Inelastic Electron Tunneling Spectroscopy at High-Temperatures

Prosper Ngabonziza, Yi Wang, Peter A. van Aken, Joachim Maier, and Jochen Mannhart*

Inelastic electron tunneling spectroscopy (IETS) is an analytical technique to monitor and analyze accurately the diffusion processes of particles in solids. IETS is highly sensitive and offers temporal resolution plus species specificity. It is used with outstanding success to identify and explore ions and other particles, defects, and elementary excitations in tunnel junctions.[1–9] By its very nature, IETS is capable of detecting particles in ultrathin barriers or even interfaces. Other spectroscopic techniques often used to characterize ion conductors such as infrared (IR) spectroscopy, Raman spectroscopy, inelastic neutron scattering (INS), and Rutherford backscattering lack this efficiency.[10–12] Moreover, IETS is sensitive to both IR and Raman-active transitions. Even the optically forbidden regions that are inaccessible to IR and Raman spectroscopy are open to IETS,[2,8] making it a promising technique for solid-state ionics. If available, it would open the door to monitoring the simultaneous propagation of one or several particle species in solids separately and in real time. IETS is widely used with great success as a spectroscopy technique for scanning tunneling microscopy.[5,9,13,14] This variant of IETS is called inelastic scanning tunneling spectroscopy. We focus here on IETS performed by using planar tunnel junctions, which offer multichannel, on-chip integration.

Despite all these attractive properties, IETS has been disregarded as a technique in solid-state ionics to analyze particle motion because the temperatures necessary to study diffusion processes are high, usually well exceeding 300 K. These temperatures were understood to be out of range for IETS. As early as 1968, J. Lambe and R. C. Jaklevic derived that, due to the thermal softening of the tunnel contacts’ Fermi–Dirac distributions, the limit of the spectral resolution of IETS worsens linearly with temperature $T$, the best possible resolution being $5.4 k_B T$, where $k_B$ is the Boltzmann’s constant.[2] Measurements of the resolution limit of Al–Al$_2$O$_3$–Pb junctions between 4.2 and 148 K are consistent with this limit.[15] Consequently, IETS has been widely considered to be useless above 150 K.[1–16] Room-temperature electron tunneling currents have been employed successfully to identify single amino acids generated by cleaving proteins.[17] In that work, conductance versus time profiles of the molecules moving through tunnel junctions, were used to identify the molecules, thereby averting the need for spectroscopical resolution. We are aware of only two publications that include room-temperature IETS spectra,[18,19] indeed room temperature appears to be the highest temperature at which IETS has ever been tried. The temperature gap between IETS and solid-state ionics has also blocked the use of IETS as an analytical tool for nanoionic studies.

However, we reveal here that the limit of $5.4 k_B T$ is not valid at temperatures $T$ above 50 K. At these temperatures, the achievable spectral resolution of IETS can be a factor of 9 better, with no limit found yet. We have obtained a minimal spectral width (full-width-at-half maximum, FWHM) of 19 meV at 400 K. Consequently, useful IETS can be performed at room temperature and even above,[19] as we have verified experimentally by our IETS-results relating to protons.
It is therefore only for temperatures, we used the same BaZrO₃-based heterostructures and scattering cross sections.

energy and therefore allows the particle under study to be identified and characterized. In this example, the tunneling barrier consists of a BaZrO₃ film, and the particle of interest is an ion, an atom, or a molecule. Here, we refer to these species as “particles under study.” An inelastic tunneling process can only occur if the proton present in the BaYOₓ layer is excited to its energy to the particle of interest. The electron reaches electrode 2 by the protons present in the BaYOₓ layer, and therefore allows it to be identified and characterized.

The operating principle of IETS is illustrated in Figure 1a. Electrons with an initial energy Eᵢ are found to tunnel elastically or inelastically across a barrier. In an inelastic tunneling process, a tunneling electron excites a quasiparticle such as a phonon, an ion, or a molecule. Here, we refer to these species, which may well be non-native to the tunneling barrier, as “particles under study.” An inelastic tunneling process can only occur if Eᵢ exceeds the energy Eₑxc required for the excitation.

