

Phonon scattering limited mobility in the representative cubic perovskite semiconductors SrGeO₃, BaSnO₃, and SrTiO₃

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Cubic perovskite oxides are emerging high-mobility transparent conducting oxides (TCOs), but Ge-based TCOs had not been known until the discovery of metastable cubic SrGeO₃. 0.5 × 0.4 × 0.2-mm³ large single crystals of the cubic SrGeO₃ perovskite were successfully synthesized employing the high-pressure flux method. The phonon spectrum is determined from the IR optical reflectance and Raman-scattering analysis to evaluate the electron transport governed by optical phonon scattering. A calculated room-temperature mobility on the order of 3.9 × 10² cm² V⁻¹ s⁻¹ is obtained, identifying cubic SrGeO₃ as one of the most promising TCOs. Employing classical phonon theory and a combined experimental-theoretical approach, a comprehensive analysis of the intrinsic electron mobility in the cubic perovskite semiconductors SrGeO₃, BaSnO₃, and SrTiO₃ is provided based on the magnitude of polarization and eigenfrequency of optically active phonons.

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I. INTRODUCTION

Transparent conducting oxides (TCOs) are emerging materials combining high electrical conductivity and optical transparency in the visible spectral region, and present important applications in optoelectronic devices. Since the discovery of the high-mobility two-dimensional electron gas in oxide heterostructures [1], perovskites became particularly attractive for advanced semiconductor technology as they facilitate a new design of future electronic devices due to the unique physics occurring at the interfaces of heterojunctions [2]. The recent reports of the remarkably high electron mobility at cryogenic temperatures in La:SrTiO₃ epitaxial films (> 50 000 cm² V⁻¹ s⁻¹) [3,4] and at room temperature (RT) in La:BaSnO₃ single crystals (320 cm² V⁻¹ s⁻¹) [5,6] sparked significant interest in understanding the fundamentals of the intrinsic electron transport in perovskite semiconductors and their application in heterostructures [7–9].

The discovery of the first Ge-based TCO, cubic perovskite SrGeO₃ [10], invites the exploration of a new, promising emerging material for application in electronics. The large conduction band (CB) dispersions in the main-group element cubic perovskites SrGeO₃ and BaSnO₃ originate from the regular octahedral coordination of the Ge⁴⁺ (Sn⁴⁺) cation to O²⁻ anions with the point symmetry O_h [11,12]. This coordination symmetry prohibits the hybridization of Ge 4s (Sn 5s) and O 2p orbitals at the Γ point in the Brillouin zone. Thus, the resulting nonbonding state at the Γ point and the antibonding states at the boundaries of the Brillouin zone have energy levels separated by several eV. The large CB curvatures

yield small effective masses of SrGeO₃ (0.22 m_e) and BaSnO₃ (0.19 m_e) [13,14], where m_e denotes the electron rest mass.

The relatively large static dielectric permittivity of perovskites is a beneficial material property which screens the electron-charge interaction and promotes the electron transport. It results from the strongly ionic character of the chemical bonds and the ion displacement from the equilibrium lattice sites. These thermally activated lattice vibrations, known as phonons, may account for a large ionic polarization even when the material is composed of only main-group elements. The static dielectric constants of SrGeO₃ (18 ± 1) and BaSnO₃ (20 [15], 20 ± 2 [16,17] (Supplemental Material), 14.8 ± 0.5 [18]) are about 2–3 times larger than those of the well-established TCOs like ZnO ($\epsilon_s^{\parallel c} = 7.4$, $\epsilon_s^{\perp c} = 8.5$) [19], In₂O₃ ($\epsilon_s = 8.5$) [20], and SnO₂ ($\epsilon_s^{\parallel c} = 14$, $\epsilon_s^{\perp c} = 9.0$) [21]. Although recent Berry phase calculations have revealed that electron transfer has a large contribution to such large dielectric polarizations, their origins have not yet been discussed in relation to phononic polarizations experimentally. Due to the large polarization, the RT electron mobility in substitutionally doped perovskite oxides is governed by electron-phonon interactions rather than ionized impurity scattering [22,23], and the dielectric screening of ionized impurities supports a high electron mobility even at enhanced carrier concentrations [14,24]. In contrast to the majority of TCOs with an $(n - 1)d^{10}ns^0$ electronic configuration (n is the principal quantum number), transition-metal based semiconductors such as SrTiO₃ and TiO₂ have rather localized unoccupied wave functions originating from the Ti 3d orbitals and a large effective mass. However, these semiconductors may nevertheless exhibit fairly good electrical transport properties. In this case, the large dielectric screening (SrTiO₃, $\epsilon_s = 310$ [25]; and TiO₂, $\epsilon_s^{\parallel c} = 173$, $\epsilon_s^{\perp c} = 89$) [26] is seen as a key property for promoting the electrical conductivity [27].

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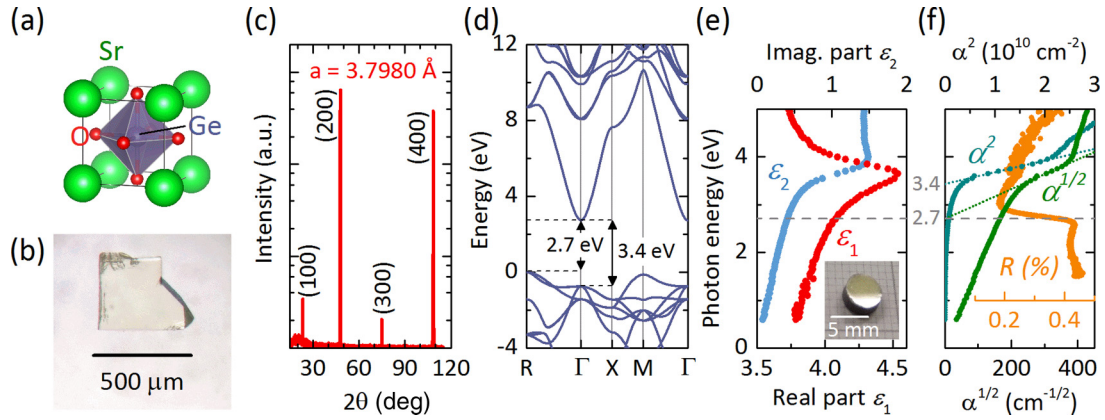


FIG. 1. (a) The cubic perovskite SrGeO_3 crystal structure. (b) Optical micrograph of a cubic SrGeO_3 single crystal. (c) The 100 out-of-plane HR-XRD pattern of a cubic SrGeO_3 single crystal with the intensity plotted on a logarithmic scale. (d) PBE0-calculated band structure along high-symmetry directions in the first Brillouin zone indicates 2.7-eV indirect and 3.4-eV direct band gaps and a large CB dispersion. (e) Reflection ellipsometry spectrum for the evaluation of (f) the absorption coefficient data $\alpha^{1/2}$ and α^2 indicate optical band gaps in agreement with the specular reflectance R edge and the calculated values.

