Graph theory ideas reveal long range conduction pathways

Maria A Gomez
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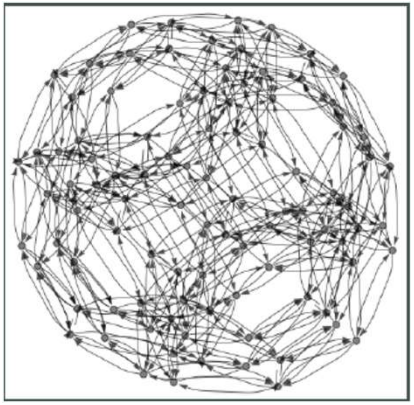
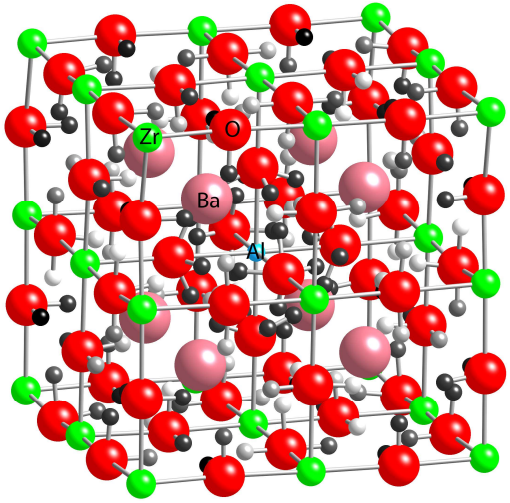
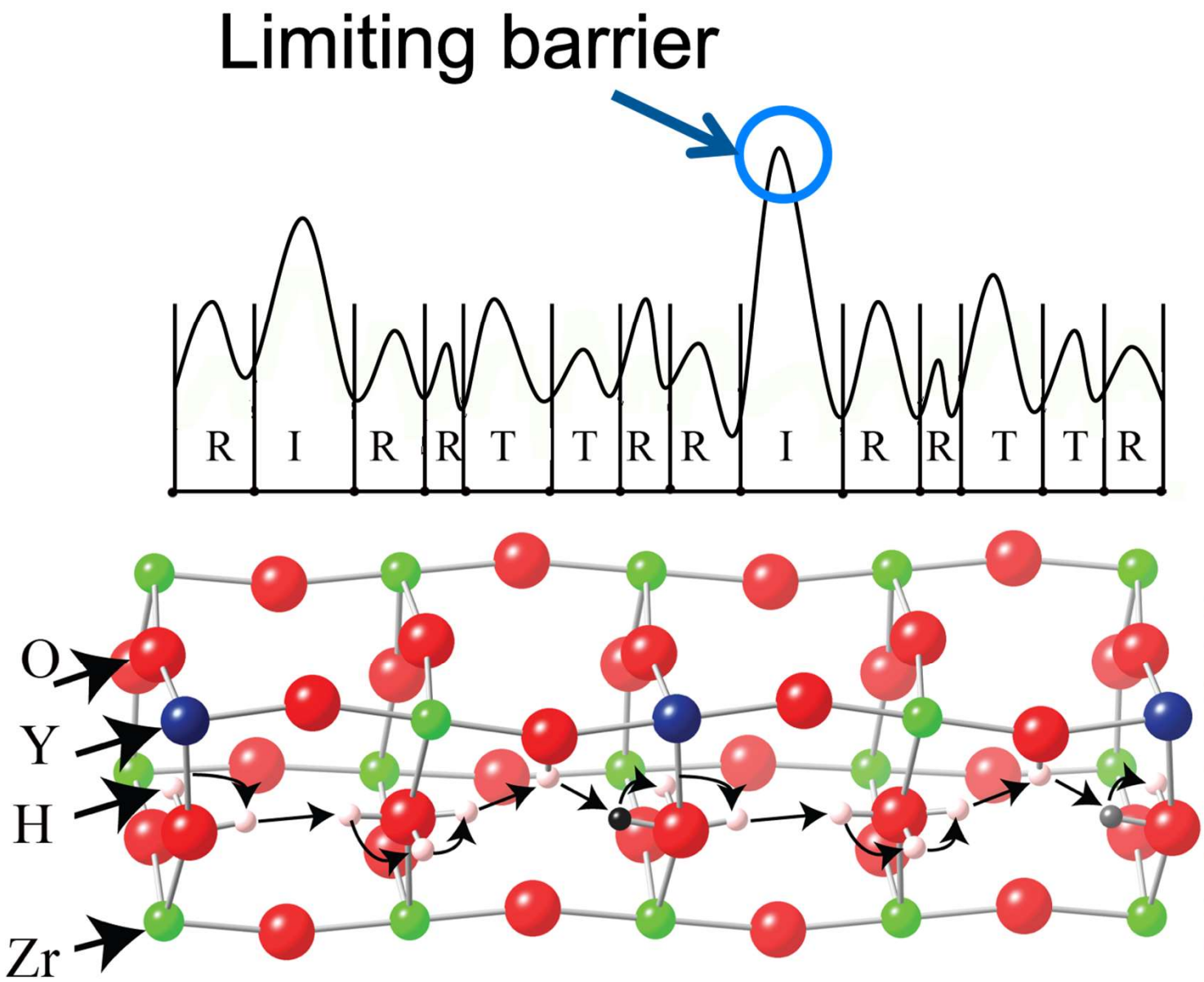




Long range proton conduction pathways can be have a dominant limiting barrier



Ways of investigating proton conduction pathways

- Energetics

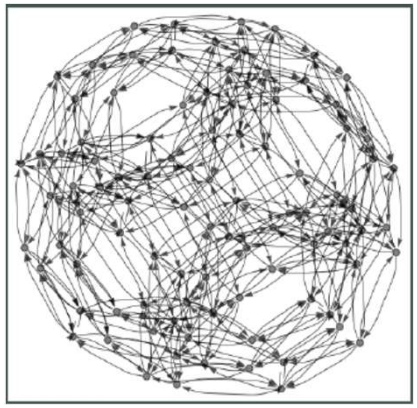
M. A. Gomez, **M. A. Griffin, S. Jindal, K. D. Rule, and V. Cooper**, "The effect of octahedral tilting on proton binding sites and transition states in pseudo-cubic perovskite oxides," J. Chem. Phys **123**, 094703 (2005)

