantalates; fergusonite solid solution; acoustic softening; thermal barrier coatings



1 Introduction

Solid-solution and multication engineering are established routes to lowering the thermal conductivity (κ) of complex oxides through chemical disorder and enhanced phonon scattering [1,2]. Most composition screening still follows the Klemens–Abeles point-defect scattering framework [3–5], in which atomic mass and ionic-radius contrasts are condensed into a scattering parameter (Γ). Γ is the Klemens–Abeles point-defect disorder parameter. It combines rare-earth (RE)-site mass and strain fluctuations and is used to rank substitution pathways [6,7]. This reduction is useful, but the mean (Debye-averaged) sound velocity (v_m) and the unit-cell volume (V_{cell}) are commonly treated as background quantities in descriptor-level screening, so that

compositional differences in elastic stiffness and unit-cell scale drop out of the descriptor. Although the Γ formalism has been generalized for multiatom crystals [8], practical screening commonly varies only the atomic mismatch terms [9]. Mean sound velocity and unit-cell volume therefore belong in a complete description alongside mass mismatch (ΔM) and radius mismatch (Δr). v_m sets the elastic stiffness, while V_{cell} sets the number density and mean bond length at fixed stoichiometry. A key unresolved question is whether the κ minimum in an isovalent RE-site solid solution is governed mainly by the maximum point-defect disorder implied by Γ -based screening or by monotonic changes in acoustic stiffness and cell volume inherited from RE-cation differences across the series.

Acoustic softening lowers κ in PbTe under internal strain [10],

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in high-entropy borides where lattice distortion dominates over mass-fluctuation scattering [11], and in half-Heusler ZrNiBi with vacancy-induced soft bonding [12]. Local bond distortion can also act through optical modes by redshifting them and shortening their lifetimes, as observed in multication RE oxides with concurrent κ reduction [2]. Consistent with these observations, Shen *et al.* [13] proposed a cross-material κ descriptor combining sound velocity and primitive-cell atom count. Such cross-material descriptors operate at the structure-type level, leaving the composition-dependent trade-off inside a single solid solution unresolved. Resolving this trade-off requires composition-resolved κ on a single RE-site solid solution, where the acoustic terms and the mass-disorder term can be tracked together against x .

RE tantalates RETaO₄ typically crystallize in the low-symmetry fergusonite structure and combine complex RE–O coordination with intrinsically low κ [14–16], making them relevant to low- κ oxide ceramics and potential thermal-barrier-coating (TBC) thermal management [17–21]. First-principles work attributes part of the low κ characteristic of fergusonite-type RETaO₄ to acoustic–optical anticrossing inside the Brillouin zone [22], a dispersion-controlled mechanism. The complementary composition dependence is addressed below within the same isostructural series. Multication and high-entropy substitution on the RE site have repeatedly been shown to lower κ , often interpreted through mass and size disorder on the RE sublattice and associated defect scattering [23–25], but concurrent changes in v_m and V_{cell} are rarely included in that interpretation. (Gd_{1– x} Sm _{x})TaO₄ provides a model solid solution for testing this issue. Gd³⁺ and Sm³⁺ are neighboring, isovalent lanthanides, so substitution occurs on the RE site without charge-compensation defects. Their mass mismatch ($\Delta M \approx 6.89$ amu, $\Delta M/\bar{M} \approx 4.5\%$) and radius mismatch ($\Delta r/\bar{r} \approx 2.4\%$) at a coordination number (CN) of 8 generate measurable mass and strain fluctuations, while the larger Sm³⁺ ion expands the RE–O coordination polyhedra and increases V_{cell} monotonically. Thus, the same series contains monotonic acoustic and structural trends together with a non-monotonic RE-site disorder term. The small formal RE-site mismatch makes this series a stringent test of whether elastic and cell-volume changes can compete with conventional mass and size disorder.

To resolve these competing composition trends, we prepared (Gd_{1– x} Sm _{x})TaO₄ ceramics at six compositions (GST- x , $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1), single-phase fergusonite (C2/c) throughout. The mean sound velocity and Debye temperature decrease by approximately 20% from GST-0 to GST-0.8 and then saturate (Section 3.3, Table 1). Room-temperature κ falls from 5.11 W·m^{–1}·K^{–1} at GST-0 to 3.48 W·m^{–1}·K^{–1} at GST-0.8 and rebounds to 3.74 W·m^{–1}·K^{–1} at GST-1. The composition spread in κ narrows from approximately 1.6 W·m^{–1}·K^{–1} at room temperature to approximately 0.5 W·m^{–1}·K^{–1} at 900 °C. At this temperature, the GST-0.8 minimum falls to approximately 1.9 W·m^{–1}·K^{–1}. Therefore, GST-0.8 remains nominally the least conductive composition at every measured temperature.

By comparing the composition dependences of κ , Γ_{PD} , v_m , Debye temperature, and V_{cell} , we show that the κ minimum is displaced from the calculated Γ_{PD} maximum and instead occurs near the composition where acoustic softening approaches saturation, while residual RE-site disorder remains finite. Here, Γ_{PD} denotes the RE-sublattice Klemens–Abeles point-defect scattering parameter and is distinct from the Raman linewidth Γ . At the composition-trend level, this offset separates the monotonic acoustic and cell-volume trends from the nonmonotonic residual-disorder term. v_m and V_{cell} should therefore be included as composition-screening descriptors, together with ΔM and Δr , for RE tantalates and structurally analogous rigid-framework oxides with compliant RE sites.

2 Materials and methods

2.1 Specimen preparation

(Gd_{1– x} Sm _{x})TaO₄ ceramics ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1) were synthesized by solid-state reaction from stoichiometric Gd₂O₃, Sm₂O₃, and Ta₂O₅ powders (99.99%, < 10 μ m) ball-milled in anhydrous ethanol at 350 r/min for 12 h. Dried powders were uniaxially pressed into 15 mm $\times$ 1.5 mm discs, cold-isostatically pressed at 500 MPa for 1 min, and sintered in air at 1600 °C for 10 h. Density was determined by the Archimedes immersion method; laser-flash specimens were machined to 6 mm diameter and approximately 1 mm thickness.

2.2 Phase, microstructure, and Raman characterization

Phase formation was characterized by a powder X-ray diffractometer (XRD; MiniFlex 600, Rigaku; Cu K α , $2\theta = 10^\circ$ – 70° , 0.01° step), with Rietveld refinements in GSAS-II [26,27]. Microstructure and elemental distributions were imaged by a scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDS; SIGMA 300, ZEISS, Germany). Room-temperature Raman spectra were collected on a LabRAM Soleil (HORIBA, Japan, 325 nm excitation); *in situ* high-temperature spectra of GST-0.8 (the κ – x minimum, Section 3.4) were acquired from room temperature to 1200 °C after a 30 min hold at each target temperature. The ν_3 (Ta–O) peak was fitted with a Lorentzian profile and a linear background, and its high-temperature position and linewidth were fitted to the symmetric three-phonon Klemens–Balkanski model (cubic term only, $B = 0$), where B is the coefficient of the quartic anharmonic term [28,29].