This work employs a combined experimental-theoretical approach to provide a fundamental understanding of how the ionic polarization, decoded into the contribution of separate phonon modes, impacts the intrinsic electron transport in cubic perovskite semiconductors. SrTiO_3 and BaSnO_3 have been well characterized, and recently, also large-size single BaSnO_3 crystals could be grown from the melt [28] and hydrothermal methods [29]. In contrast, up to present, the cubic perovskite SrGeO_3 [Fig. 1(a)] has remained widely unexplored due to the difficulty in the synthesis, requiring high-pressure conditions [30]. So far, only a $0.1 \times 0.08 \times 0.08\text{-mm}^3$ small single crystal was obtained employing the high-pressure sintering of a polycrystalline sample [31]. We report the successful single-crystal growth of cubic SrGeO_3 employing the high-pressure flux method. The phonon spectrum of cubic SrGeO_3 was determined, which allows for a quantitative analysis of the intrinsic mobility, in comparison with SrTiO_3 and BaSnO_3 . We conclude that the particular combination of properties, a large polarization of the hardest longitudinal optical (LO) phonon mode *and* a small effective mass, would be effective for the design of electronic materials with an exceptionally high-RT electron mobility.

II. MATERIALS AND METHODS

A. Experimental

Cubic SrGeO_3 single crystals were grown using a belt-type high-pressure apparatus [32]. The precursor powder, monoclinic SrGeO_3 (space group $C2/c$), was prepared by calcination of stoichiometric quantities of SrCO_3 and GeO_2 at 1100°C for 12 h on Pt foil. The monoclinic SrGeO_3 powder (100 mg) was mixed in the 1:7 molar ratio with a $\text{SrCl}_2/\text{NaCl}$ flux of the molar composition 3:2. The eutectic point in the $\text{SrCl}_2\text{-NaCl}$ system lies at 544°C and 53 mol.% SrCl_2 [33]. SrCl_2 and NaCl were dehydrated at 350°C prior to the mixing. The powder mixture was filled into a Au capsule, pressed, and inserted into a NaCl/ZrO_2 cell of the weight ratio 9:1 with a carbon heater. A 5-GPa pressure was applied and the specimen was annealed at 1100°C for 4 h, then slowly cooled down to 800°C within 18 h, at

which point the heating was turned off and the specimen was water cooled to room temperature. After washing out the flux with deionized water, yellowish transparent cubic SrGeO_3 ($Pm\bar{3}m$) single crystals of up to $0.5 \times 0.4 \times 0.2\text{ mm}^3$ size and naturally grown 100 facets were obtained [Fig. 1(b)]. Colorless, orthorhombic $\beta\text{-SrGe}_2\text{O}_5$ ($Pnma$) single crystals were obtained as side product [34]. We also prepared dense, cubic SrGeO_3 and $\text{La}_{0.02}\text{Sr}_{0.98}\text{GeO}_3$ polycrystalline pellets of 5-mm diameter by sintering the precursor powder in a BN capsule at 1100°C for 2 h at 5-GPa pressure. The pellets were cleaved and the surface was mirror polished for optical reflectance measurements.

The 100 out-of-plane high-resolution x-ray diffraction (HR-XRD) pattern of cubic SrGeO_3 single crystals and the rocking curve of the 200 peak were recorded using a Rigaku SmartLab diffractometer equipped with a monochromatic $\text{Cu K}\alpha_1$ x-ray source (1.5406 Å) and utilizing parallel beam optics. Reflection ellipsometry spectra (Jobin Yvon UVISEL) were recorded from 0.6–5 eV. Specular reflectance spectra (Hitachi U-4100) were recorded from 1.5–5.0 eV and using vacuum Fourier-transform IR spectroscopy (Bruker Vertex 70v) from 100–8000- cm^{-1} wave number. Al and Au mirrors were used as 100% reflectance standards, respectively. For measuring the nonpolarized Raman spectrum of cubic SrGeO_3 single crystals, we used a Horiba LabRAM HR system in the backscattering configuration employing the 457-nm wavelength of a Nd:YVO₄ laser (Cobolt Twist 50) and a liquid N₂-cooled charge-coupled device detector.

B. Computational

We performed the theoretical calculations using hybrid density-functional theory (DFT) and the projector augmented-wave method [35] as implemented in the Vienna *Ab initio* Simulation Package (VASP) [36,37]. As the cubic perovskite has no degree of freedom for internal atomic coordinates, only the lattice parameter a was relaxed by using the Perdew-Burke-Ernzerhof (PBE0) hybrid functional [38]. A plane-wave cutoff of 500 eV and a Γ -centered $6 \times 6 \times 6$ k mesh were used. The relaxed ground-state cubic SrGeO_3 structure

has the calculated lattice parameter of 3.80 Å, which is in excellent agreement with the experimental value at room temperature, 3.7978 Å [31]. The electronic band structure was calculated employing maximally localized Wannier functions using the code WANNIER90 [39]. We employed the PBE0 functional because it gave a reasonable band gap for related oxides, GeO₂ (tetragonal, $P4_2/mnm$, $E_g^{\text{calc}} = 4.55$ eV, $E_g^{\text{exp}} = 4.68$ eV) [40] and BaSnO₃ ($E_g^{\text{calc}} = 3.17$ eV, $E_g^{\text{exp}} = 2.95$ eV) [24].

We used the PHONOPY code [41] and adopted the experimental lattice parameters at room temperature since they largely affect the phonon frequencies. For the exchange-correlation functional, we adopted the generalized gradient approximation with a very high accuracy of total energy criteria for self-consistent convergence, 10^{-8} eV. $2 \times 2 \times 2$ 40-atom supercells were used along with a plane-wave cutoff of 400 eV and a Γ -centered $4 \times 4 \times 4$ k mesh.