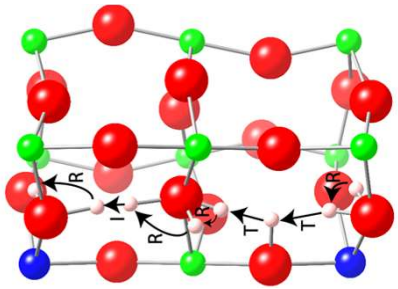
- Ab initio Molecular Dynamics

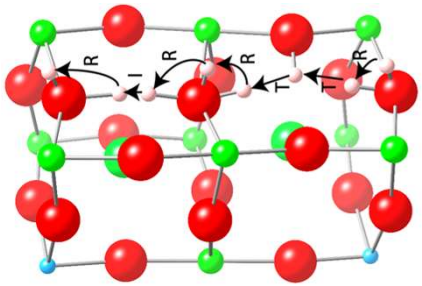
M. A. Gomez, **Saryu Jindal, Katharyn M. Fletcher, Leigh S. Foster, Nanna Dufie A Addo, Debbie Valentin, Cristina Ghenoiu, and Abigail Hamilton**, "A comparison of proton conduction in $KTaO_3$ and $SrZrO_3$," J. Chem. Phys. **126**, 194701 (2007); Amaldeldi Torayev, Luke Sperrin, Maria A Gomez, John A Kattirtzi, Celine Merlet, and Clare P. Grey*, "Local distortions and dynamics in hydrated Y-doped BaZrO3," Submitted to J. Physical Chemistry C.

- Ensemble of pathways

M. A. Gomez, **M. Chunduru,L. Chigweshe, L. S. Foster, S. J. Fensin, K. M. Fletcher, and L. F. Fernandez**, "The effect of yttrium dopant on the proton conduction pathways of BaZrO3, a cubic perovskite," J. Chem. Phys. **132**, 214709 (2010); M. A. Gomez, **M. Chunduru, L. Chigweshe, K. M. Fletcher**, "The effect of Al an Y dopant on the proton conduction pathways of SrZrO3, an orthorhombic perovskite," J. Chem. Phys. **133**, 064701 (2010); M. A. Gomez, D. Shepardson, **L. T. Nguyen, T. Kehinde,** "Periodic long range proton pathways in pseudo-cubic and orthorhombic perovskites," Solid State Ionics, **213**, 8 (2012).



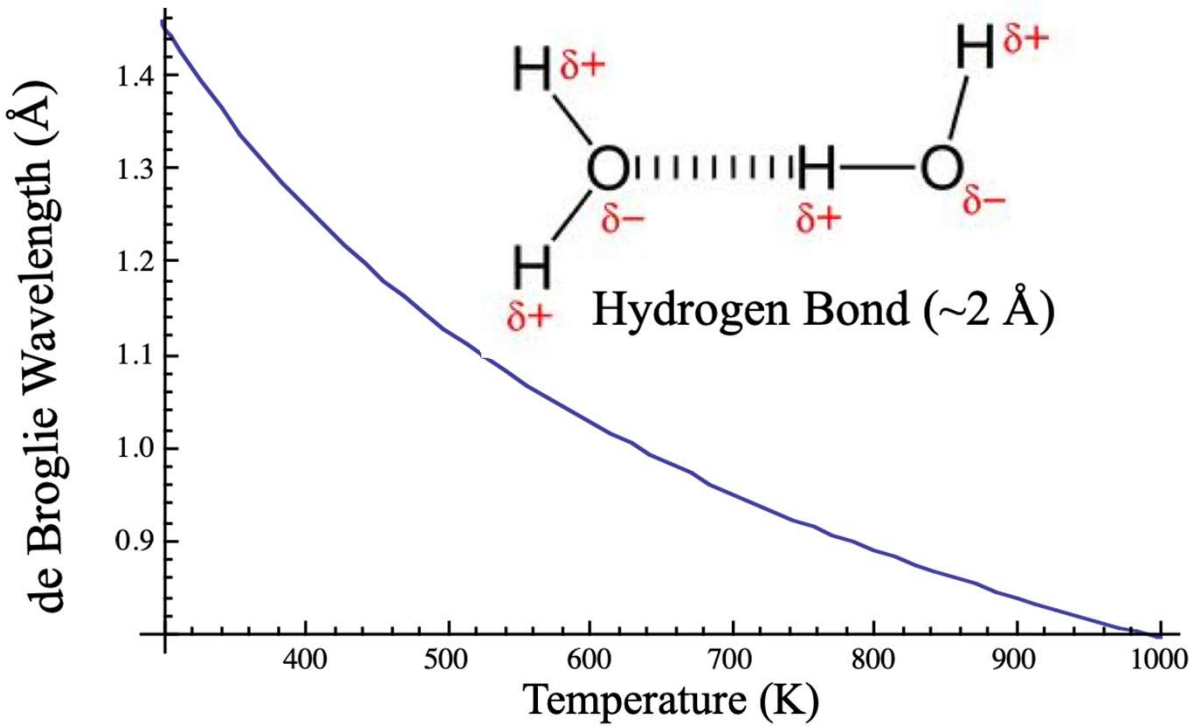




- Kinetic Monte Carlo trajectories
- Centrality measures

M. A. Gomez, **Fan-Jean Liu** "Protons in Al doped $BaZrO_3$ escape dopant traps to access long range conduction highways," Solid State Ionics, 252, 40 (2013); **Rachel Krueger,** F. G. Haibach, **Dana L Fry,** and Maria A Gomez "Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories,"J. Chem. Phys. **142**, 143110 (2015).