2.3 Acoustic properties, elastic moduli, and hardness

Longitudinal (v_L) and transverse (v_T) sound velocities were measured at room temperature by an ultrasonic pulse-echo instrument (UMS-100, Teclab, China). Table 1 lists the values measured on one specimen per composition, and repeat measurements on two to three independently sintered pellets per composition quantify the pellet-to-pellet reproducibility (Table S7 in the Electronic Supplementary Material (ESM)). v_m , Poisson's

Table 1 Acoustic and elastic parameters of (Gd_{1– x} Sm _{x})TaO₄

Sample	x_{Sm}	ρ (kg·m ^{–3})	v_T (m·s ^{–1})	v_L (m·s ^{–1})	v_m (m·s ^{–1})	ν	γ	E (GPa)	G (GPa)	B (GPa)	θ_D (K)
GST-0	0.0	8475	2393	4923	2688	0.345	2.09	130.5	48.5	141	344
GST-0.2	0.2	8408	2264	4588	2541	0.339	2.04	115.4	43.1	120	324
GST-0.4	0.4	8363	2107	3938	2353	0.300	1.77	96.5	37.1	80	300
GST-0.6	0.6	8324	2024	3765	2260	0.297	1.75	88.4	34.1	73	288
GST-0.8	0.8	8271	1942	3392	2158	0.256	1.53	78.4	31.2	54	275
GST-1	1.0	8165	1938	3444	2156	0.269	1.59	77.8	30.7	56	274

ratio (ν), shear modulus (G), Young's modulus (E), bulk modulus (B), and Debye temperature (θ_D) were computed from ν_T , ν_L , ρ , and V_{cell} via standard isotropic-elasticity relations, as shown in Eqs. (1)–(6):

$$\nu_m = \left[\frac{1}{3} \left(\frac{2}{\nu_T^3} + \frac{1}{\nu_L^3} \right) \right]^{-1/3} \quad (1)$$

$$\nu = \frac{\nu_L^2 - 2\nu_T^2}{2(\nu_L^2 - \nu_T^2)} \quad (2)$$

$$G = \rho \nu_T^2 \quad (3)$$

$$E = 2G(1 + \nu) \quad (4)$$

$$B = \frac{E}{3(1 - 2\nu)} \quad (5)$$

$$\theta_D = \frac{\hbar}{k_B} \nu_m \left(\frac{6\pi^2 n}{V_{\text{cell}}} \right)^{1/3} \quad (6)$$

where, E is Young's modulus, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and Z is the number of formula units per monoclinic conventional cell. The monoclinic conventional cell contains $n = 24$ atoms ($Z = 4$). The Grüneisen parameter used in the point-defect strain prefactor (Eq. (9)) is taken from the quasi-isotropic Belomestnykh–Tesleva relation $\gamma = 3(1 + \nu)/[2(2 - 3\nu)]$ [30]. This relation provides a Debye-model elastic estimate of the acoustic-mode Grüneisen parameter. In the long-wavelength continuum, the volume dependence of the acoustic branches is carried by the elastic response of the medium. Poisson's ratio captures this response through the ratio of longitudinal to transverse sound velocities. The relation therefore gives an elastic, acoustic estimate of γ . It is not extracted directly from anharmonicity.

The indentation modulus and hardness were obtained by Berkovich nanoindentation [31] at a 100 mN peak load with no dwell on a 10×10 grid ($N = 100$ indents) over $100 \mu\text{m} \times 100 \mu\text{m}$ per sample. Oliver–Pharr analysis reports the reduced modulus (E_r) directly, without conversion to sample Young's modulus.

2.4 Thermal property measurement

Thermal diffusivity (α) was measured by a laser flash analyzer (NETZSCH, LFA-457, Germany) [32] on graphite-coated specimens. Specific heat capacity (c_p) was estimated from end-member oxide $c_p(T)$ data (Ta₂O₅, Gd₂O₃, and Sm₂O₃) via the Neumann–Kopp rule [33]. Thermal conductivity is given by Eq. (7):

$$\kappa = \alpha \rho c_p \quad (7)$$

Three derived quantities used in Section 3.4—the Cahill amorphous limit scale, the Klemens–Abeles point-defect parameter, and a kinetic-theory phonon mean free path—are defined below. The Cahill scale is defined as Eq. (8) [34]:

$$\kappa_{\text{Cahill}} = \frac{k_B}{2.48} n_V^{2/3} (2\nu_T + \nu_L) \quad (8)$$

with $n_V = n/V_{\text{cell}}$. The RE sublattice point defect scattering parameter Γ_{PD} (distinct from the Raman linewidth Γ) follows the Klemens–Abeles form [3,4,6,8], as shown in Eq. (9):

$$\Gamma_{\text{PD}} = x(1 - x) \left[\left(\frac{\Delta M}{M} \right)^2 + \varepsilon^2 \left(\frac{\Delta r}{r} \right)^2 \right] \quad (9)$$

Here, x is the Sm fraction on the RE site, with $0 \leq x \leq 1$. The strain prefactor is $\varepsilon^2 = (2/9)[6.4\gamma(1 + \nu)/(1 - \nu)]^2$, where M and r are the RE-site cation mass and radius, respectively. The intrinsic phonon mean free path is given by Eq. (10):

$$l_{\text{int}} = \frac{3\alpha_{\text{fit}}(T)}{\nu_m} \quad (10)$$

where T is the absolute temperature in kelvin (K). The $\alpha_{\text{fit}}(T)$ term is obtained from weighted linear fits of $1/\alpha$ against T in the Umklapp-dominated window (Table S5 and Fig. S4 in the ESM).

Linear thermal expansion was measured on a thermomechanical analyzer (TMA-402F3, NETZSCH, Germany) from room temperature to 1200 °C. The coefficient of thermal expansion (CTE) was extracted as the slope of $\Delta L/L_0$ vs. T .

2.5 First-principles calculations

First-principles calculations were performed with CP2K v2026.1 [35] in the Gaussian and plane-wave framework [36] using Perdew–Burke–Ernzerhof (PBE) [37] with Grimme D3 (Becke–Johnson, BJ) dispersion [38,39], norm-conserving Goedecker–Teter–Hutter (GTH) pseudopotentials [40,41], and DZVP-MOLOPT basis sets [42]. Gd and Sm employed LnPP2* q11 4f-in-core pseudopotentials and basis sets [43–45], whereas q13 and q6 GTH pseudopotentials were used for Ta and O, respectively. Magnetic ordering and crystal-field excitations are therefore not addressed.

Four systems were modeled: GdTaO₄, SmTaO₄, Sm-doped GdTaO₄ ($x = 1/8$), and Gd-doped SmTaO₄ ($x = 7/8$). Full cell and atomic relaxations used no symmetry constraints. CUTOFF/REL_CUTOFF, set from per-system planewave-density convergence tests, was 1300/50 Ry for GdTaO₄-based cells and 1100/60 Ry for SmTaO₄-based cells; Monkhorst–Pack meshes [46] were $4 \times 2 \times 5$ (24-atom end-member cells) and $4 \times 1 \times 5$ (48-atom substituted supercells). The self-consistent field (SCF) threshold was 10^{-7} Ha; the force thresholds were 4.5×10^{-5} Ha·Bohr⁻¹ (end-member cells) and 1.0×10^{-4} Ha·Bohr⁻¹ (substituted supercells).

Per-formula-unit mixing enthalpies were computed at $x = 1/8$ and $7/8$ and combined with the ideal random mixing configurational entropy to give $\Delta G_{\text{mix}}(x, T)$, as shown in Eqs. (11) and (12):

$$\Delta H_{\text{mix}}(x) = E_{\text{alloy}}(x) - (1 - x)E_{\text{GdTao}_4} - xE_{\text{SmTaO}_4} \quad (11)$$

$$\Delta S_{\text{conf}}(x) = -k_B[x \ln x + (1 - x) \ln(1 - x)] \quad (12)$$

DOS, PDOS, and OPDOS were obtained in Multiwfn v2026.3.27 [47,48] from Γ -only single-point calculations on $2 \times 4 \times 2$ supercells (384 atoms). Bader charges were evaluated with pybader [49] on CP2K total-density cubes including the pseudopotential core density (required for norm-conserving pseudopotentials). Electron localization function (ELF) maps [50] were generated in CP2K and visualized in Multiwfn.