The conductance of the tunnel junction increases stepwise at the tunneling voltage V = Eₑxc, and so the second derivative of the junction’s current–voltage characteristic ²V/²V²(V) shows a peak. As this peak is centered at Eₑxc, it quantifies the excitation energy and therefore allows the particle under study to be identified. The peak’s strength is a measure of the particles’ concentration and scattering cross sections.

To explore the potential of IETS to study ionic species at high temperatures, we used the same BaZrO₃-based heterostructures to act simultaneously as proton conductors and tunnel barriers. BaZrO₃-based multilayers feature excellent dielectric properties (electronic bandgap 5.33 eV at 300 K), chemical and thermal stability, and high ionic conductivity.[25–28] Indeed, as proton conductors, perovskite heterostructures are of great interest for various applications such as solid oxide fuel cells, hydrogen sensors, electrochromic displays, and electrolyzers.[25–28]

In the experiments, we used Y-doped BaZrO₃ films. Doping with trivalent acceptor impurities such as Y³⁺ or In³⁺ on the Zr⁴⁺ site is the common strategy to create oxygen vacancies that enable dissociate water uptake. The water uptake leads to the formation of internal OH⁻ groups that give rise to proton conductivities in bulk[29] and thin films[30] exceeding 10⁻² S cm⁻¹ at 500 °C (for 20% Y-doping). In uniformly doped Ba(Zrₓ₋ₓYₓ)O₃ barriers, protons effectively occupy the complete tunnel barrier. This is not always desirable for IETS. To provide a defined local environment for the particles under study and to minimize their interactions with the contacts of the tunnel junctions, we also explored a second approach to enhance proton conduction of BaZrO₃ and take advantage of proton diffusion through interfaces in BaZrO₃−BaYOₓ-based multilayers.[31] Strong enhancements of ion conduction at interfaces in heterostructures have already been found for several heterostructures, e.g., for CaF₂−BaF₂ and SrCeO₃−SrZrO₃ superlattices.[32,33]

Therefore, the architecture of some of the tunneling barrier was chosen to take advantage of 2D doping.[33] The tunnel barrier comprises of a BaYOₓ layer embedded between BaZrO₃ layers (Figure 1b). In such a structure, a ZrO₂ layer is replaced in the growth sequence by a YOₓ layer, which is intercalated between BaOₓ layers, thereby generating oxygen vacancies along the Y-doped layers.[31] In hydrated conditions, hydroxide ions partially fill these oxygen vacancies, yielding the desired proton-conducting channels located in the middle of the barrier. For reference, we also explored tunnel junctions with barriers consisting of undoped and Y-doped BaZrO₃ layers.

The devices were fabricated by in situ pulsed laser deposition controlled by reflection high-energy electron diffraction and a photolithographic process as described in the Supporting Information. To obtain desirable tunnel resistances, the thicknesses of the BaZrO₃-based films and heterostructures δ were chosen to be between 2.5 and 3 nm, and the tunnel junction areas A are 10 × 10, 20 × 20, and 40 × 40 µm². After the photolithography step, which subjected the samples to water and C₆H₁₃NO-based developer (pH = 13), the samples underwent photoresist baking at 125 °C. To induce further proton (deuteron) diffusion into the samples, several of the tunnel junctions bonded to their carrier chips were soaked in heated regular water or heavy water at later times (see the Supporting Information).