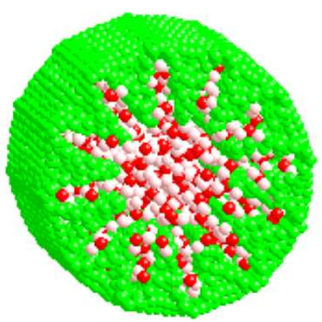
Proton conduction at different temperatures



$$\lambda = \frac{h}{m\mathrm{v}}$$

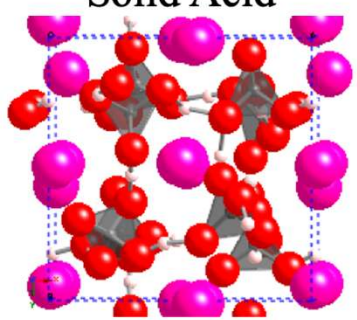
$$\left\langle \frac{1}{2} m\mathrm{v}^2 \right\rangle = \frac{3}{2} k_B T$$

Nafion



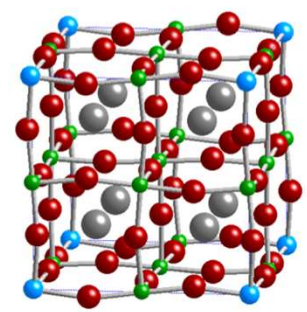
Pt Catalyst

Solid Acid



Pd Catalyst

Perovskites



Ni Catalyst

M. A. Gomez, and P. Peart, "Including quantum subsystem character within classical equilibrium simulations," J. Chem. Phys. **125**, 034105 (2006).

P. Grabowski, D. Riccardi, M. A. Gomez, D. Asthagiri, and L. R. Pratt, "Quasi-chemical theory and the standard free energy of H+ (aq)," J. Phys. Chem. A. 106, 9145 (2002).

Annu. Rev. Mater. Res. 2003. 33:333–59
doi: 10.1146/annurev.matsci.33.022802.091825

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PROTON-CONDUCTING OXIDES

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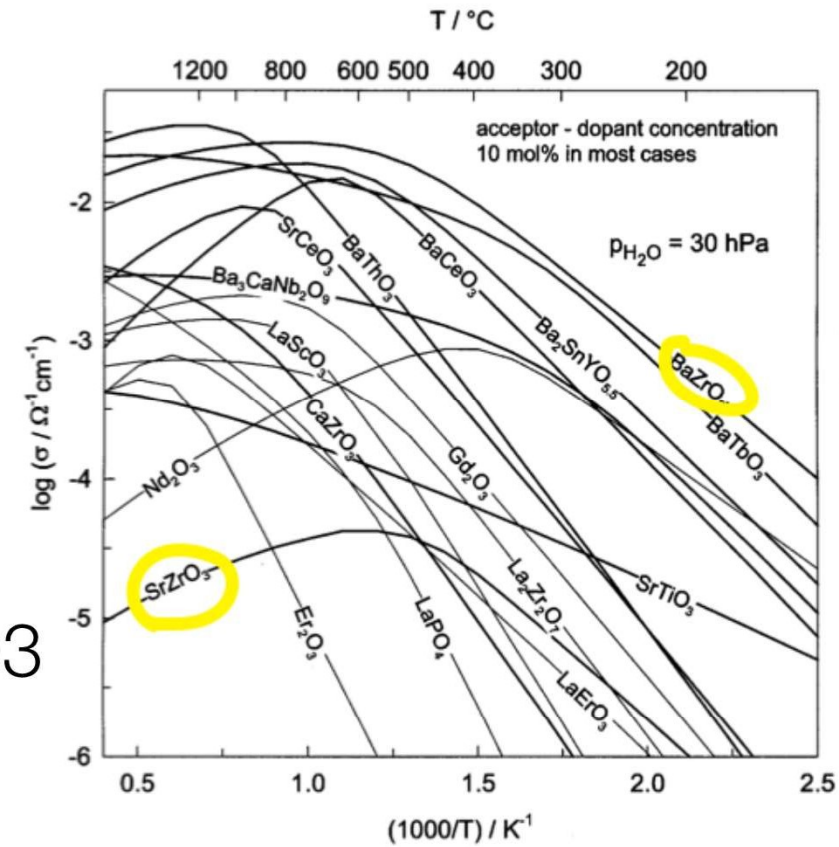


BaZrO3

SrZrO3

Figure 1 Proton conductivities of various oxides as calculated from data on proton concentrations and mobilities, according to Norby & Larring [type of dopant is not indicated, for source data, see (21)]. Conductivities of oxides with perovskite-type structure are shown by bold lines.

x

Solid State Ionics 51 (1992) 101–107
North-Holland

SOLID STATE IONICS

Protonic conduction in $SrZrO_3$-based oxides

T. Yajima, H. Suzuki, T. Yogo and H. Iwahara [1]
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received 29 October 1991; accepted for publication 13 December 1991

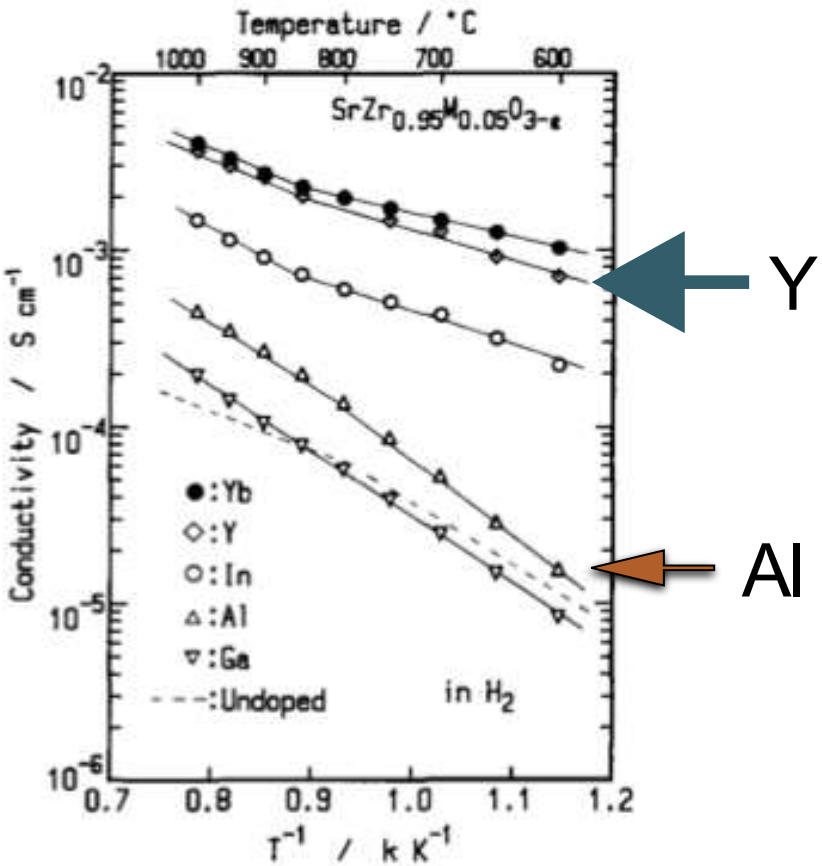


Fig. 3. Conductivity of $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ in hydrogen atmosphere.