3 Results and discussion

3.1 Single-phase fergusonite solid-solution formation

Room-temperature XRD patterns of (Gd_{1-x}Sm_x)TaO₄ ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1 , denoted GST- x) are shown in Fig. 1(a). All

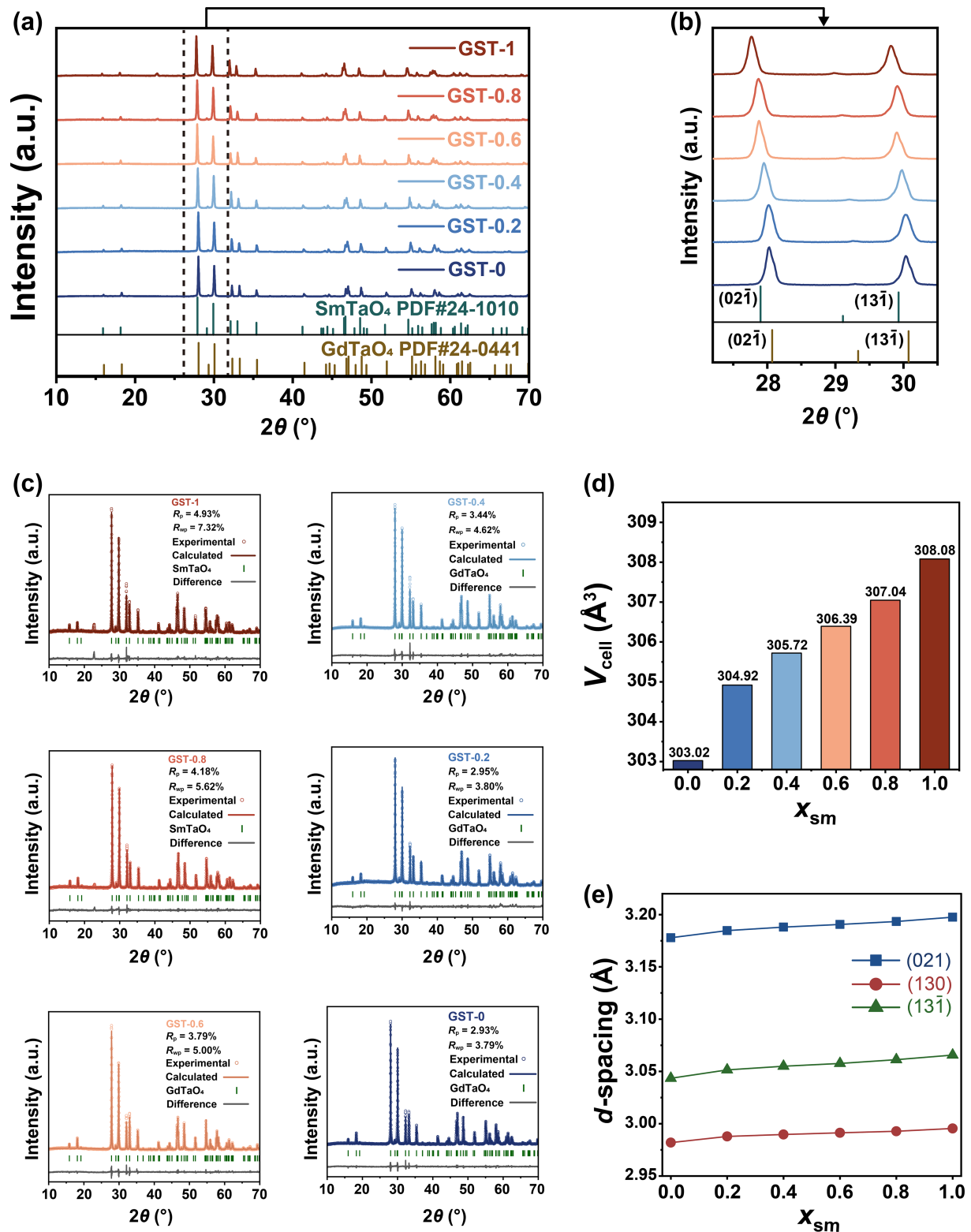


Fig. 1 XRD of $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$. (a) Room-temperature patterns for $x_{\text{Sm}} = 0$ –1 with SmTaO_4 (PDF#24-1010) and GdTaO_4 (PDF#24-0441) references. (b) Magnified 27° – 31° range showing low-angle shift of (021) , (130) , and (131) . (c) Rietveld refinements with observed, calculated, and difference profiles (full parameters in Table S1 in ESM). (d) Unit-cell volume V_{cell} vs. x_{Sm} . (e) $d_{(021)}$, $d_{(130)}$, and $d_{(131)}$ vs. x_{Sm} .

reflections index to the monoclinic fergusonite structure (space group $C2/c$), with no secondary-phase reflections or peak splitting observed at any composition, indicating that the GdTaO_4 – SmTaO_4 system retains a common crystallographic framework. In the magnified 27° – 31° range (Fig. 1(b)), the (021) , (130) , and (131) reflections shift monotonically to lower 2θ with

increasing x_{Sm} , consistent with a continuous increase in lattice spacing.

Rietveld refinement confirms the single-phase picture (Fig. 1(c)), with good agreement between the observed and calculated patterns (full parameters in Table S1 in the ESM). The unit-cell volume increases monotonically with x_{Sm} (Fig. 1(d)), and the