Figure 1b and Figure 2a show a schematic side view of a device and a top-view scanning electron microscopy image of a tunnel junction, respectively. In total, ten junctions on five substrates were measured: two junctions per substrate for five different substrates labeled A–E.
Characterization of the samples by X-ray diffraction and atomic force microscopy reveals a high sample quality (see the Supporting Information). No indications of pinholes were seen. The cross section of a sample was investigated by scanning transmission electron microscopy (STEM). Figure 2b depicts a high-angle annular dark-field-STEM image of a representative SrTiO$_3$−SrRuO$_3$−BaZrO$_3$−BaYO$_x$−BaZrO$_3$−Au sample. All layers in the stack are coherent despite the large lattice mismatch between SrRuO$_3$ (a = 3.93 Å) and BaZrO$_3$ (a = 4.19 Å) which induces compressive strain in the BaZrO$_3$. The barrier thicknesses extracted from STEM data agree well with the X-ray reflectivity measurements (4.8 vs 4.6 nm for the samples of Figure 2b; and Figure S1b (Supporting Information), respectively).

The junctions are highly resistive, and their resistances rise by one order of magnitude if d is enhanced from 2.5 to 3 nm (see Supporting Information). The I(V) characteristics of junction C1 (d = 2.5 nm, A = 20 × 20 µm$^2$) are shown in Figure S3b (Supporting Information) for T = 2–400 K. These data were taken on the junction as fabricated, i.e., after photolithography but prior to being soaked in H$_2$O or D$_2$O. The maximal voltage range of ±650 mV was chosen to prevent electric breakdown and excessive heating. The curves are nominally symmetric and overlap for T ≤ 150 K. At higher T, the conductance of the junctions increases in accordance with a growing contribution of thermally activated electron transport. These properties match the behavior expected for electron transport by tunneling plus thermally activated electron hopping over the barrier.

Having established that the devices act as tunnel junctions, we now present the IETS spectra. IETS measurements were performed between 2 and 400 K. The upper limit was chosen by wiring-induced constraints. The $\partial^2 I/\partial V^2$ characteristics were directly measured using a standard 4-terminal lock-in-amplifier technique that recorded the second harmonic response of the tunnel junctions (see Supporting Information).
characteristics were reproducible, also with respect to different deposition runs on different SrTiO$_3$ substrates (Figure 3a) and were stable for at least 6 weeks. Small voltage differences, at which characteristic features occur among different samples, are attributed to the 4-point geometry being not perfect and, possibly, to minor sample heating.

The $\partial^2 I/\partial V^2(V)$ characteristic of sample C1 is shown in Figure 4. In forward (positive) bias, electrons tunnel from the bottom SrRuO$_3$ film to the Au top contact. The $\partial^2 I/\partial V^2(V)$ curve shows a rich spectrum of features, which we found reproducibly in all junctions with barriers consisting of Ba(Zr$_{0.8}$Y$_{0.2}$)O$_3$ films or of $(\text{BaZrO}_3)_x-(\text{BaYO}_x)_y-(\text{BaZrO}_3)_z$ multilayers. The details of these features are also independent of deposition run, SrTiO$_3$ substrate, and scan direction (see Figure 3a; and Supporting Information). However, tunnel junctions with undoped BaZrO$_3$ barriers showed only a minute peak structure (see Supporting Information). As the proton conductivity is much lower in BaZrO$_3$ than in Ba(Zr$_{0.8}$Y$_{0.2}$)O$_3$ or BaZrO$_3$–BaYO$_x$–BaZrO$_3$, this observation suggests that the observed peaks are associated with the presence of protons in the barrier.

The spectra reveal three ranges of energy with distinct characteristics: first, a low-energy region (<60 mV) with several small but sharp peaks of $\partial^2 I/\partial V^2(V)$ (Figure 4b), second, an energy window from 60 to 230 mV that is nominally devoid of IETS structures (Figure 4a) and, third, the energy range above 230 mV, which features a rich spectrum of large, crisp peaks (Figure 4c). We now analyze the peaks found in the low and high-energy ranges.