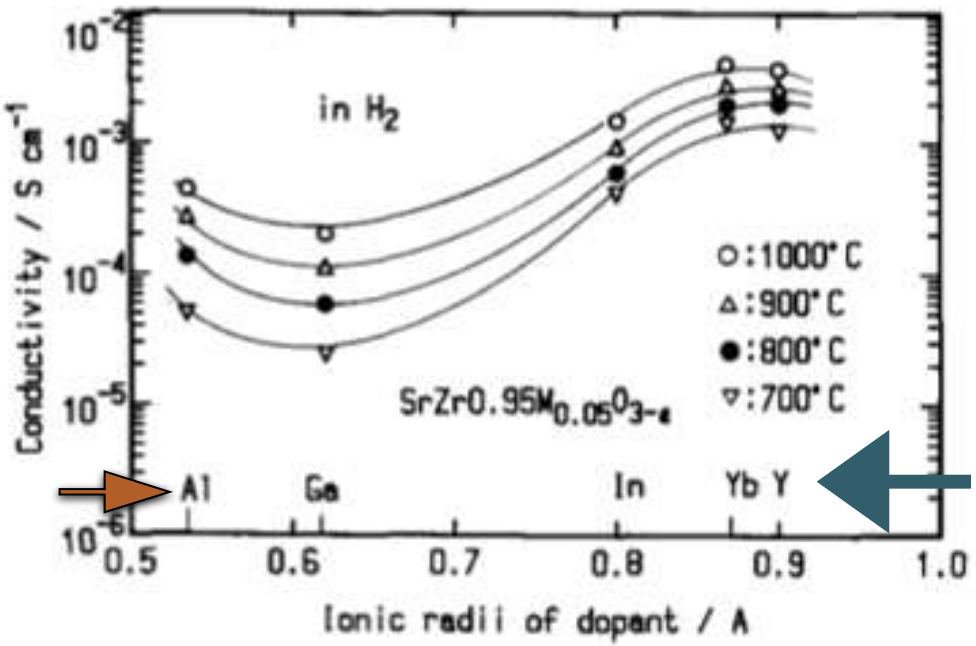
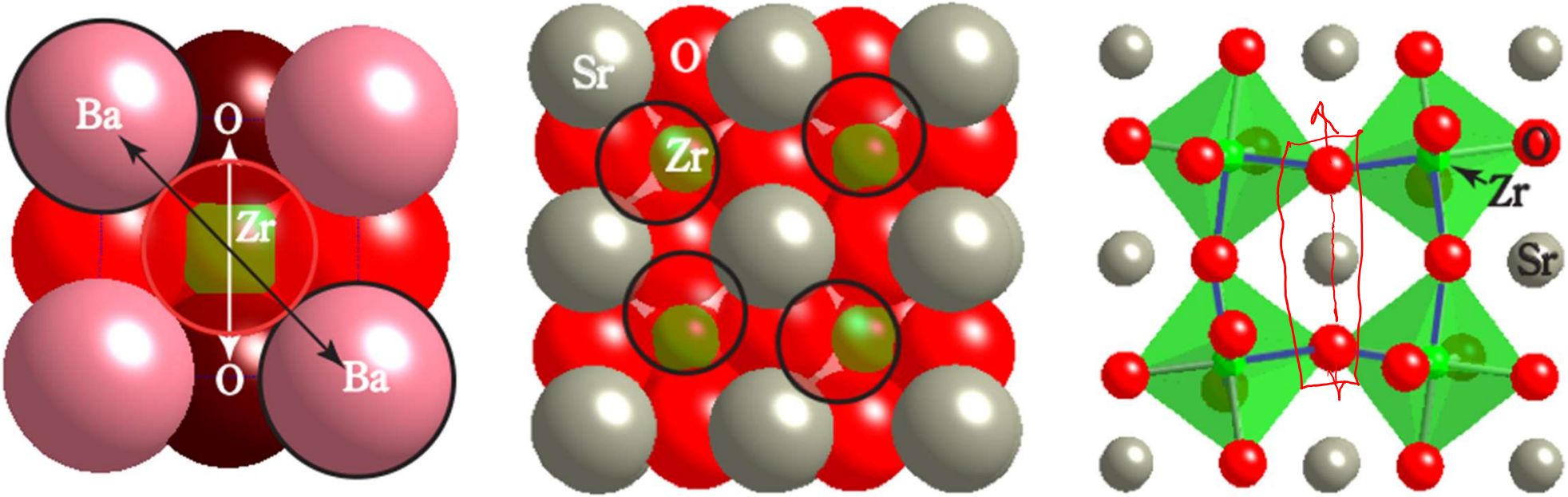


Fig. 4. Dependence of proton conductivity on ionic radii of dopant cations.