III. CRYSTAL STRUCTURE, ELECTRONIC STRUCTURE, AND OPTICAL CHARACTERIZATION OF CUBIC SrGeO₃

The 100 out-of-plane HR-XRD pattern of the SrGeO₃ single crystal confirms the cubic structure and a 3.7980-Å lattice parameter is obtained using Bragg's law [Fig. 1(c)]. The narrow, 0.023° wide full width at half maximum of the rocking curve of the 200 peak indicates a low degree of mosaicity of the single crystal (Fig. S1 [17]). The PBE0-calculated band structure of the cubic perovskite SrGeO₃ shows a 2.7-eV indirect band gap of the CB minimum at the Γ point and the valence-band (VB) maximum at the R point of the first Brillouin zone [Fig. 1(d)]. The effective mass of 0.22 m_e is determined from the CB curvature at the Γ point [42],

$$m_e^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}, \quad (1)$$

where \hbar is the reduced Planck constant and k is the reciprocal space vector. Using a cleaved and mirror-polished cubic SrGeO₃ polycrystalline pellet, we obtained the reflection ellipsometry spectrum [Fig. 1(e)] to evaluate the absorption coefficient α . Note that the absorption below the optical band gap is a measurement artifact due to the residual surface roughness which causes diffuse scattering or trace subgap absorption from in-band-gap defects. The linear fits to the $\alpha^{1/2}$ and α^2 -photon energy plots in the vicinity of the absorption edge allow for the determination of 2.7-eV indirect and 3.4-eV direct optical band gaps, respectively, in agreement with the specular reflectance edge and the calculated values [Fig. 1(f)].

IV. PHONON SPECTRA OF CUBIC PEROVSKITES

A. IR dispersion function of cubic SrGeO₃

To investigate the intrinsic electron mobility in cubic SrGeO₃, we first determine the phonon spectrum. Materials crystallizing in the cubic perovskite structure (one SrGeO₃ chemical unit) have a total of 15 phonon modes [43]; 3 acoustic modes, 4 pairs of doubly degenerate transverse optical (TO) modes, and 4 longitudinal optical (LO) phonon modes. Only three of the four triplets of optical modes are IR active, having a net ionic dipole moment which contributes to the macroscopic static polarization. Thus, we construct the optical

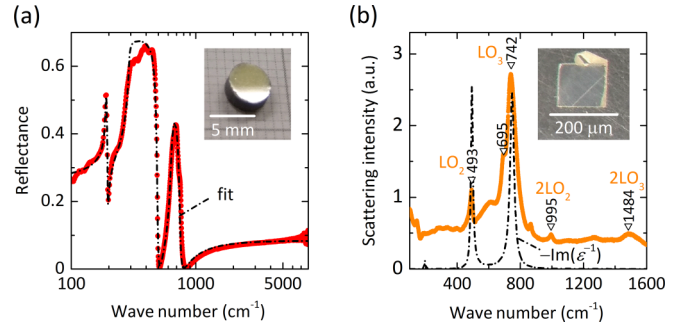


FIG. 2. (a) IR reflectance spectrum of a mirror-polished cubic SrGeO₃ polycrystalline pellet. (b) Raman-scattering spectrum of a cubic perovskite SrGeO₃ single crystal. The first-order Raman peaks at 493 and 742 cm⁻¹ provide the LO₂ and LO₃ phonon frequencies in the dispersion model, as given by the maxima of the loss function $-\text{Im}(\epsilon^{-1})$.

dispersion model using a Lorentz oscillator [44] for each of the three IR-active TO phonon modes,

$$\epsilon(\omega) = \epsilon_\infty + \sum_{\mu} \frac{\epsilon_{t\mu} \omega_{t\mu}^2}{\omega_{t\mu}^2 - \omega^2 - i\gamma_{\mu}\omega}, \quad (2)$$

where ϵ_∞ is the high-frequency dielectric constant, $\omega_{t\mu}$ is the TO phonon eigenfrequency, and γ_{μ} is the damping frequency, both given as angular frequencies. The contribution of the individual phonon modes to the static polarization is given by the TO phonon oscillator strength $\epsilon_{t\mu}$. Following the classical theory of polarization waves in crystals [45], the TO phonon oscillator strength is given by

$$\epsilon_{t\mu} = \frac{(\sum_i e_i^* x_{t\mu,i})^2}{\omega_{t\mu}^2 \epsilon_0 V \sum_i M_i x_{t\mu,i}^2}, \quad (3)$$

where ϵ_0 is the vacuum permittivity and V is the unit-cell volume. The ionic polarization results from the displacement $x_{t\mu,i}$ of ions with the Born effective charge e_i^* and the atomic mass M_i . This classical theory holds for the harmonic vibration regime, in which ion displacements are sufficiently small, such that the induced polarization can be described as a linear function of $x_{t\mu,i}$. In fact, the displacement of a certain ion would also induce a polarization on other ions as well, giving a rather complicated description of the total polarization.

For the determination of the dispersion parameters in Eq. (2), we fit the specular IR reflectance spectrum of a mirror-polished cubic SrGeO₃ polycrystalline pellet [Fig. 2(a)]. In addition, we measured the Raman spectrum for a cubic SrGeO₃ single crystal. The first-order Raman peaks provide the LO phonon frequencies, which are given by the maxima of the loss function $-\text{Im}(\epsilon^{-1})$ [46]. According to theory, cubic perovskites shall not show any first-order Raman active modes [43], but we observe the LO₂ and LO₃ phonons at 493- and 742-cm⁻¹ wave number, respectively, as well as their overtones at 995 and 1484 cm⁻¹ [Fig. 2(b)]. The shoulder peak at 695 cm⁻¹ may relate to the LO₁ + LO₂ overtone. The LO₁ mode cannot be identified due to its negligibly small polarization. The Raman spectrum of cubic SrGeO₃ is strikingly similar to that of BaSnO₃, and a large scattering intensity of the LO₂ and LO₃ phonons is observed [16]. The

TABLE I. TO phonon frequency ω_{μ} , damping frequency γ_{μ} , and oscillator strength ε_{μ} describing the SrGeO₃, BaSnO₃, and SrTiO₃ IR dielectric functions using three Lorentz oscillators [Eq. (2)]. The high-frequency dielectric constants are $\varepsilon_{\infty}^{\text{SrGeO}_3} = 4.2 \pm 0.2$, $\varepsilon_{\infty}^{\text{BaSnO}_3} = 4.3$ [16], and $\varepsilon_{\infty}^{\text{SrTiO}_3} = 5.2$ [25]. Values in brackets denote calculation results using the PBE functional. The theoretical TO phonon oscillator strength ε_{μ} is obtained from the phonon calculation results of the ion displacement vectors and Born effective charges [Eq. (3)].