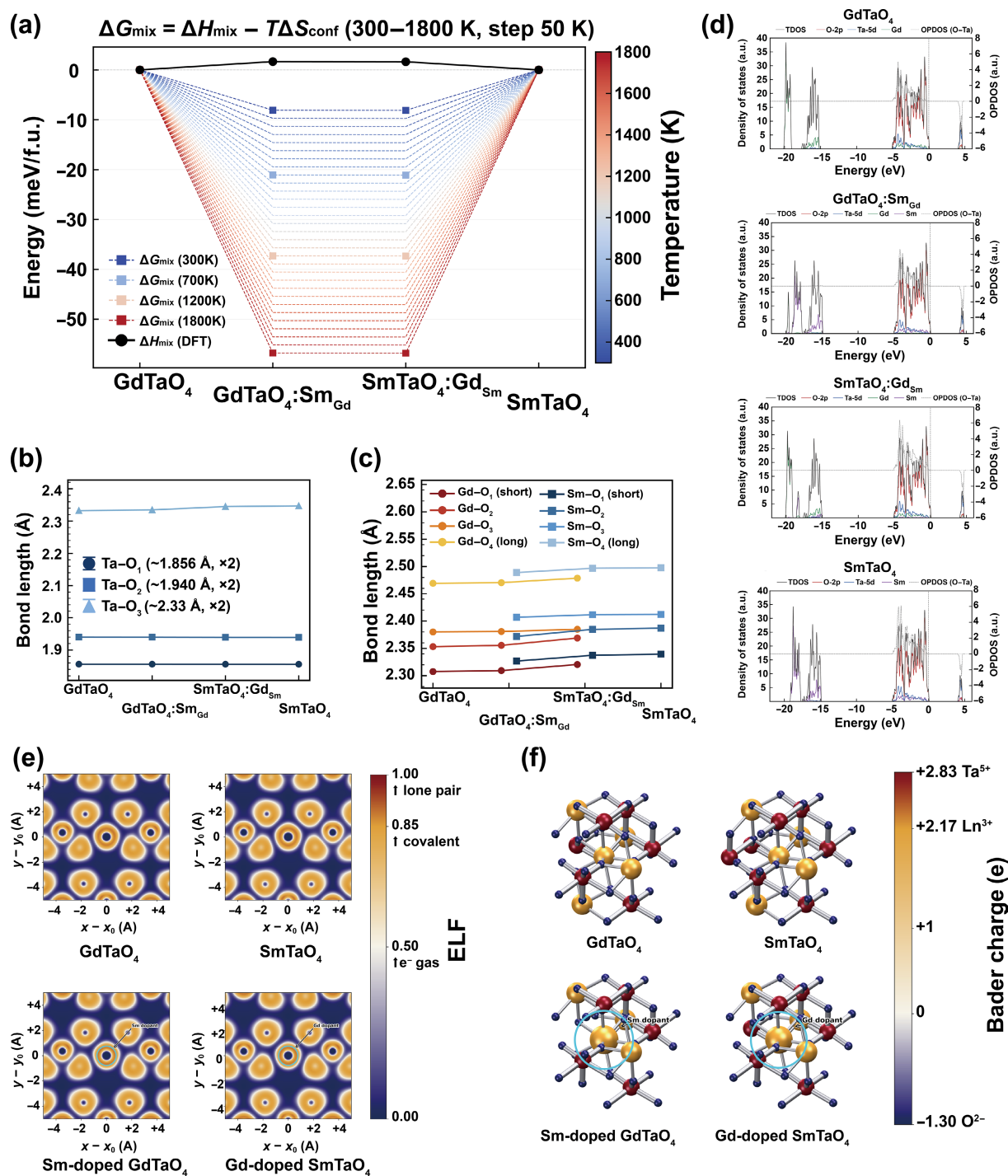


Fig. 2 First-principles structure and electronic response of (Gd,Sm)TaO₄. (a) $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{conf}}$ across 300–1800 K for four CP2K models (GdTaO₄, SmTaO₄, Sm-doped GdTaO₄, and Gd-doped SmTaO₄). (b) Ta–O and (c) RE–O bond-length groupings across four models. (d) DOS and OPDOS (O–Ta) on the same energy axis, with total DOS, O-2p, Ta-5d, and RE projections shown separately. (e) ELF maps sliced through dopant–RE cation layer. (f) RE-site Bader charges visualized on relaxed structures (full data in Table S4 in ESM).

monoclinic angle (β) varies continuously over a narrow range (Table S1 in the ESM). The $d_{(021)}$, $d_{(130)}$, and $d_{(131)}$ spacings in Fig. 1(e) also increase monotonically, in line with the low-angle peak shift in Fig. 1(b). This continuous expansion follows the Shannon ionic radii [51]. Sm³⁺ (CN = 8, 1.079 Å) is larger than Gd³⁺ (1.053 Å), so Sm substitution drives a cooperative expansion of the RE–O coordination polyhedra and the unit cell.

First-principles calculations (Methods, Section 2.5) account for the continuous solid-solution behavior at the atomic scale through

mixing thermodynamics and local relaxation. The density functional theory (DFT)-optimized end-member volumes increase from GdTaO₄ to SmTaO₄, in line with the XRD trend (Table S2 in the ESM). For the Sm-doped GdTaO₄ and Gd-doped SmTaO₄ models, ΔH_{mix} values of +1.7 and +1.6 meV/f.u. (Fig. 2(a)) indicate a negligible enthalpic penalty for Gd/Sm interchange. The configurational entropy term plotted in Fig. 2(a) is large enough to render ΔG_{mix} negative across 300–1800 K [52]. The relaxed structures show that the Gd/Sm radius difference is

accommodated primarily by cooperative adjustment of the first-nearest-neighbor RE–O bond lengths, with the Ta–O bond lengths essentially unchanged. The two short Ta–O bond groups nearly coincide across all four models, and the long Ta–O₃ bond elongates by less than 1%, whereas the equivalent RE–O bond groups elongate systematically as the matrix shifts from the Gd to the Sm end-member (Figs. 2(b) and 2(c)). This pattern, with limited Ta–O bond-length change and an RE–O adjustment that follows the RE radius, matches the structural behavior reported for related RENbO₄, in which the Nb–O coordination polyhedron remains relatively rigid while the RE–O polyhedron evolves with the RE radius [53]. Bond groupings and raw bond lengths are listed in Table S3 in the ESM.

The valence electronic structure is consistent with this picture. The DOS and OPDOS (Fig. 2(d)) reveal a valence band dominated by O-2p states co-distributed with Ta-5d states between –5 and 0 eV. OPDOS (O–Ta) is positive throughout the occupied valence region and turns negative in the low-energy Ta-5d conduction region, corresponding to a stable Ta–O bonding–antibonding distribution [47,54,55]. Sm/Gd interchange does not measurably alter this distribution, and the RE projections contribute little near the O-2p and Ta-5d band edges. ELF maps sliced through the dopant-RE cation layer (Fig. 2(e)) show the same O 2p lone-pair localization projected from the neighboring O layers and the same Ta-centered ELF depletion across all four configurations [50,56], and the Bader charge of a given RE element differs by no more than 0.003 e between its end-member and the corresponding doped model (Fig. 2(f) and Table S4 in the

ESM). Gd/Sm interchange is therefore accommodated within the fergusonite framework at low enthalpic cost and without resolvable site-charge changes. Structurally, this interchange adjusts the RE–O bond lengths and leaves the Ta–O bonding–antibonding distribution, the valence-electron localization, and the RE site charges intact.

The single-phase behavior across all compositions and the continuous unit-cell evolution from XRD Rietveld refinement, combined with the low mixing enthalpy and local structural and electronic stability from DFT, establish that (Gd_{1–x}Sm_x)TaO₄ forms a continuous single-phase fergusonite solid solution over $0 \leq x \leq 1$. This provides a consistent structural basis for the thermal-transport analysis in the following sections. Sm substitution localizes the structural response in the RE–O coordination environment and at the unit-cell scale, while the Ta–O bonding network remains stable across the series.

3.2 Raman evidence for weak local vibrational response, high-temperature reversibility, and microstructural homogeneity

Sm substitution only weakly perturbs the local Raman response associated with the Ta–O framework and the RE–O coordination environment across the (Gd_{1–x}Sm_x)TaO₄ series, and the Raman response of GST-0.8 is reversible across a 25–1200 °C thermal cycle. Room-temperature Raman spectra for the six compositions (Fig. 3(a)) share a common vibrational signature consistent with previously reported experimental and computed spectra of fergusonite-type RETaO₄ [57–59]. External modes dominate the