x

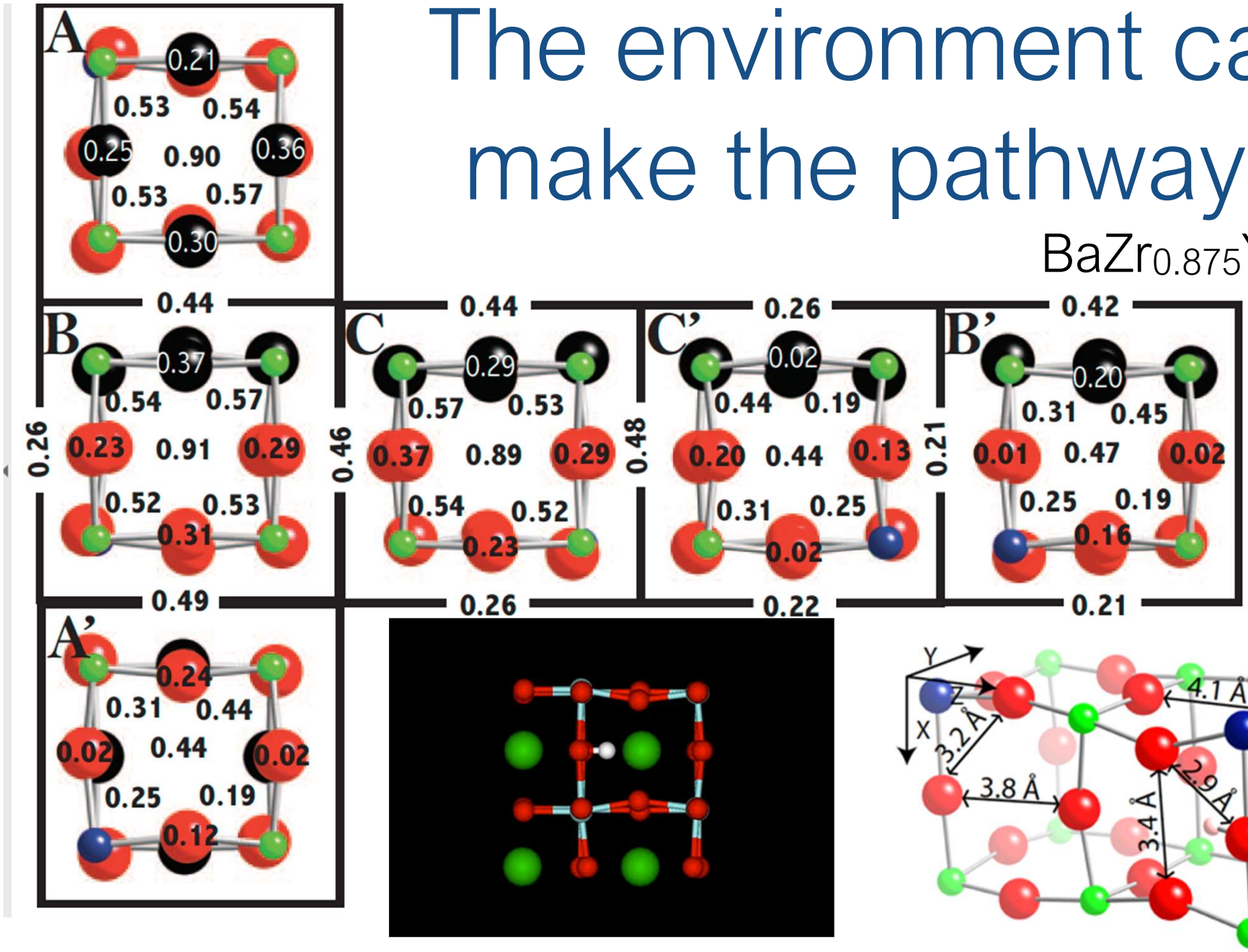
Perovskite Geometry



Ionic size: $Al^{3+} < Ga^{3+} < Zr^{4+} < Sc^{3+} < In^{3+} < Er^{3+} < Y^{3+}$

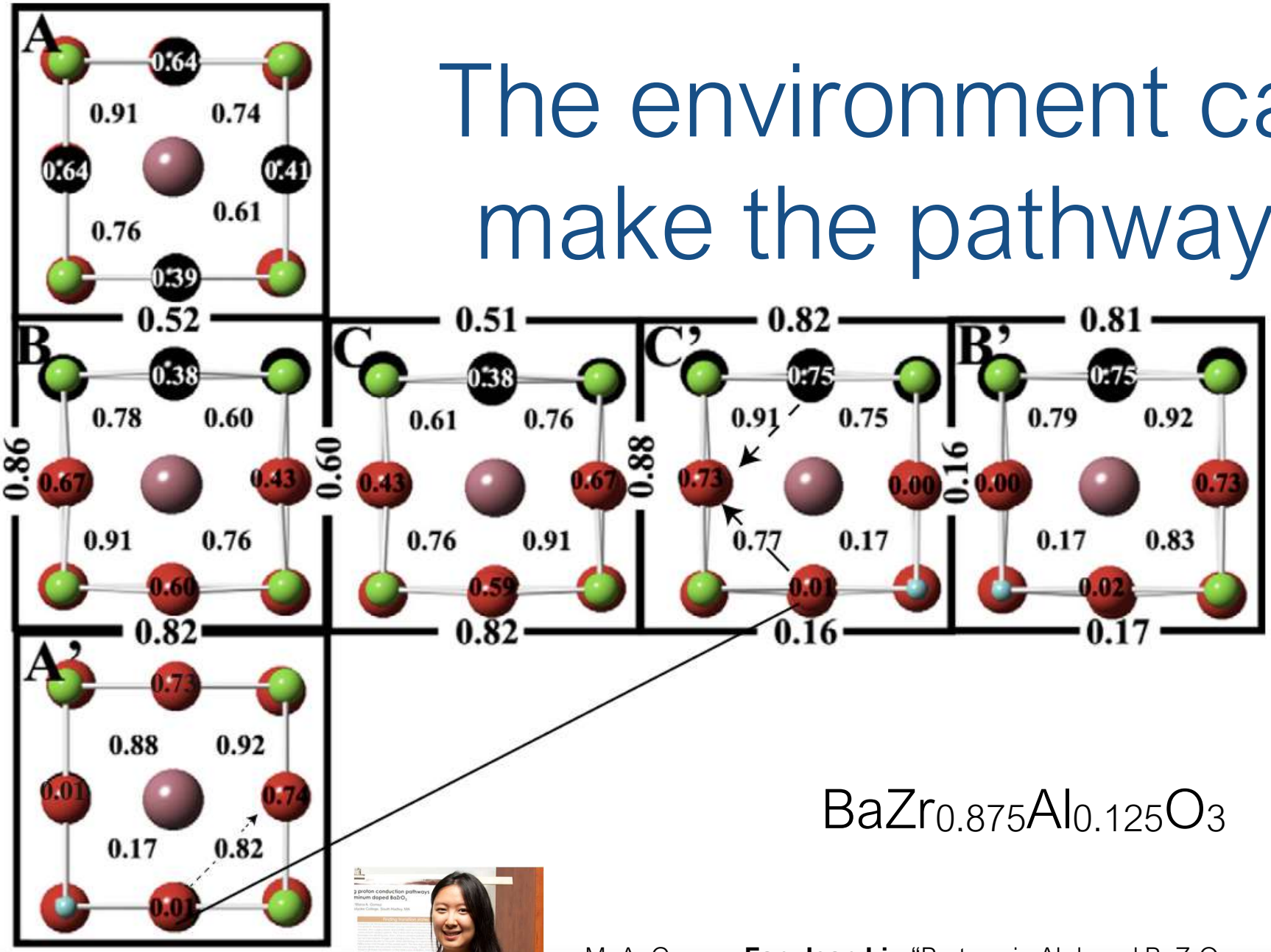
The environment can make the pathways

$BaZr_{0.875}Y_{0.125}O_3$



M. A. Gomez, **M. Chunduru,L. Chigweshe, L. S. Foster, S. J. Fensin, K. M. Fletcher, and L. F. Fernandez**, "The effect of yttrium dopant on the proton conduction pathways of BaZrO3, a cubic perovskite," J. Chem. Phys. **132**, 214709 (2010)

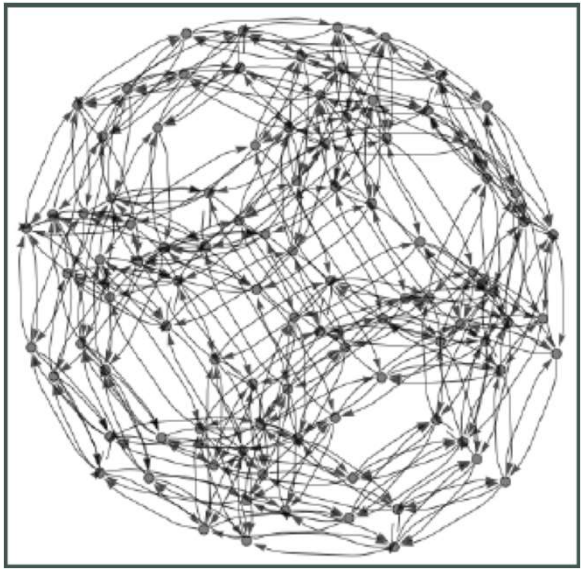
The environment can make the pathways



$BaZr_{0.875}Al_{0.125}O_3$

M. A. Gomez, **Fan-Jean Liu** "Protons in Al doped $BaZrO_3$ escape dopant traps to access long range conduction highways," Solid State Ionics, **252**, 40 (2013);