As Figure 4b shows, the height of the peaks in this energy range is partly asymmetric with respect to bias direction, whereas the peak energies are symmetric. The asymmetry in the peak height is common for inelastic tunneling processes. The intensity of a peak in an IETS spectrum is high if the inelastic interaction occurs close to the electrode via which the electrons leave the tunneling barrier,$^{14,14}$ which for the spectra shown in Figure 4b is the Au contact. The energy of these peaks is in the range of tens of meV, which is the range of phonon energies. Indeed, the two main peaks (15 and 53 mV) labeled 1 and 2 in Figure 4b, match optical phonon modes (14.5 and 55 meV) measured by IR and Raman spectroscopy.$^{11,35,36}$ In BaZrO$_3$, the $\text{Ba}^\text{2+}–\text{ZrO}_6$ stretching mode (in our case also the $\text{Ba}^\text{2+}–\text{ZrO}_6$ stretching mode)

![Figure 4](image)

**Figure 4.** a) IETS spectra of sample C1 measured at a range of temperatures. The low-energy IETS features (<60 meV, peaks 1 and 2) weaken and soften with increasing temperature, giving way to a rounded dip. The high-energy features (>230 meV) are well-resolved and traced up to 400 K, the highest temperature used. The curves have been shifted along the y-axis for clarity. b) Low-energy IETS spectrum of sample C1 measured at 2 K revealing peaks 1 and 2 (15 and 53 meV) resulting from two optical phonon modes in BaZrO$_3$. The V-shape dip at $V\approx 0$ has only been observed in samples containing Y (see the Supporting Information). c) High-energy IETS spectrum of sample C1 measured at 2 K displaying the assigned vibrational modes. Peaks 5 and 8 have not been identified.
Ba–Yo₆ stretching) is known to generate a vibrational band at 15 meV, whereas the O–Zr–O bending mode induces a band at 53 meV. As expected for phonon-assisted tunneling, the energies of the modes remain unchanged with increasing temperature, and the width of the peaks increases (Figure S6, Supporting Information). The peaks start to merge above 10 K.

In the high-energy range, the IETS spectrum resolves ten pronounced, reproducible peaks (Figure 4c). A comparison with reported IR spectra, INS spectra, and results of ab initio molecular dynamics calculations allows us to attribute most peaks to vibrational modes involving hydrogen or to their higher-order transitions. Hydrogen is supposed to be absent in the idealized barrier structure of our samples, but hydration causing proton, hydrogen, hydroxyl, or water diffusion is bound to occur during the photolithography steps and subsequent sample heating. Most peaks observed in Figure 4c match vibrational modes in proton-conducting oxides. We use the labeling scheme of Figure 4c in this discussion.

The 2δ(O–H) higher-order transitions of the O–H bend mode have been found by INS to occur in In-doped BaZrO₃ at 260 and 315 meV. These energies precisely match peaks 3 and 4 of the IETS spectrum. Peak 7 at 450 meV is a peak that has been prominent in the IETS spectra of a variety of metal–oxide–metal tunnel junctions since the 1960s. It has been attributed to a $\delta$(O–H) mode, with free OH− being generated by oxidation processes in the presence of water and subsequent redistribution of hydrogen bonds. As reported in Ref. [17], this 450 meV $\delta$(O–H) mode is usually redshifted in hydrated oxides. Peak 6 (410 meV) agrees well with this redshifted mode so that we tentatively attribute it to the $\delta$(O–H) mode arising from hydration in the oxide barrier. Hydration of the junctions is to be expected, as described above. Furthermore, peaks arising from higher-order transitions and combinations of the $\delta$(O–H) and the $\tau$(O–H) modes are anticipated. Indeed, peaks 9–12 at 525, 560, 580, and 635 meV, respectively, match the expected energies of the $2\delta$(O–H)+$\tau$(O–H) and $2\delta$(O–H)+$\tau$(O–H) modes (Figure 4c). We cannot assign the remaining peaks 5 (365 meV) and 8 (510 meV) to any combination of $\delta$(O–H) and $\tau$(O–H) modes reported for acceptor-doped BaZrO₃. We therefore suggest that these peaks indicate modes associated with oxygen vacancies or related defects present in the barrier.