Material	Eigenfrequency ω_{μ} (cm ⁻¹)	Energy $\hbar\omega_{\mu}$ (meV)	Damping frequency γ_{μ} (cm ⁻¹)	Oscillator strength ε_{μ}
SrGeO ₃	189 (180)	23	4.0	1.8 (3.1)
	291 (270)	36	7.6	11.2 (9.8)
	634 (671)	79	39	0.83 (1.4)
BaSnO ₃ ^a	135 (136)	17	10	3.8 ± 2 (3.8)
	246 (231)	30	18	10.8 (13.8)
	629 (641)	78	26	0.76 (1.0)
SrTiO ₃ ^b	88 (81)	11	26	299 (288)
	178 (173)	22	6.1	3.6 (21)
	546 (561)	68	27	1.9 (2.9)

^aReferences [16,17].

^bReference [25].

large Raman response of LO modes has been attributed to resonant multiphonon scattering known to occur in materials of large lattice polarizability.

The IR reflectance spectrum was fitted by first constraining the LO₂ and LO₃ frequencies to 493 and 792 cm⁻¹, respectively, and determining the high-frequency dielectric constant $\varepsilon_{\infty} = 4.2 \pm 0.2$ from the position of the reflectance edge near a frequency of 760 cm⁻¹. Then, all dispersion parameters were allowed to vary for the final fitting to obtain a reliable dispersion model which can very well reproduce both, the IR reflectance spectrum and the frequencies of the first-order LO₂ and LO₃ Raman peaks. We do not attempt to fit the Raman-scattering intensity, which is a complicated function of wave number that cannot be simply described by considering only the loss function $-\text{Im}(\varepsilon^{-1})$ [47]. The fitting was performed using the RefFIT program [48] and the obtained dispersion parameters are given in Table I. The cubic SrGeO₃ static dielectric constant $\varepsilon_s = 18 \pm 1$ is obtained from the sum of the high-frequency dielectric constant and all three TO phonon oscillator strengths ε_{μ} . The largest contribution to the total static polarization originates from the TO₂ mode ($\varepsilon_{\text{t}_2} = 11.2$).

The result of our dispersion model contradicts the finding of the apparently very high static dielectric constant ($\varepsilon_s = 114$) and largely polar TO₁ mode ($\varepsilon_{\text{t}_1} = 100.5$) in cubic SrGeO₃ reported by Grzechnik [49–51]. Our experimental results are further supported by the agreement with the theoretical calculation of the cubic SrGeO₃ static dielectric constant $\varepsilon_s^{\text{calc}} = 21$ using density-functional perturbation theory [52]. Moreover, it is reasonable that the cubic SrGeO₃ dispersion parameters are comparable to those reported for BaSnO₃ ($\varepsilon_s = 20$ [15], 20 ± 2 [16,17], 14.8 ± 0.5 [18]), due to the similarities in the chemical bonding and electronic structure. We also calculated the high-frequency dielectric constant $\varepsilon_{\infty}^{\text{calc}} = 4.9$ of cubic SrGeO₃, which is slightly larger as compared to the experimental value.

B. LO phonon oscillator strength

The LO phonon oscillator strength ε_{l_v} is calculated from the dispersion model parameters, after the expansion of the

longitudinal mode displacements x_{l_v} in terms of those of the transverse modes x_{t_μ} [53], according to

$$\varepsilon_{\text{l}_v} = \varepsilon_{\infty}^2 \left(\omega_{\text{l}_v}^2 \sum_{\mu} \frac{\varepsilon_{\text{t}_\mu} \omega_{\text{t}_\mu}^2}{(\omega_{\text{l}_v}^2 - \omega_{\text{t}_\mu}^2)^2} \right)^{-1}, \quad (4)$$

with the results given in Table II. The matrix elements of Eq. (4) describe the coupling strength between TO and LO modes (Table III).

C. Comparison of the cubic perovskites SrGeO₃, BaSnO₃, and SrTiO₃

In Fig. 3 we provide the IR dispersion functions of cubic SrGeO₃ in comparison with BaSnO₃ and SrTiO₃, which were determined by optical analyses of single crystals [16,17,25]. The maxima of the imaginary part ε_2 of the dielectric function provide the TO phonon frequencies ω_{t_μ} . The maxima of the loss function $-\text{Im}(\varepsilon^{-1})$ provide the LO phonon frequencies ω_{l_v} , which correspond to the zeros of the real part ε_1 . The peak heights of the TO and LO phonons indicate the magnitude of polarization, but it must be considered that the peak broadening due to damping ($\gamma_{\mu} > 0$) is taken into account. The phonon spectra of SrGeO₃ and BaSnO₃ are very similar, and both materials show large polarizations for the TO₂, LO₂, and LO₃ modes [Fig. 3(b)]. However, the SrGeO₃ eigenfrequencies of these modes are noticeably shifted to higher frequencies. The SrTiO₃ phonon spectrum is distinctly different and shows a remarkably large polarization of the TO₁ and LO₃ modes.

To understand the differences in the phonon spectra between cubic SrGeO₃ and BaSnO₃, and SrTiO₃ on the other hand, we calculated the phonon band structures and displacement vectors of all eigenmodes (Fig. 4). The SrGeO₃ and SrTiO₃ phonon band structures show imaginary frequencies at the Brillouin zone boundaries, because at ambient pressure and absolute-zero temperature, the thermodynamically stable crystal structures are not cubic ($Pm\bar{3}m$), but monoclinic ($C2/c$) and tetragonal ($I4/mcm$) [55], respectively. The three

TABLE II. LO phonon frequency ω_{lv} , LO phonon oscillator strength ε_{lv} for SrGeO₃, BaSnO₃, and SrTiO₃. Values in brackets denote calculation results using the PBE functional. The theoretical LO phonon oscillator strength ε_{lv} is obtained from the phonon calculation results of the ion displacement vectors and Born effective charges [Eq. (3)]. The polaron coupling constant α_v and RT relaxation time τ_v^{RT} is calculated according to Eqs. (5) and (6), respectively.