Map to graph: Each binding site is a vertex and are connected by an edge when there is a single transition state between them.



$$probability = \rho(x_{i_1}) P_{i_1 i_2} P_{i_2 i_3} \ldots\ldots P_{i_{N-1} i_N}$$

Rate constant between sites

$$k_{i\to j}^{HTST} = \frac{\prod_{k=1}^{N_{vib}} \nu_k^{\min}}{\prod_{k=1}^{N_{vib}-1} \nu_k^{TS}} \exp\left(-\beta E_{i\to j}^{barrier}\right)$$

Probability between sites

$$p_{i\to j} = \frac{k_{i\to j}^{HTST}}{\sum_{m=1}^{N_{neighbors}} k_{i\to m}^{HTST}}$$

Weight of an edge

$$w_{i\to j} = -\ln(p_{i\to j})$$

Weight of a path

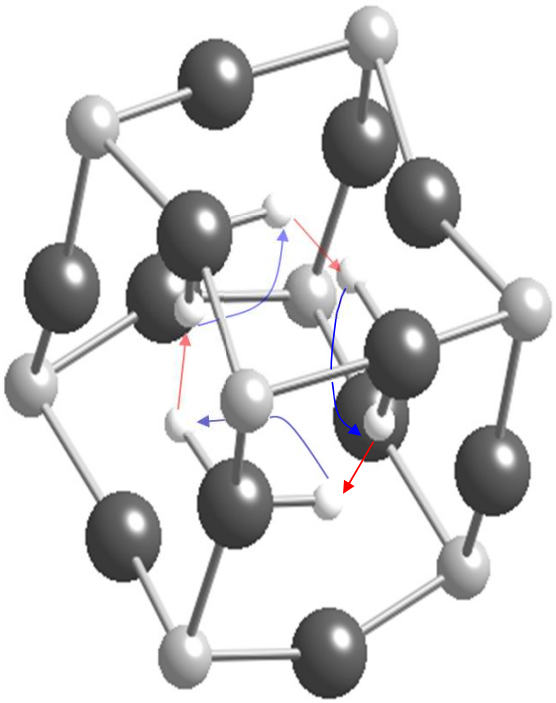
$$-\ln(\rho_{i_1}) + \sum_{n=1}^{N} w_{i_n \to i_{n+1}}$$

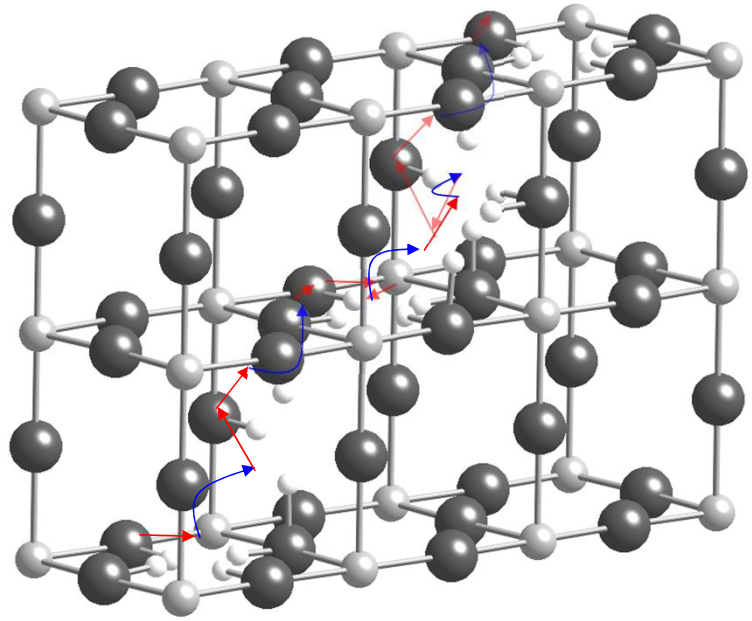
Some paths are loops while others are longer range pathways.