It is noteworthy that some of the known O–H bending or stretching modes are weak or even absent from the spectrum. Such a behavior of IETS spectra was already noted and analyzed in the early days of IETS. Although no strict selection rules exist for IETS, propensity rules for the peak strengths have been defined that take into account the effects at the position, orientation, and screening of the dipole electric field of the modes interacting with the tunneling electrons. In addition, the spectra of our junctions are characterized by the almost featureless energy range from 60 to 230 meV. The peaks expected in this range are muted by an unknown phenomenon.

Isotope replacement is a control experiment capable of revealing the role of protons in vibrational modes. We therefore inserted deuterons into the barriers by subjecting the tunnel junctions to D₂O (see Supporting Information). Figure 3b shows the $\partial^2\hat{I}/\partial\nu^2(V)$ characteristics of a SrTiO₃–SrRuO₃–BaZrO₃–BaYO₆–BaZrO₃–Au tunnel junction (B3, $d = 2.5$ nm) before and after exposure to deuterium, which induces the marked peak at 328 mV that matches the O–D stretching mode. The same peak was reported for deuterated Al–Al₂O₃–Pb junctions as being the only peak above 230 mV.[8] Its presence confirms that deuterons have penetrated the tunnel barrier and thereby provides evidence that i) protons indeed readily diffuse into the barrier and ii) their vibrational modes generate peaks in the high-energy range of the $\partial^2\hat{I}/\partial\nu^2(V)$ characteristics.

Although one might expect that during the D₂O-soaking experiment some of the protons in the OH-groups to be exchanged with deuterons, the IETS spectra reveal no noticeable shifts of the O–H peaks. It seems that the D₂O-soaking parameters used did not lead to a general replacement of the protons embedded in the crystal lattices. These results suggest that it is much easier to add protons during sample fabrication than to replace them afterward.

IETS could be highly useful if it were possible to perform tunneling spectroscopy above room temperature. This requires a spectral resolution sufficient to yield a peak structure in the $\partial^2\hat{I}/\partial\nu^2(V)$ characteristics that allows the modes to be identified and possibly quantified. Figure 4a displays high-resolution IETS spectra of sample C1 taken between 2 and 400 K that clearly show temperature-driven changes in the characteristics. Importantly, however, the spectra show well-resolved sets of peaks at all temperatures, even at 400 K. Many of these peaks are connected to the previously identified low-temperature modes (Figure 4c). The intensity of the phonon peaks (peaks 1 and 2) weakens with rising temperature. Above 100 K, the sharp zero-bias V-shaped depression of the $\partial^2\hat{I}/\partial\nu^2(V)$ characteristic smoothens into a dip. This behavior is expected from the thermal softening of the electrodes’ Fermi–Dirac distributions.

Above 200 meV, the measured IETS peaks, which reflect the O–H vibration bands, persist up to 400 K (Figure 4a). Starting at 150 K, the spectra show that the O–H modes shift by ~10 mV with temperature increasing to 400 K (for peak 3, e.g., by 15 mV). The mechanism causing the observed peak shift, which at its face value would imply a thermal softening of the O–H stretching modes, remains to be investigated.

The peak widths of the 450 meV $\tau$(O–H) modes (15.2 meV) at low temperatures are much smaller than the corresponding peak widths observed in IR and Raman measurements on polycrystalline BaZrO₃-based bulk samples, but are comparable to the IETS peak widths obtained at Al–Al₂O₃–Pb junctions (~17 meV). It is reasonable to expect that the peak widths of our samples are smaller than those of the bulk polycrystals because the epitaxially oriented, few-unit-cell thick tunnel barriers provide a more regular microstructure.