Material	Eigenfrequency ω_{lv} (cm ⁻¹)	Energy $\hbar\omega_{lv}$ (meV)	Oscillator strength ε_{lv}	Coupling constant $\alpha_v(\frac{m_e}{m_\xi}^*)^{1/2}$	RT relax. time τ_v^{RT} (10 ⁻¹⁴ s)
SrGeO ₃	196 (191)	24	0.047 ± 0.01 (0.09)	0.062	72
	493 (426)	61	1.4 ± 0.2 (1.9)	1.2	7.5
	748 (791)	93	1.8 ± 0.2 (1.4)	1.2	17
BaSnO ₃	146 ^a (148)	18	0.11 ± 0.07 (0.15)	0.17	25
	425 ^a (370)	53	1.9 ± 0.1 (2.1)	1.6	4.4
	720 ^a (726)	89	1.4 ± 0.1 (1.3)	0.92	24
SrTiO ₃	174 (154)	22 ^b	0.02 (0.08)	0.017 ^b	89
	461 (438)	57 ^b	0.94 (1.7)	0.54 ^b	4.8
	816 (807)	101 ^b	4.2 (1.6)	1.8 ^b	2.8

^aReference [16].

^bCf. Ref. [54].

IR-active TO eigenmodes in SrGeO₃ and BaSnO₃ are very similar, and one schematic is given to illustrate these modes in both materials. There are different displacement vectors for the following ions: A²⁺ and B⁴⁺ cations, and O_{||}²⁻ and 2 × O_⊥²⁻ anions with displacements vectors parallel and perpendicular to the axis of the B–O bond, respectively.

Despite having the same cubic perovskite crystal structure, the SrTiO₃ eigenvectors are distinctly different from those of SrGeO₃ and BaSnO₃. For example, the displacements of the TO₁ mode depend on the electronic structure and whether the B⁴⁺ cation valence orbitals are comprised of Ge 4s (Sn 5s) or Ti 3d orbitals. In SrGeO₃ (BaSnO₃), the Ge⁴⁺ (Sn⁴⁺) cation is displaced along the Ge⁴⁺–O_{||}²⁻ (Sn⁴⁺–O_{||}²⁻) bond axis and as part of the GeO₆ (SnO₆) octahedron in the same direction as the O_{||}²⁻ and O_⊥²⁻ anions [Fig. 4(b)]. This is in contrast to the TO₁ mode in SrTiO₃, for which the Ti⁴⁺ cations and the O_{||}²⁻ anions of the TiO₆ octahedron are displaced in opposite directions [Fig. 4(c)]. The variation of the Ti⁴⁺–O_{||}²⁻ bond length compresses the bonding O 2p orbital and increases its *d* character [56]. The dynamic charge transfer from O_{||}²⁻

to Ti⁴⁺ ions results in anomalously large Born effective charges $e_{O_{||}}^*$ and e_{Ti}^* (Table IV). Consequently, the TO₁ mode polarization in SrTiO₃ is excessively large, which gives rise to a pronounced TO-LO splitting and a strikingly large LO₃ polarization.

We do not consider the triply degenerate, IR-inactive eigenmode any further, which is characterized by the displacement of two O_⊥²⁻ ions in opposite directions without a net ionic dipole moment (Fig. S3). The calculation data of eigenmodes at various points in the phonon band structures is provided as Supplemental Material for interactive visualization of ion displacements using the website of Miranda [57]. Our results for the BaSnO₃ and SrTiO₃ eigenmodes agree with a recent phonon calculation [58], and the analyses of experimental dispersion data obtained from single crystals [25,59], respectively.

V. LO PHONON SCATTERING

A. Determination of the scattering limited electron mobility

In all cubic perovskites of this study, the LO₁ phonon polarization is negligibly weak. Thus, the electron-phonon interaction is governed by the large polarization of the LO₂ and LO₃ phonons. We describe the electron-phonon interaction quantitatively by polaron coupling constants α_v according to [53,60]

$$\alpha_v = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r_p \hbar \omega_{lv}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \frac{\varepsilon_{lv}}{\sum_v \varepsilon_{lv}}, \quad (5)$$

where e is the electron charge and $r_p = (\hbar/2m_e^* \omega_{lv})^{1/2}$ is the polaron radius. The polaron binding energy $\alpha_v \hbar \omega_{lv}$, as derived by Fröhlich [60] is shown to be valid for weak coupling interactions ($\alpha_v < 10$). Fröhlich's model was extended to describe the coupling constants of materials having more than one optical phonon mode, by weighting them according to their phonon oscillator strength, as given by the term $\varepsilon_{lv}/\sum_v \varepsilon_{lv}$ [53]. The electron-phonon coupling is weak when (I) the effective mass m_e^* is small, (II) the high-frequency dielectric constant ϵ_∞ is large to promote screening of the polarization,

TABLE III. The matrix elements of Eq. (4) describe the strength of coupling between TO and LO phonon modes, from which the LO phonon oscillator strength ε_{lv} is obtained.

Material	ν	$\omega_{lv}^2 \frac{\varepsilon_{lv} \omega_{lv}^2}{(\omega_{lv}^2 - \omega_{\nu\mu}^2)^2}$			$\omega_{lv}^2 \sum_\mu \frac{\varepsilon_{lv} \omega_{lv}^2}{(\omega_{lv}^2 - \omega_{\nu\mu}^2)^2}$
		$\mu = 1$	$\mu = 2$	$\mu = 3$	
SrGeO ₃	1	364	17.1	0.1	381
	2	0.4	9.2	3.2	12.8
	3	0.1	2.4	7.5	10.0
BaSnO ₃	1	154	9.1	0.1	163
	2	0.5	8.1	1.3	9.9
	3	0.1	1.6	11.7	13.4
SrTiO ₃	1	137	1372	0.2	1510
	2	11.6	0.7	16.4	28.7
	3	3.5	0.2	2.8	6.5