TT
RR

TTTT
RRRR

RTRTRT





T T R T R T T T R T

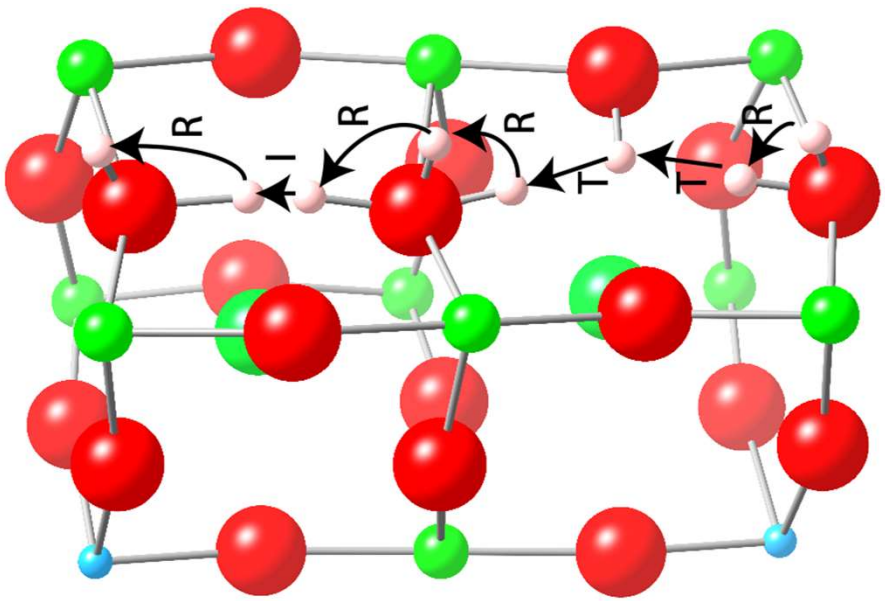
Highest probability ten step building block

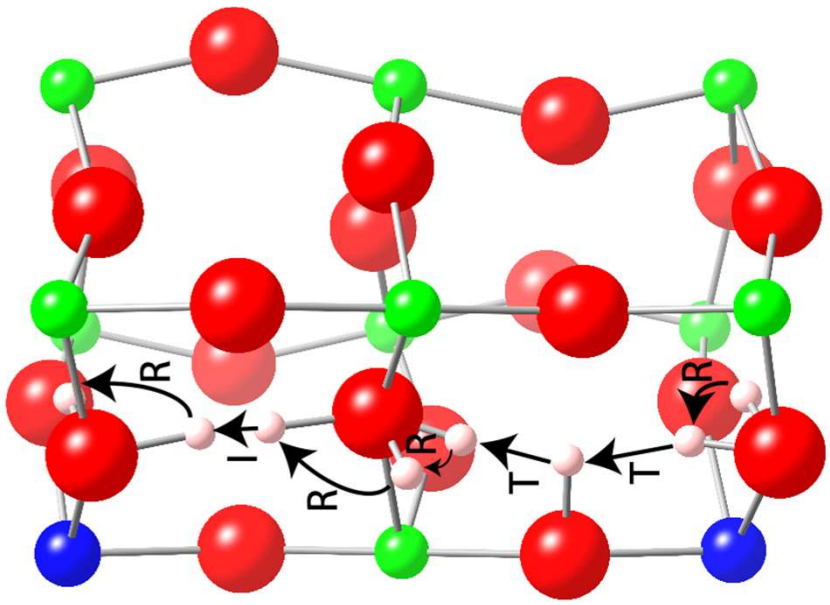
T R T T R T

Highest probability six step building block

M. A. Gomez, D. Shepardson, **L. T. Nguyen, T. Kehinde,** "Periodic long range proton pathways in pseudo-cubic and orthorhombic perovskites," Solid State Ionics, **213**, 8 (2012).

Most probable periodic paths in Al/$SrZrO_3$ avoid dopant while those in Y/$SrZrO_3$ hug dopant.



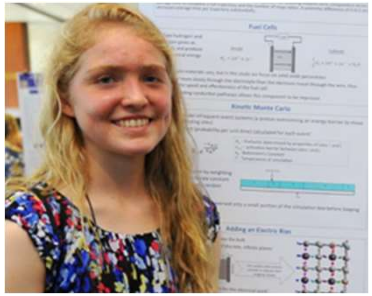


M. A. Gomez, **M. Chunduru, L. Chigweshe, K. M. Fletcher**, "The effect of Al an Y dopant on the proton conduction pathways of $SrZrO_3$, an orthorhombic perovskite," J. Chem. Phys. **133**, 064701 (2010).

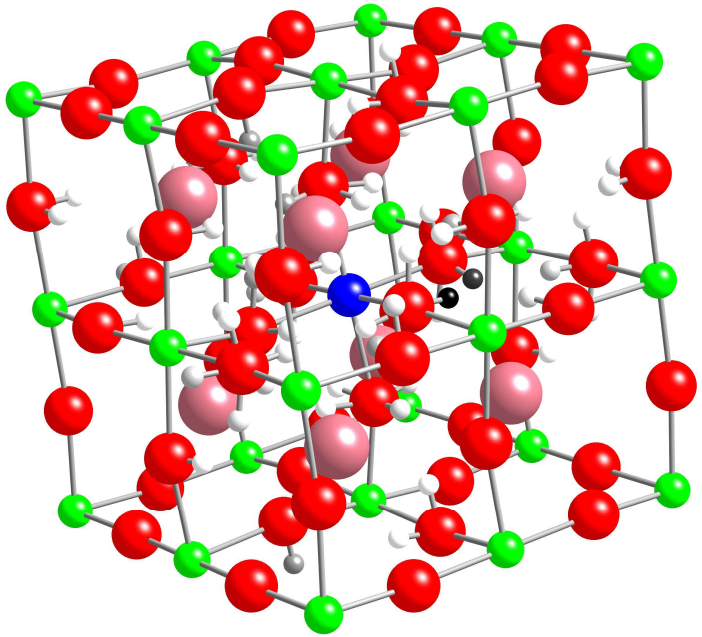
M. A. Gomez, **M. Chunduru,L. Chigweshe, L. S. Foster, S. J. Fensin, K. M. Fletcher, and L. F. Fernandez**, "The effect of yttrium dopant on the proton conduction pathways of $BaZrO_3$, a cubic perovskite," J. Chem. Phys. **132**, 214709 (2010).

kMC suggests that individual proton motion is characterized by trapping and escape to fast conduction barriers.