We did not expect that the IETS spectra would exhibit spectral peaks that are sufficiently distinct at 400 K to identify the presence of protons at interfaces. Indeed, this finding disagrees with the Lambe–Jaklevic limit of the temperature-dependent spectral resolution of 5.4 $k_B T$ for the minimal peak width (FWHM). As Figure 3c shows, the measured peak widths, determined as described in the Supporting Information, indeed violate this limit above a sample-specific temperature of 30–150 K. This is shown most pronouncedly by sample C1. For this sample, the width of the 580 meV mode (peak 11) equals 20.1 meV at 400 K, which is a factor of 9 smaller than the 5.4 $k_B T$ limit of ~186 meV. At 300 K, the peak width equals ~19 meV, corresponding to 0.75 $k_B T$. Such peak widths were found in
most—but not all—of the samples investigated. For example, the peak widths of sample D1 are larger (75.5 and 81 meV at 300 and 400 K, respectively, see Figure 3c), but still less than half of the Lambe–Jaklevic limit. We attribute the observed resolution enhancement to a spectral sharpening of the tunneling electrons induced by sample-dependent resonant states.

In this hypothetical scenario, the standard energy distribution of the tunneling electrons is sharpened by resonant electron tunneling, which occurs in addition to direct tunneling, in case the resonant states have a spectral width that is much smaller than the thermal energy distribution of the electrons in the electrodes (see Figure S7 in the Supporting Information). This resonant tunneling is reminiscent to the previously reported orbital-mediated tunneling through molecules.[49,50] In our case, defects of the oxide-crystal lattices or interface states may provide for the resonant states. With this high resolution, IETS has the capability to yield valuable spectral information even at temperatures above 400 K. To achieve such high operation temperatures requires further optimization of the junctions’ thermal stability, including their contacts and wiring.

Having demonstrated that IETS with planar tunnel junctions is a viable high-resolution technique to analyze mobile species in solids, we draw attention to the fact that this technique is only useful to perform spectroscopy on solids that can be integrated in tunneling barriers. This implies that the materials must be excellent insulators, even at layer thicknesses as small as several nanometers. There is no explicit need for the layers to be grown with epitaxial order. The requirement to embed the materials of interest in tunnel junctions implies that IETS is not a suitable technique to study test samples of random bulk materials. Nevertheless, we foresee IETS as a highly valuable tool to analyze materials and heterostructures grown as thin layers specifically for the task of exploring their ionic dynamics. In this case, lithography with all its available freedom for design can be used to design experimental setups. Figure 5 shows a corresponding, envisaged nanoionic device that utilizes nanostructured tunnel junctions for time resolved, 2D mapping of ionic diffusion in heterostructure devices.

In conclusion, we have designed and validated tunnel junctions in which the tunnel barrier consists of efficient proton conductors. The barriers of these junctions therefore have a double function. They act as a vertical tunneling barrier for electrons and as a horizontal diffusion path for ions. The tunnel junctions yield meaningful IETS spectra of diffused ions up to at least 400 K with no upper bound identified. The excellent fit of the peak energies in the IETS spectra enables them to be attributed to established phonon modes and to O–H bend and stretch modes, which has been confirmed by spectroscopy of tunnel junctions subjected to D$_2$O.

This work provides evidence that, despite a well-accepted tenet to the contrary, IETS is a powerful spectroscopic tool, capable to analyze ions above room temperature. At 400 K, the achieved spectral resolution of the junctions is at least a factor of 9 better than the established theoretical limit. Applying IETS to ionic conductors opens the door to studying diffusion in solids in real time with a spatial resolution limited only by the minimum size of the tunnel junctions. We expect future IETS to utilize even smaller tunnel junctions, including junctions fabricated from 2D van der Waals materials, to operate at even higher temperatures, and to monitor the motion of several ionic species, such as protons, lithium, and sodium ions simultaneously. With the capability of high-temperature operation, IETS has the potential to become a valuable item in the suite of analytical tools for future solid-state ionics.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge valuable discussions in particular with R. Merkle, H. Boschker, D. Braak, P. Bredol, S. Kivelson, T. Harada, and T. Whittles. They also thank M. Hagel and H. Hoier for technical support, and L.-M. Pavka for editorial help. Y. Wang and P. A. van Aken acknowledge funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 823717-ESTEEM3.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
high-temperature tunneling spectroscopy, inelastic tunneling spectroscopy, ionic diffusion, nanoionics, tunnel junctions