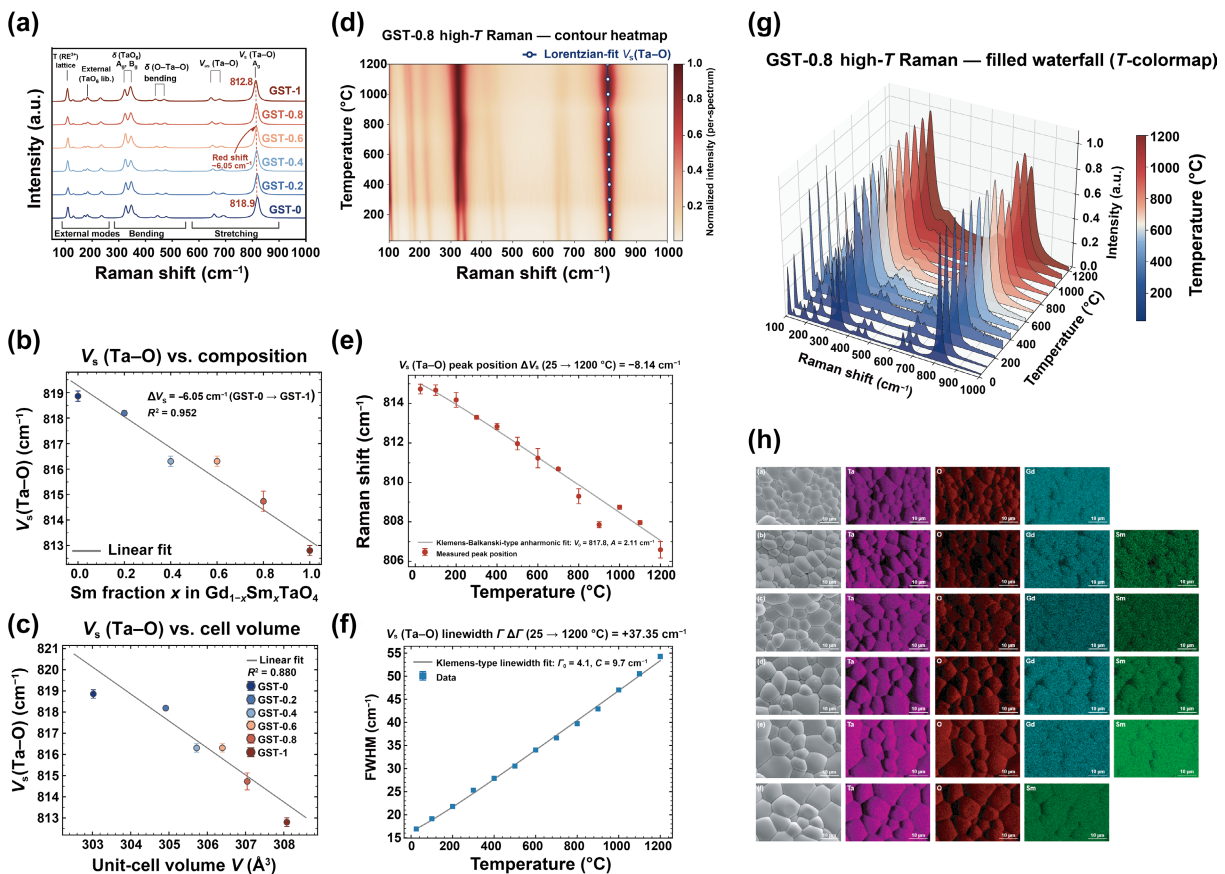


Fig. 3 Raman spectra and microstructure of (Gd_{1–x}Sm_x)TaO₄. (a) Room-temperature Raman spectra of six compositions, with external, bending, and Ta–O stretching regions labeled. (b) $\nu_s(\text{Ta–O})$ vs. x_{Sm} (weighted linear fit, $R^2 = 0.952$). (c) $\nu_s(\text{Ta–O})$ vs. unit-cell volume ($R^2 = 0.880$). (d, g) *In situ* Raman contour map and waterfall plot of GST-0.8 from 25 to 1200 °C. (e) Klemens–Balkanski symmetric three-phonon fit to ν_s peak position. (f) Klemens symmetric three-phonon fit to FWHM. (h) Secondary-electron SEM images and co-located EDS maps (Ta, O, Gd, and Sm) for six compositions, arranged from GST-0 (top) to GST-1 (bottom).

low-frequency region and combine RE³⁺ translations with rigid-unit translations and librations of the [TaO₆] octahedra, while TaO₆-related internal modes occupy the mid- and high-frequency regions [58]. No new peaks, peak splitting, or abrupt line-shape changes appear across the series. The symmetric Ta–O stretching mode $\nu_s(\text{Ta–O})$, corresponding to the highest-frequency internal TaO₆ mode in fergusonite GdTaO₄ [58], lies at 813–819 cm⁻¹ and redshifts by 6.05 cm⁻¹ as x_{Sm} increases from 0 to 1 (Fig. 3(b)), a relative change of only 0.74%. The external RE and lattice modes, by contrast, soften more strongly with Sm substitution (Fig. S9 in the ESM).

This redshift follows the DFT-relaxed bond-length redistribution (Figs. 2(b) and 2(c), Table S3 in the ESM). As expected from the Shannon-radius-driven expansion in Section 3.1, Sm/Gd substitution redshifts $\nu_s(\text{Ta–O})$ for $\gamma > 0$ [58]. Across the GdTaO₄–SmTaO₄ series, the four short Ta–O bonds in TaO₆ barely change in mean length. The long apical Ta–O bond elongates by 0.6%. The RE–O coordination polyhedron absorbs most of the 1.3% volume change. Because the short Ta–O bond group is nearly invariant, the 6.05 cm⁻¹ redshift is most conservatively interpreted as indirect modulation of the TaO₆ stretching force constant by the expanded RE–O environment. ν_s varies linearly with x_{Sm} (Fig. 3(b), weighted fit $R^2 = 0.952$), and combining this trend with the Rietveld cell volume gives $d\nu/dV = -1.28 \text{ cm}^{-1}\text{Å}^{-3}$ (Fig. 3(c), $R^2 = 0.880$). The corresponding apparent mode-volume coefficient is $\gamma_{\text{vapp}} = 0.48 \pm 0.09$ [60,61], setting the volume sensitivity of $\nu_s(\text{Ta–O})$ under Sm/Gd substitution. This matches the hydrostatic mode-Grüneisen $\gamma = 0.53$ reported for $\nu_s(\text{Ta–O})$ (A_g , 812 cm⁻¹) in end-member GdTaO₄ [58] within 10%, indicating that substitution and hydrostatic loading drive ν_s with the same $d\nu/dV$. Both values lie below the $\gamma \approx 2.4$ reported for a low-frequency external mode of the same lattice [58]. $\nu_s(\text{Ta–O})$ is therefore the low- γ internal channel of (Gd,Sm)TaO₄, and the external mode is the high- γ mode.

In situ Raman spectra of GST-0.8 between 25 and 1200 °C track the high-temperature evolution of ν_s . The contour map and waterfall plot (Figs. 3(d) and 3(g)) show a continuous redshift and broadening of the observed modes across the heating range, with no new peaks, peak splitting, or abrupt intensity changes. Lorentzian fits give an 8.14 cm⁻¹ redshift of $\nu_s(\text{Ta–O})$ and a full width at half maximum (FWHM) increase from ~17 to ~54 cm⁻¹ ($\Delta\Gamma = 37.35 \text{ cm}^{-1}$) over this range. The peak shift follows the symmetric three-phonon term ($B = 0$) of the Klemens–Balkanski model [28,29] (Fig. 3(e)), and the linewidth follows the symmetric Klemens three-phonon lifetime model [28] (Fig. 3(f)). Anharmonic frequency redshift and ν_s phonon lifetime shortening therefore dominate the high-temperature response, and no structural transition signature appears. Upon cooling to room temperature, ν_s and Γ return to within ~1 cm⁻¹ of their initial values (Fig. S1 in the ESM), so no irreversible signature is resolvable in the $\nu_s(\text{Ta–O})$ channel of GST-0.8 across 25–1200 °C.

Secondary-electron SEM images of the six compositions (Fig. 3(h), arranged from top to bottom) show dense micron-scale polyhedral grains without obvious pore clusters, secondary-phase precipitates, or compositionally distinct regions (Fig. S11 and Table S8 in the ESM). In the equivalent-circle-diameter analysis, we traced the boundaries to exclude the intragranular ferroelastic domain walls. The mean grain size is near 5 μm for GST-0 and GST-0.2, and approximately 7 μm for the GST-0.4 to GST-1 compositions. The κ minimum at GST-0.8 therefore falls among the coarser-grained, not the finest-grained, compositions. This is the reverse of what grain-boundary-limited transport would require. Coarsening also lowers the grain-boundary density as Sm

content increases. Boundary-limited transport would therefore raise, not lower, the conductivity across the series. All compositions have a relative density of approximately 96% by the Archimedes method, leaving 3%–4% residual porosity. The micron-scale grains are far larger than the phonon mean free path (1.85–2.18 nm). Grain-boundary scattering is therefore a minor, compositionally uniform channel. It cannot generate the observed composition trend. Applying the standard porosity correction $(1 - P)$ shifts the absolute values by a few percent. It leaves the trend and the GST-0.8 minimum unchanged. Colocated EDS maps for Ta, O, Gd, and Sm display uniform contrast in every channel, and no RE segregation or local enrichment is detected within the SEM/EDS spatial resolution and detection limit. The FWHM of $\nu_s(\text{Ta–O})$ stays within 17–18 cm⁻¹ across the series. Together with the 0.74% peak shift and the reversible anharmonic response from 25 to 1200 °C, this shows that the symmetric Ta–O stretch responds weakly to RE-site Sm/Gd substitution, in contrast to the stronger acoustic-channel softening over the same composition window (Section 3.3).