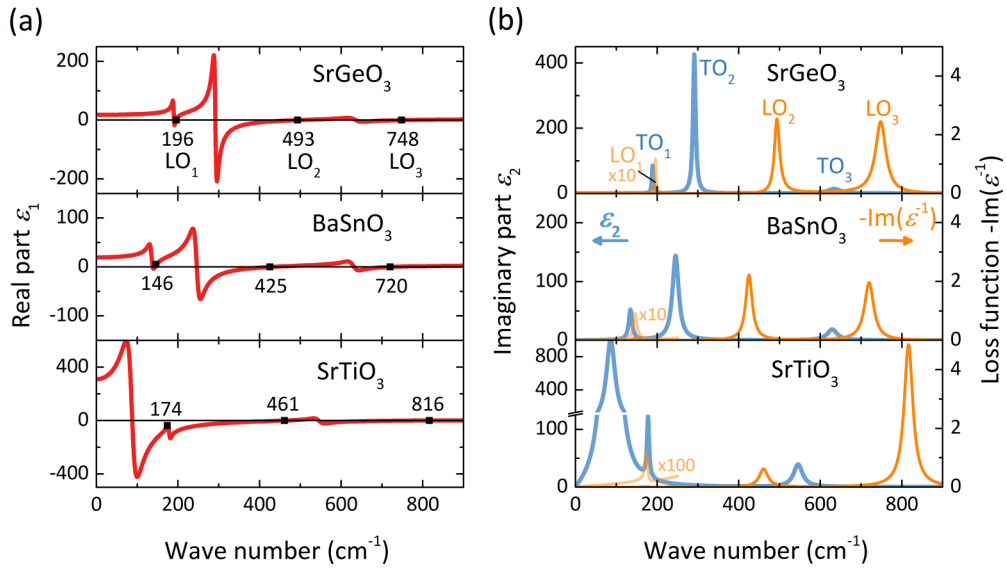


FIG. 3. (a) Real part of ϵ_1 of the dielectric function of cubic SrGeO₃, BaSnO₃, and SrTiO₃. The LO phonon frequencies correspond to the zeros of ϵ_1 . (b) The maxima of the imaginary part ϵ_2 of the dielectric function and the loss function $-\text{Im}(\epsilon^{-1})$ correspond to the frequency of TO and LO phonon modes, respectively. The peak heights of the TO and LO phonons indicate the magnitude of polarization, but it must be considered that the peak broadening due to damping ($\gamma_\mu > 0$) is taken into account.

and (III) the oscillator strength $\epsilon_{1\nu}$ of the LO phonon mode is weak. The polaron coupling constants α_ν for all LO phonon modes are summarized in Table II.

The LO phonon energy $\hbar\omega_\nu$ and the coupling parameter α_ν determine the relaxation time τ_ν of momentum loss by carrier scattering due to electron-LO phonon interactions. It is calculated for each of the LO phonon modes according to [61]

$$\tau_\nu = \frac{1}{2\alpha_\nu\omega_\nu} \left(\frac{m_e^*}{m_p} \right)^2 f(\alpha_\nu) \left[\exp\left(\frac{\hbar\omega_\nu}{k_B T}\right) - 1 \right], \quad (6)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and $f(\alpha_\nu)$ is a dimensionless function, slowly increasing from 1.0 to 1.2 for $0 < \alpha_\nu < 3$. The polaron mass $m_p = (1 + \alpha_\nu/6)m_e^*$ [44] describes the larger effective mass of an electron which creates a local polarization due to the Coulombic interaction with the ions of the crystal. Equation (6) for

the relaxation time is valid for temperatures smaller than the Debye temperature of the phonon mode ($T \ll \hbar\omega_\nu/k_B$). This condition is satisfied at RT for all considered phonon modes with the exception of the soft LO₁ modes, which in any case can be neglected due to their negligibly small polarization.

The relaxation time τ_ν is largely dependent on the LO phonon energy $\hbar\omega_\nu$ and the oscillator strength $\epsilon_{1\nu}$ as shown in Fig. 5. In general, a hard LO phonon mode exhibits a large coupling parameter, but the thermal occupation at RT, as given by the term $\exp(-\hbar\omega_\nu/k_B T)$, is small as compared to soft modes. The smallest relaxation time τ_ν among all LO phonon modes in each material is crucial for the effective relaxation time τ_{LO} , following Mathiessen's rule [53],

$$\tau_{\text{LO}} = \left(\sum_\nu \frac{1}{\tau_\nu} \right)^{-1}. \quad (7)$$

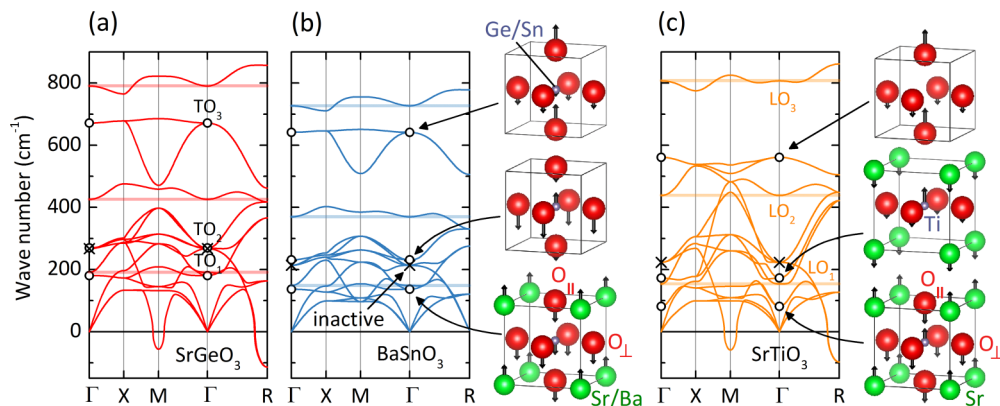


FIG. 4. Calculated phonon band structures of cubic SrGeO₃, BaSnO₃, and SrTiO₃ obtained by density-functional perturbation theory. The three IR-active TO modes at the Γ point of the first Brillouin zone (empty circles) are schematically illustrated based on the calculated ion displacement vectors. The inactive eigenmodes are indicated with a cross. The LO eigenfrequencies at the Γ point are indicated by the horizontal lines.

TABLE IV. Calculated Born effective charge e^* (in units of the electron charge e) of ions in cubic SrGeO₃, and BaSnO₃ and SrTiO₃ from density-functional perturbation theory.