Received: October 25, 2020
Revised: December 4, 2020
Published online: January 18, 2021
[1] R. C. Jaklevic, J. Lambe, Phys. Rev. Lett. 1966, 17, 1139.
[2] J. Lambe, R. C. Jaklevic, Phys. Rev. 1968, 165, 821.
[3] S. K. Khanna, J. Lambe, Science 1983, 220, 1345.
[4] J. W. Reiner, S. Cui, Z. Liu, M. Wang, C. H. Ahn, T. P. Ma, Adv. Mater. 2010, 22, 2962.
[5] S. You, J.-T. Lü, J. Guo, Y. Jiang, Adv. Phys. X 2017, 2, 907.
[6] C. J. Adkins, W. A. Phillips, J. Phys. C: Solid State Phys. 1985, 18, 1313.
[7] M. A. Reed, Mater. Today 2008, 11, 46.
[8] K. W. Hipps, U. Mazur, in Tunneling Spectroscopy (Ed: P. K. Hansma), Springer, Boston, MA, 1982, p. 229–269.
[9] E. L. Wolf, Principles of Electron Tunneling Spectroscopy, 2nd ed., Oxford University Press, Oxford, 2012.
[10] A. Perrichon, M. Jiménez-Ruiz, L. Mazzei, S. M. H. Rahman, M. Karlsson, J. Mater. Chem. A 2019, 7, 17626.
[11] F. Giannici, M. Shirpour, A. Longo, A. Martorana, R. Merkle, J. Maier, Chem. Mater. 2011, 23, 2941.
[12] L. Mazzei, M. Wolff, D. Pergolesi, J. A. Dura, L. Börjesson, P. Gutfreund, M. Bettinelli, T. Lippert, M. Karlsson, J. Phys. Chem. C 2016, 120, 28415.
[13] A.-S. Hallbäck, N. Oncel, J. Huskens, H. J. W. Zandvliet, B. Poelsena, Nano Lett. 2004, 4, 2393.
[14] L. J. Lauhon, W. Ho, Phys. Rev. B 1999, 60, R8525.
[15] R. J. Jennings, J. R. Merrill, J. Phys. Chem. Solids 1972, 33, 1261.
[16] P. K. Hansma, in Tunneling Spectroscopy (Ed: P. K. Hansma), Springer, Boston, MA 1982, p. 1.
[17] T. Ohshiro, M. Tsutsui, K. Yokota, M. Furuhashi, M. Taniguchi, T. Kawai, Nat. Nanotechnol. 2014, 9, 835.
[18] J. S. Mooker, J. Nowak, R. J. M. van de Veerdonk, Phys. Rev. Lett. 1998, 80, 2941.
[19] V. Bommisetty, S. Bhandari, R. L. Karmacharya, D. A. Rislov, R. D. Mileham, D. Galipeau, D. W. Galipeau, IEEE Sens. J. 2008, 8, 983. Note: Figure 6 in this reference shows a characteristic of a tunnel junction with a 300 K FWHM of ≈136 meV = 5.8 k_BT, and the authors of this reference point out that this width is smaller than the 5.4 k_BT limit.
[20] K. D. Kreuer, Annu. Rev. Mater. Res. 2003, 33, 333.
[21] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Adv. Mater. 2012, 24, 195.
[22] J. H. Shim, T. M. Gür, F. B. Prinz, Appl. Phys. Lett. 2008, 92, 253115.
[23] D. Pergolesi, E. Fabbri, A. D’Epifanio, E. Di Bartolomeo, A. Tebano, S. Sanna, S. Licoccia, G. Balestrino, E. Traversa, Nat. Mater. 2010, 9, 846.
[24] A. Fluri, A. Marcolongo, V. Roddatis, A. Wokaun, D. Pergolesi, N. Marzari, T. Lippert, Adv. Sci. 2017, 4, 1700467.