3.3 Sound velocity and elastic response

Sm substitution expands the RE–O coordination shell (Section 3.1) but leaves the Ta–O stretching modes nearly unchanged (~1%, Section 3.2). Ultrasonic pulse-echo measurements (Table 1) and Berkovich nanoindentation (Fig. 4) show much stronger softening at acoustic frequencies. From GST-0 to GST-0.8, v_m decreases from 2688 to 2158 m·s⁻¹ and θ_D from 344 to 275 K, both falling by ~20%, compared with only ~1% for the Ta–O optical mode. Between GST-0.8 and GST-1, v_m and θ_D plateau (Table 1).

The elastic moduli derived from these velocities also decrease: E from 130.5 to 78.4 GPa and G from 48.5 to 31.2 GPa from GST-0 to GST-0.8 (Fig. S10 and Table S7 in the ESM). The softening is asymmetric between bulk and shear. B falls by 62% (from 141 to 54 GPa), while G falls by only 36%, and the Poisson's ratio follows this contrast from 0.345 to 0.256 [62]. At GST-1, ν rebounds to 0.269 as B increases slightly to 56 GPa, while G settles at 30.7 GPa.

This asymmetry is explained by the bonding architecture established in Sections 3.1 and 3.2. The TaO₆ subnetwork preserves its short bond lengths within 1%, and its Ta-5d–O-2p bonding–antibonding distribution (Section 3.1) and $\nu_s(\text{Ta–O})$ shift by only 0.74% across the composition series (Section 3.2). The Ta–O force constants are therefore conserved across $0 \leq x_{\text{Sm}} \leq 1$. Shear deformation loads the lattice through bond-angle distortion, which the directional Ta–O bonding strongly resists, so G softens only weakly. Volumetric deformation instead loads the most compliant bonds in the cell, which the expanding ionic RE–O polyhedron supplies, and B collapses by 62% over the same window. The ν rebound at GST-1 coincides with the disappearance of Sm/Gd mixing on the RE sublattice and matches the κ rebound developed in Section 3.4.

Nanoindentation follows the ultrasonic trend. The Berkovich reduced the modulus E_r from 156.5 to 98.2 GPa and H from 8.45 to 5.85 GPa (Fig. 4). The maps in Figs. 4(a) and 4(c) show no spatial gradient within any single composition, and for $x_{\text{Sm}} \geq 0.6$, the H and E_r distributions broaden. From GST-0 to GST-0.8, (Gd_{1-x}Sm_x)TaO₄ thus exhibits substantial acoustic softening, while the high-frequency Ta–O optical mode remains nearly invariant. Thermal expansion is only weakly composition dependent, with the CTE within 6×10^{-6} – $11 \times 10^{-6} \text{ K}^{-1}$ from 200 to 1200 °C across all samples (Fig. S2 in the ESM). The GST-0 dilatometric curve is smooth across the whole range. It shows no discontinuity or slope break near 600 °C. This confirms the absence of a reconstructive phase transition over this range. High-temperature Raman spectra

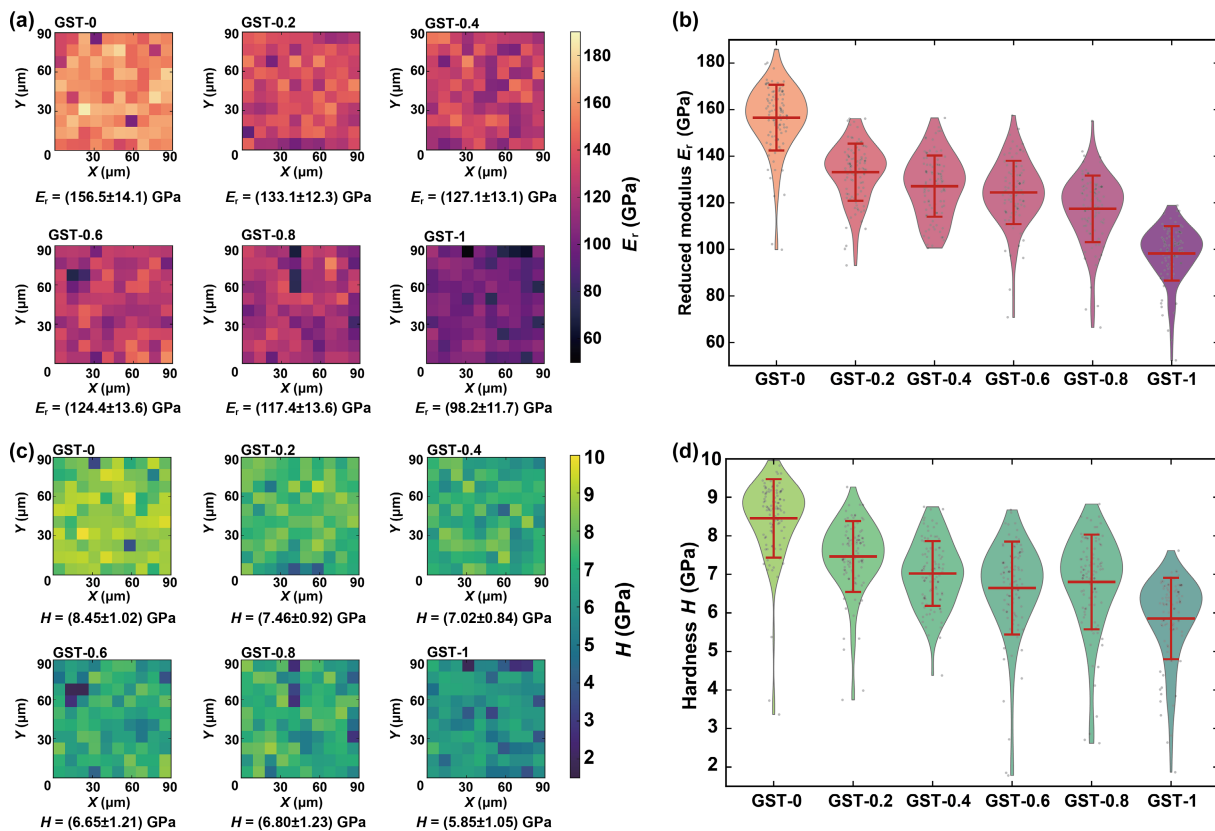


Fig. 4 Berkovich nanoindentation of $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$. (a, c) 10×10 spatial maps of E_r and H for six compositions, with mean $\pm$ standard deviation annotated in each panel. (b, d) Violin distributions of E_r and H vs. x_{Sm} .

also remain continuous and fully reversible up to 1200 °C. The differential scanning calorimetry (DSC) traces show no endothermic or exothermic anomalies from room temperature to 1197 °C (Fig. S6 in the ESM). The DSC measurements were not calibrated for absolute specific heat capacity and were used only to check for thermal anomalies. The absence of a thermal anomaly is consistent with the smooth heat-capacity trend assumed in the Neumann–Kopp estimate. The $\kappa(T)$ curve also passes smoothly through 600 °C. Together, these observations corroborate the absence of a reconstructive phase transition. The CTE rises monotonically to 1200 °C without a plateau because the dominant mechanism shifts with temperature. Up to approximately 900 °C, the stiff Ta–O stretching modes near 800 cm^{-1} (Einstein temperature ≈ 1150 K) are still being populated. The lattice heat capacity has therefore not reached its Dulong–Petit limit and continues to rise (Fig. S12 in the ESM). This lifts the CTE through the Grüneisen relation. Above this range, the heat capacity is nearly saturated. The continued increase is instead sustained by intrinsic anharmonicity, principally the softening of the elastic moduli with temperature. This raises the expansion coefficient even at a fixed heat capacity. The absence of a plateau across the full window is consistent with the monotonic rise reported for related RETaO_4 ceramics [14].