Material	e_A^*	e_B^*	$e_{O_{\parallel}}^*$	$e_{O_{\perp}}^*$
SrGeO ₃	2.6	4.5	-3.7	-1.7
BaSnO ₃	2.7	4.4	-3.3	-1.9
SrTiO ₃	2.5	7.7	-6.1	-2.1

The electron mobility μ_{LO} is determined from the ratio of effective scattering relaxation time τ_{LO} and effective mass m_e^* , according to [44]

$$\mu_{LO} = \frac{e\tau_{LO}}{m_e^*}. \quad (8)$$

We calculate the intrinsic RT mobilities for cubic SrGeO₃, BaSnO₃, and SrTiO₃ of 3.9×10^2 , 3.0×10^2 , and $2 \times 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Table V).

The uncertainties in the determination of the high-frequency dielectric constant ϵ_{∞} , the electron effective mass m_e^* , and the LO phonon oscillator strength $\epsilon_{1\nu}$ are the critical parameters for the error in determining the electron mobility. The combined evaluation of the IR reflectance and Raman scattering of cubic SrGeO₃ presented in this study allows for a very reliable determination of both phonon energies and oscillator strengths. Therefore, the resulting error of the mobility calculation from these parameters is comparably small. Despite the experimental uncertainty, the present method for calculating the electron mobility is powerful from the viewpoint of providing a very intuitive understanding of how individual phonon modes contribute to the effective relaxation time. In addition, it allows one to circumvent the large computational effort of DFT calculations. Furthermore, theoretical papers on DFT calculations of the phonon scattering-limited mobility often adopt experimental values such as the effective mass, dielectric constants, and phonon energies as input parameters, without consideration of the experimental error. Thus, the rather generous error limits of the present calculation results shall not be surprising.

B. Differences between the phonon spectra and implications for the scattering relaxation time

1. SrGeO₃ and BaSnO₃

In both materials, SrGeO₃ and BaSnO₃, the LO₂ phonon mode is the most crucial one for the scattering (Fig. 5). This mode is described by a vibration of the Ge⁴⁺(Sn⁴⁺) cation against the two O_⊥²⁻ anions in the equatorial positions of the GeO₆ (SnO₆) octahedron, while the displacement vectors of Sr²⁺(Ba²⁺) and O_∥²⁻ are comparably small [cf. Fig. 4(b)]. Considering only the displacement of Ge⁴⁺(Sn⁴⁺) and O_⊥²⁻ ion sublattices, and regarding other ions are fixed on their equilibrium lattice sites, the phonon eigenfrequency is proportional to the square root of the reduced mass of the Ge⁴⁺(Sn⁴⁺) and $2 \times \text{O}_{\perp}^{2-}$ ions [44],

$$\omega_{\mu}^2 = 2k_{\mu} \left(\frac{1}{M_{\alpha}} + \frac{1}{M_{\beta}} \right), \quad (9)$$

as follows from the analogy to the case of a diatomic crystal. Here, M_{α} and M_{β} denote the mass of the ions in the two ion sublattices and k_{μ} is the force constant. Thus, it is concluded that the TO₂ and LO₂ eigenfrequencies in SrGeO₃ (291 and 493 cm⁻¹) are increased with respect to the corresponding modes in BaSnO₃ (246 and 425 cm⁻¹) due to the smaller atomic mass of Ge (72.6 u) as compared to Sn (118.7 u). The TO₃ eigenfrequencies in SrGeO₃ (634 cm⁻¹) and BaSnO₃ (629 cm⁻¹) are nearly identical, since they are mainly described by a vibration of only O_∥²⁻ and O_⊥²⁻ anions. As is seen from the expansion coefficient matrix to obtain the LO phonon oscillator strengths (Eq. (4) and Table III), the increased TO₂ and LO₂ eigenfrequencies in SrGeO₃ result in a stronger coupling between the LO₂-TO₃ modes and a weaker coupling between the TO₃-LO₃ modes as compared to the corresponding ones in BaSnO₃. Thus, the relative LO₂ oscillator strength $\epsilon_{12}/\sum_{\nu} \epsilon_{1\nu}$ in SrGeO₃ (1.2/3.2) is smaller as compared to that of BaSnO₃ (1.9/3.4), resulting in a somewhat longer RT scattering relaxation time τ_2^{RT} (Tables II and V).

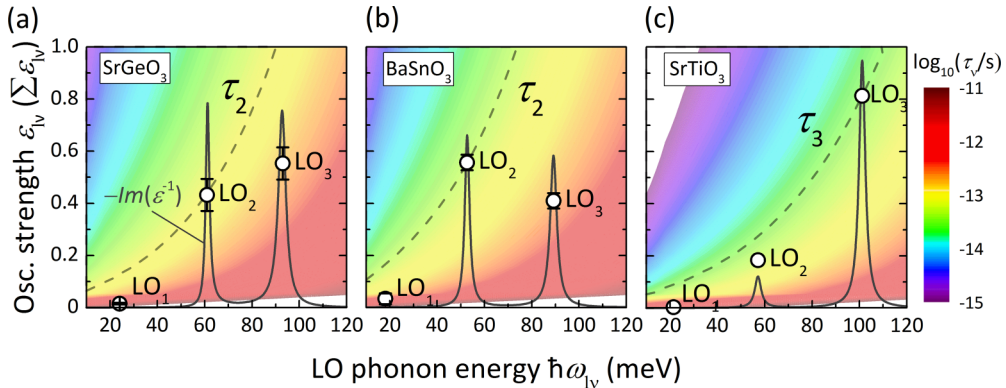


FIG. 5. Relaxation time of carrier scattering τ_v at $T = 298 \text{ K}$ by LO phonons as a function of the phonon energy $\hbar\omega_v$ and oscillator strength $\epsilon_{1\nu}$ for cubic (a) SrGeO₃, (b) BaSnO₃, and (c) SrTiO₃, according to Eqs. (5) and (6). The smallest relaxation time among the three LO phonon modes, which is the most crucial for the intrinsic electron mobility, is indicated by the dashed line. The LO peak heights of the loss function $-\text{Im}(\epsilon^{-1})$ indicate the magnitude of polarization, but it must be considered that the peak broadening due to damping ($\gamma_{\mu} > 0$) is taken into account.

TABLE V. Lattice parameter a , optical and static dielectric constants ϵ_∞ and ϵ_s , and effective mass m_e^* of cubic SrGeO₃, BaSnO₃, and SrTiO₃. The effective RT relaxation time τ_{LO}^{RT} and RT electron mobility μ_{LO}^{RT} is calculated according to Eqs. (7) and (8), respectively.