[25] H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martínez, D. Beeaff, S. H. Morejudo, P. K. Vestre, T. Norby, R. Haugsrud, J. M. Serra, C. Kjelseth, Nat. Energy 2017, 2, 923.
[26] S. H. Morejudo, R. Zanón, S. Escolalístico, I. Yuste-Tirados, H. Malerød-Fjeld, P. K. Vestre, W. G. Coors, A. Martínez, T. Norby, J. M. Serra, C. Kjelseth, Science 2016, 353, 563.
[27] J. A. Kilner, M. Burriel, Annu. Rev. Mater. Res. 2014, 44, 365.
[28] L. Malavasi, C. A. J. Fisher, M. S. Islam, Chem. Soc. Rev. 2010, 39, 4370.
[29] K. D. Kreuer, Solid State Ionics 1999, 125, 285.
[30] Y. B. Kim, T. M. Gür, H.-J. Jung, S. Kang, R. Sinclair, F. B. Prinz, Solid State Ionics 2011, 198, 39.
[31] P. Ngabonziza, R. Merkle, Y. Wang, P. van Aken, T. S. Bjørheim, J. Maier, J. Mannhart, Adv. Energy Mater. 2020, 2003267, https://doi.org/10.1002/aenm.202003267.
[32] N. Kata, K. Eberman, K. Eberl, J. Maier, Nature 2000, 408, 946.
[33] H. Yugami, H. Naito, H. Arashi, Appl. Surf. Sci. 1997, 113–114, 222.
[34] W. He, T. P. Ma, Appl. Phys. Lett. 2003, 83, 2605.
[35] C. H. Perry, D. J. McCarthy, G. Rupprecht, Phys. Rev. B 1965, 138, A1537.
[36] M. Karlsson, I. Ahmed, A. Matic, G. S. Eriksson, Solid State Ionics 2010, 181, 126.
[37] L. Mazzei, A. Perrichon, A. Mancini, G. Wahnström, L. Malavasi, S. F. Parker, L. Börjesson, M. Karlsson, J. Mater. Chem. A 2019, 7, 7360.
[38] M. Karlsson, M. E. Björketun, P. G. Sundell, A. Matic, G. Wahnström, D. Engberg, L. Börjesson, I. Ahmed, S. Eriksson, P. Berastegui, Phys. Rev. B 2005, 72, 094303.
[39] T. Ornata, M. Takagi, S. Otsuka-Yao-Matsuo, Solid State Ionics 2004, 168, 99.
[40] M. C. Gallagher, Y. B. Ning, J. C. Adler, Phys. Rev. B 1987, 36, 6651.
[41] J. Kirtley, D. J. Scalapino, P. K. Hansma, Phys. Rev. B 1976, 14, 3177.
[42] D. J. Scalapino, S. M. Marcus, Phys. Rev. Lett. 1967, 18, 459.
[43] A. Gagliardi, G. C. Solomon, A. Pecchia, T. Frauenheim, A. Di Carlo, N. S. Hush, J. R. Reimers, Phys. Rev. B 2007, 75, 174306.
[44] J. Kirtley, J. T. Hall, Phys. Rev. B 1980, 22, 848.
[45] N. Lorente, M. Persson, L. J. Lauhon, W. Ho, Phys. Rev. Lett. 2001, 86, 2593.
[46] A. Troisi, M. A. Ratner, Nano Lett. 2006, 6, 1784.
[47] J. Igalson, J. C. Adler, Phys. Rev. B 1983, 28, 4970.
[48] R. C. Jaklevic, M. R. Gaerttner, Appl. Phys. Lett. 1977, 30, 646.
[49] U. Mazur, K. W. Hips, J. Phys. Chem. B 1999, 103, 9721.
[50] L. Scudiero, D. E. Barlow, U. Mazur, K. W. Hips, J. Am. Chem. Soc. 2001, 123, 4073.