3.4 Sound velocity and residual RE sublattice disorder contributions to thermal conductivity reduction

Thermal conductivity decreases in an Umklapp-dominated manner [63] with a slight high-temperature upturn from a radiative contribution [19] (Fig. 5(a)). The 25 °C κ decreases from 5.11 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at GST-0 to 3.48 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at GST-0.8 (–32%) and rebounds to 3.74 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at GST-1. Across all isotherms, the nominal κ – x minimum lies at $x_{\text{Sm}} = 0.8$, with GST-0.8 and GST-1

overlapping within uncertainty at the highest temperatures (Fig. 5(b)).

Normalizing v_m , ρC_p , κ_{Cahill} , and the measured κ to their GST-0 values (Fig. 5(c)) shows that ρC_p varies by $\leq 4\%$ across the series since the density decrease and the C_p increase compensate. From GST-0 to GST-0.8, v_m and κ_{Cahill} from Eq. (8) (built from v_T , v_L , and n_V), the measured κ decreases by 19.7%, 25.7%, and 32%, respectively. The measured drop exceeds but closely follows the Cahill geometric scale, so acoustic softening and unit-cell expansion account for most of the κ reduction across compositions [11,64]. κ_{Cahill} here serves only as an acoustic geometric reference, and the measured lattice conductivity is compared with the ultimate acoustic limits in Fig. S5 in the ESM.

Raw thermal diffusivity and specific heat inputs appear in Fig. S3 in the ESM. Per-sample fit windows for α_{fit} in Eq. (10) span 25–400, 25–500, or 25–600 °C (Fig. S4 and Table S5 in the ESM). All three fit windows lie below the onset of the high-temperature radiative upturn near 700 °C. The fitted regime is therefore governed by intrinsic Umklapp scattering rather than radiative transfer. The radiative contribution is only approximately 3%–7% of the conductivity at 900 °C (Fig. S7 in the ESM). The intrinsic phonon mean free path in Fig. 5(d) is 1.85–2.18 nm at 25 °C, and the spread of l_{int} across compositions narrows to $\leq 5\%$ above 300 °C. l_{int} remains larger than the ~ 3 Å nearest-neighbor spacing even at the highest temperatures, so $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$ remains above the amorphous limit throughout the measurement range.

The Klemens–Abeles Γ_{PD} from Eq. (9) reaches its lowest value among the doped compositions at GST-0.8, approximately 60% below the GST-0.4 value (Fig. 5(e)). A κ – x minimum set by the Klemens–Abeles mass and strain fluctuations alone would require Γ_{PD} to peak near the low- κ composition. Γ_{PD} instead peaks at $x_{\text{Sm}} = 0.2$ – 0.6 , displaced from the κ minimum at $x_{\text{Sm}} = 0.8$. The scalar

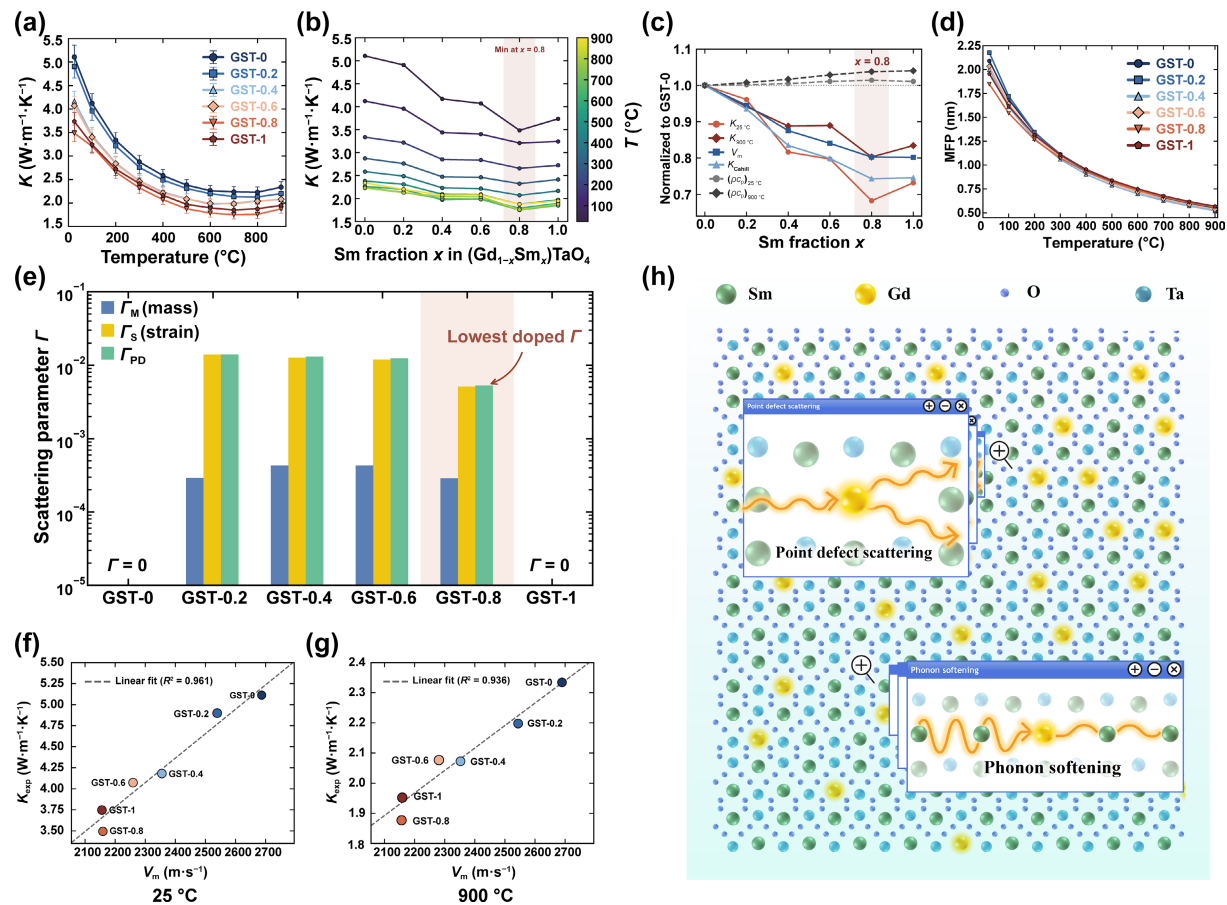


Fig. 5 Decomposition of $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$ thermal conductivity into a sound-velocity- V_{cell} channel and residual RE-sublattice disorder scattering. (a) $\kappa(T)$ for six compositions across 25–900 °C. (b) Isotherm-resolved κ - x with $x_{\text{Sm}} = 0.8$ minimum shaded. (c) v_m , ρc_p , κ_{Cahill} , and measured κ at 25 and 900 °C, normalized to GST-0. (d) Mean free path $l_{\text{mt}} = 3\alpha_{\text{fit}}/v_m$ vs. temperature (per-sample fits in Table S5 and Fig. S4 in ESM). (e) Klemens–Abeles Γ_M , Γ_S , and Γ_{PD} . (f, g) κ - v_m at 25 and 900 °C with linear regressions. (h) Schematic of two coexisting κ -reduction channels: An acoustic–volumetric channel, in which RE-site lattice distortion expands V_{cell} and softens acoustic branches (“phonon softening” inset), and a residual RE-sublattice point-defect scattering channel (“point defect scattering” inset). Error bars in (a) denote $\pm 5\%$ uncertainty in κ .