Material	Lattice parameter	Dielectric constants		Effective mass	Effective RT relaxation time	RT electron mobility
	a (Å)	ϵ_∞	ϵ_s	m_e^* (m_e)	τ_{LO}^{RT} (10^{-14} s)	μ_{LO}^{RT} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
SrGeO ₃	3.798 ^a	4.2 ± 0.2	18 ± 1	0.22	4.9 ± 0.4	3.9 ± 0.5 × 10 ²
BaSnO ₃	4.117 ^b	4.3 ^d	20 ± 2 ^d	0.19 ± 0.02 ^f	3.2 ± 0.3	3.0 ± 0.6 × 10 ²
SrTiO ₃	3.905 ^c	5.2 ^e	310 ^e	1.8 ^g	1.7	2 × 10

^aReference [31].

^bReference [62].

^cReference [63].

^dReferences [16,17].

^eReference [25].

^fReference [14].

^gReference [64].

2. SrTiO₃

Among the SrTiO₃ LO phonons, the hard LO₃ mode exhibits the largest polarization and it is the most crucial one for the intrinsic mobility [Fig. 5(c)]. However, the hard LO₃ mode is the least thermally occupied mode at RT among all three LO modes [cf. Eq. (6)]. Considering the large SrTiO₃ effective mass of 1.8 m_e , the resulting 17-ps scattering relaxation time is nevertheless remarkably long, and only by a factor of 2-3 shorter than that obtained for SrGeO₃ and BaSnO₃ (cf. Table V).

C. Implications for the design of high-RT electron mobility semiconductors

The results of our analysis provide an important guideline for the design of high-RT mobility semiconductors. The most promising candidate materials shall combine both properties, a small effective mass *and* a comparably large polarization for the hardest LO mode. A large static dielectric constant is indicative of a strongly polar TO phonon mode which in turn yields an increased polarization of hard LO modes. Transition-metal oxides commonly exhibit a large static dielectric constant due to the dynamic charge transfer between ions and increased Born effective charges, but the compromise is a large effective mass, since d orbitals are generally more localized than s orbitals. Thus, it would be very exciting to explore transition-metal based compound semiconductors which, in analogy to cubic SrGeO₃ and BaSnO₃, show a nonbonding character of the cation-derived CB, and consequently, a reduced effective mass. The recently synthesized tetragonal ZrOS semiconductor with a dispersive CB derived from a Zr $4d$ nonbonding state and small 0.36 m_e effective mass proves that such materials design is feasible [65], providing very interesting candidates for future investigation.

D. Comparison of the calculated electron mobility with experimental results

The calculated RT mobility on the order of $3.0 \pm 0.6 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for BaSnO₃ is in very good agreement with experimental values determined by Hall-effect measurements

of La-doped single crystals ($220\text{--}320 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [6,28]. Furthermore, the calculation result of $2 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for SrTiO₃ agrees well with the measured Hall mobility of about $5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ determined for La-doped SrTiO₃ epitaxial thin films [22].

To determine the electrical transport properties in cubic SrGeO₃ experimentally, we fit the IR reflectance spectrum of a mirror-polished 2 at.% La-doped SrGeO₃ polycrystalline pellet (Fig. 6). At such high doping level, the phonon spectrum is screened due to the large electronic contribution of free carriers to the dielectric function. Thus, the fitting is performed by only using the Drude model [44],

$$\epsilon_D(\omega) = \epsilon_\infty - \frac{\epsilon_\infty \omega_p^2}{\omega^2 + i\omega/\tau_p}, \quad (10)$$

where ω_p denotes the unscreened plasma frequency and τ_p denotes the carrier scattering relaxation time. We determine the optical mobility of $42 \pm 3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [Eq. (8)], the carrier concentration of $1.3 \pm 0.1 \times 10^{20} \text{ cm}^{-3}$ [Eq. (S1)], and the optical resistivity of $1.1 \pm 0.1 \times 10^{-3} \Omega \text{ cm}^{-1}$ [Eq. (S2)]. The reduced optical mobility as compared to the calculation

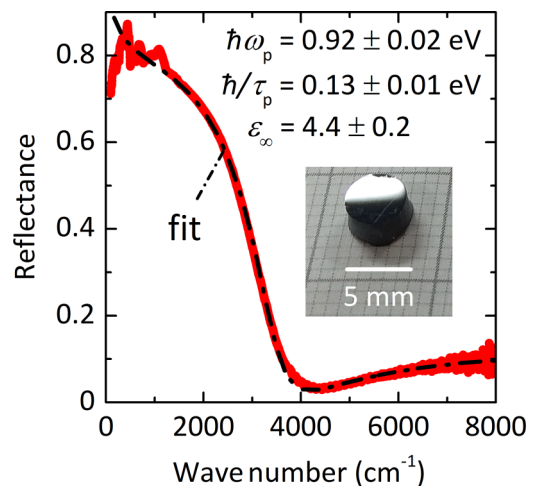


FIG. 6. IR reflectance spectrum of a mirror-polished, 2 at.% La-doped cubic SrGeO₃ (La_{0.02}Sr_{0.98}GeO₃) polycrystalline pellet.

result may indicate the presence of defects, including the possibility of Ge vacancy formation or a reduction of Ge⁴⁺ to Ge²⁺. The Hall-effect measurement of substitutionally doped SrGeO₃ single crystals will be the subject of further investigation, when crystals of larger size can be grown and characterized.

VI. CONCLUSION

In summary, we have successfully synthesized cubic SrGeO₃ perovskite single crystals using the high-pressure flux growth. The optical phonon spectrum is determined from IR optical reflectance and Raman analyses to evaluate the electron transport governed by LO phonon scattering. Employing the classical phonon theory and a combined experimental-theoretical approach, we analyzed the individual eigenmodes to gain a fundamental understanding of the similarities and differences in the phonon spectra for the cubic perovskites SrGeO₃, BaSnO₃, and SrTiO₃. Cubic SrGeO₃ exhibits a calculated RT mobility on the order of $3.9 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,

demonstrating great promise as a high-performance TCO. We suggest a universal guideline for the exploration of high-RT mobility semiconductors. The combined properties of a small effective mass *and* a large polarization of the hardest LO mode is in favor of supporting an exceptionally high-RT mobility despite the electron-phonon interactions.

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