Klemens–Abeles scattering parameter therefore cannot by itself predict the location of the κ - x minimum. A point-defect-controlled minimum thermal conductivity would lie near $x = 0.5$, whereas the measured minimum tracks the monotonic decline of the sound velocity to $x = 0.8$. The scalar form thus underestimates the true RE sublattice scattering at GST-0.8, as the κ rebound from GST-0.8 to GST-1 below demonstrates directly.

In the κ - v_m plane, the 25 and 900 °C data both show clear positive correlations, with linear regression R^2 values of 0.961 and 0.936 (Figs. 5(f) and 5(g)). Lower- v_m compositions have lower κ across the series. This cross-temperature covariation is consistent with the sound-velocity- V_{cell} channel that dominates the κ reduction in Fig. 5(c). The κ - x minimum, however, falls at the near-velocity-matched GST-0.8 rather than at the lowest- v_m end-member GST-1. This displacement, together with the fact that Γ_{PD} is lowest at GST-0.8 among the doped compositions (Fig. 5(e)), indicates residual RE-sublattice disorder scattering at the κ minimum beyond the scalar Klemens–Abeles Γ_{PD} description [65].

The GST-0.8 to GST-1 step provides a local comparison at nearly identical sound velocities. The two compositions differ in v_m by only 0.09% (Table 1), and κ_{Cahill} from Eq. (8) rebounds by only 0.37%, whereas the measured 25 °C κ rebounds by 7.2% (0.25 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, Fig. 5(a)). Sound velocity and unit-cell changes cannot account for this rebound. The κ rebound at the end-member GST-1, where Sm/Gd mixing disorder vanishes, is

consistent with residual RE-sublattice disorder scattering at GST-0.8 (Fig. 5(h)).

Together with Figs. 5(a)–5(g), the schematic in Fig. 5(h) captures the composition dependence of κ in $(\text{Gd}_{1-x}\text{Sm}_x)\text{TaO}_4$ through two coexisting channels. The first is a sound-velocity- V_{cell} channel. Sm/Gd substitution distorts the RE–O coordination environment while leaving the short Ta–O bonds essentially unchanged (Sections 3.1 and 3.2). This lattice distortion is accompanied by a monotonic expansion of V_{cell} across the series, and v_m and θ_D accordingly fall by approximately 20% from GST-0 to GST-0.8 (acoustic softening, Section 3.3) [66]. The Cahill geometric scale predicts a 25.7% relative drop that captures most of the measured 32% reduction. First-principles phonon dispersions confirm a monotonic redshift of the low-frequency acoustic branches with increasing Sm content (Fig. S8 in the ESM). The second is residual RE-sublattice disordered scattering. The Klemens–Abeles Γ_{PD} peaks at compositions offset from the κ minimum, and the near-velocity-matched GST-0.8 to GST-1 step shows a κ rebound once Sm/Gd mixing disappears at the end member. From GST-0 to GST-0.8, the κ reduction is therefore set primarily by the sound-velocity- V_{cell} channel, while the κ minimum at $x_{\text{Sm}} = 0.8$ is consistent with residual RE-sublattice disorder scattering [67]. This decomposition separates end-member screening through v_m and V_{cell} from substitution-ratio optimization. The two channels are nonetheless not independent at the microscopic level. The group velocity and relaxation time

remain coupled, and an absolute partition into velocity, velocity-dependent Umklapp, and disorder-limited lifetime contributions awaits a full anharmonic Boltzmann transport calculation with disorder-resolved phonon lifetimes. The framework applies to RETaO₄-based composition design [22] and complex oxide solid solutions with large end-member elastic or unit-cell contrast. Ta₂O₅ can direct mullite growth and improve wear resistance [68]. Volume strain can govern anode contact interfaces [69]. However, the present thermal-transport framework is limited to structurally analogous rigid-framework oxides. It does not extend to perovskites or fluorites, where other mechanisms may govern. For example, fluctuating bonding can cause glass-like transport in perovskite tantalates [67].

Within the RE tantalate family, we compare the present (Gd_{1-x}Sm_x)TaO₄ series with published data. Radiation-corrected lattice κ values for monoclinic RETaO₄ range from approximately 1.3 to 1.8 W·m⁻¹·K⁻¹ at 900 °C, including EuTaO₄ and HoTaO₄ [14]. We also include the (Gd_{1-x}Y_x)TaO₄ solid solution [70] (Table S6 in the ESM). The (Gd_{1-x}Y_x)TaO₄ series provides useful control. Its mean sound velocity is non-monotonic. The minimum occurs at $x = 1/6$. Its κ minimum coincides with the point-defect Γ maximum at $x = 3/6$. Point-defect scattering controls this trend. The present system behaves differently. Its κ minimum follows the decrease in sound velocity and is offset from the Γ maximum. The isostructural fergusonite RENbO₄ family offers an independent test of how the conductivity tracks the sound velocity. In the RENbO₄ series, the softest member also has the lowest derived phonon thermal conductivity, with the Cahill acoustic lower bound following the same ordering [71,72], consistent with an acoustic contribution. Across the family, the cation mass and structural subtype vary together with the RE element, so a single sound-velocity law cannot be isolated from the reported data, and the descriptor developed here is bounded to the isovalent (Gd,Sm) substitution.

4 Conclusions

(Gd_{1-x}Sm_x)TaO₄ forms a single-phase fergusonite solid solution across $0 \leq x \leq 1$, with Sm/Gd substitution accommodated by RE–O polyhedral expansion and a comparatively rigid Ta–O subnetwork. From GST-0 to GST-0.8, v_m and θ_D decrease by 19.7% and 20.1%, respectively, and the 25 °C κ falls from 5.11 to 3.48 W·m⁻¹·K⁻¹ (–32%). A Cahill geometric scale reproduces a 25.7% relative drop, capturing most of the measured reduction through a sound-velocity– V_{cell} channel. The Klemens–Abeles Γ_{PD} peaks at $x_{\text{Sm}} = 0.2$ – 0.6 are displaced from the κ – x minimum at $x_{\text{Sm}} = 0.8$. Together with the κ rebound across the near-velocity-matched GST-0.8 to GST-1 step, the κ – x minimum lies outside the scalar Klemens–Abeles locus and is consistent with residual RE-sublattice disorder scattering.

Conventional RETaO₄ low- κ screening uses Klemens–Abeles mass and radius mismatches as a single descriptor. The sound-velocity– V_{cell} channel established here adds a second, distinct descriptor. GST-0.8 lies near the acoustic-softening lower bound under this combined criterion. Its Raman response is reversible to 1200 °C, and its CTE is within 6×10^{-6} – 11×10^{-6} K⁻¹. This makes it a potential low- κ candidate. The same principle extends to other rigid-framework oxides that combine a stiff covalent skeleton with compliant, low-mismatch RE sites, although not universally. Perovskites and fluorites lack this structural separation, and different scattering mechanisms govern these materials. The zirconate pyrochlore RE₂Zr₂O₇, with a rigid ZrO₆ framework and a softer RE A-site, is a promising but untested case.

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Author contributions

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article. The author Jing Feng is the Editorial Committee member of this journal.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.26599/JAC.2026.9221355>.

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