Rachel Krueger, F. G. Haibach, **Dana L Fry,** and Maria A Gomez "Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories,"J. Chem. Phys. **142**, 143110 (2015).

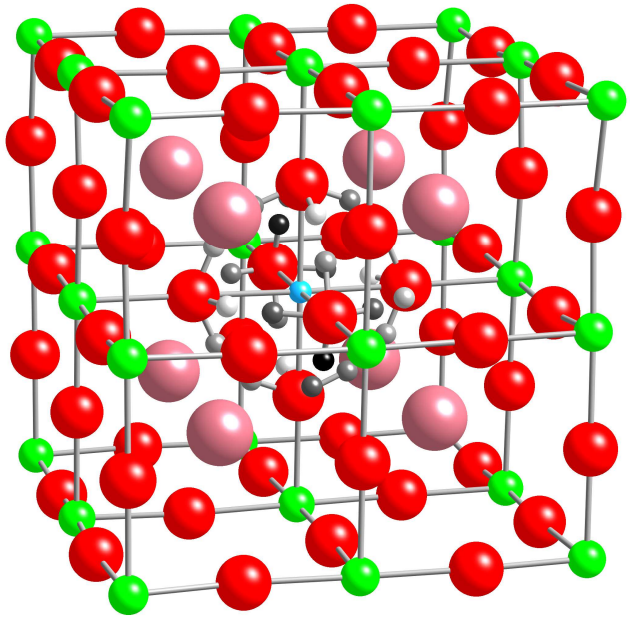


Y/$BaZrO_3$

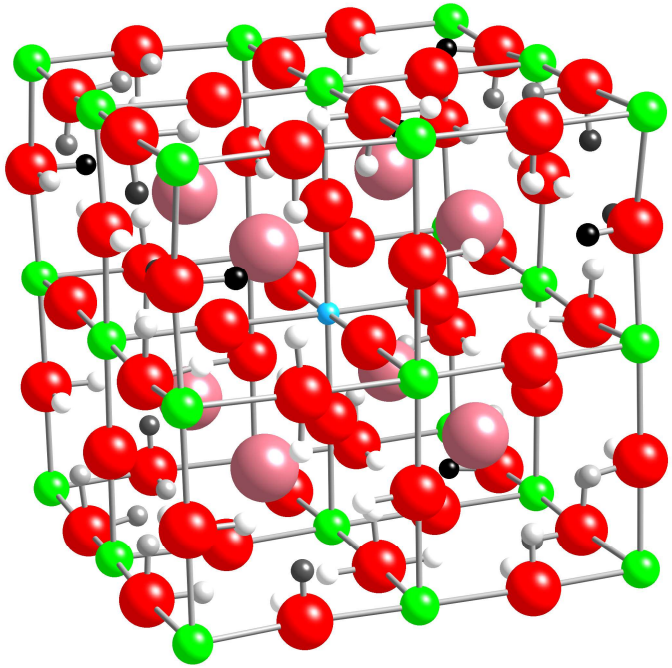


(0-16 ps)

Al/$BaZrO_3$



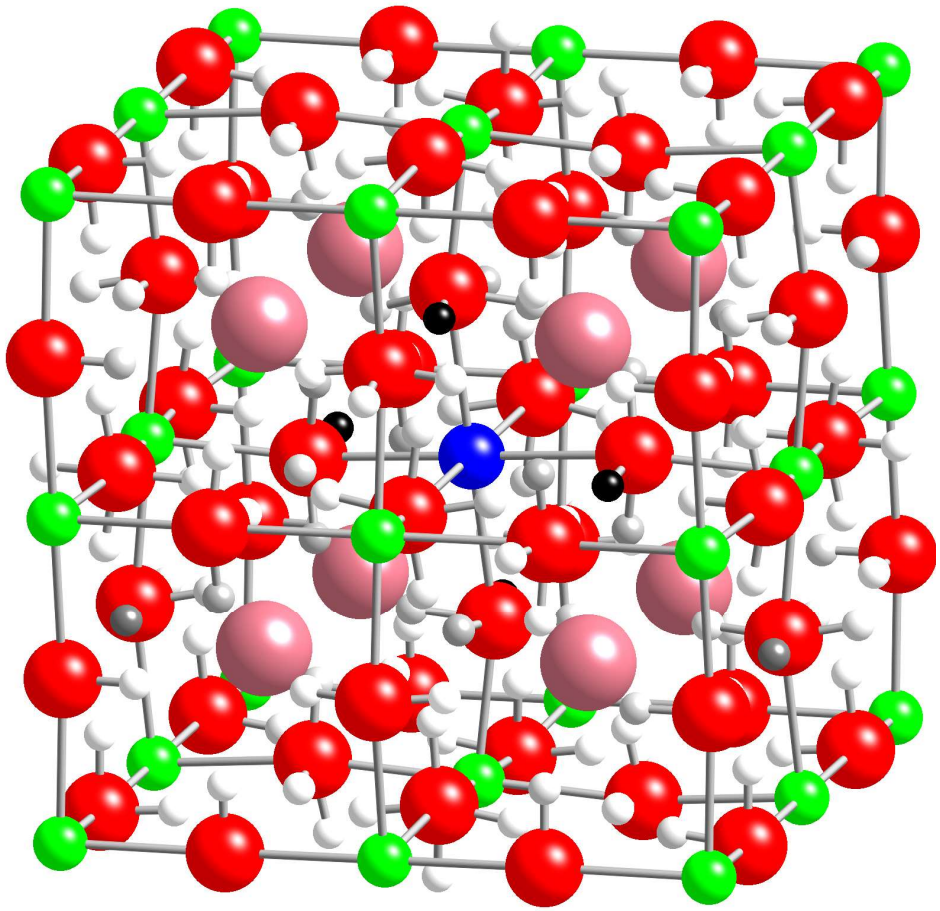
(0-1271 ps)



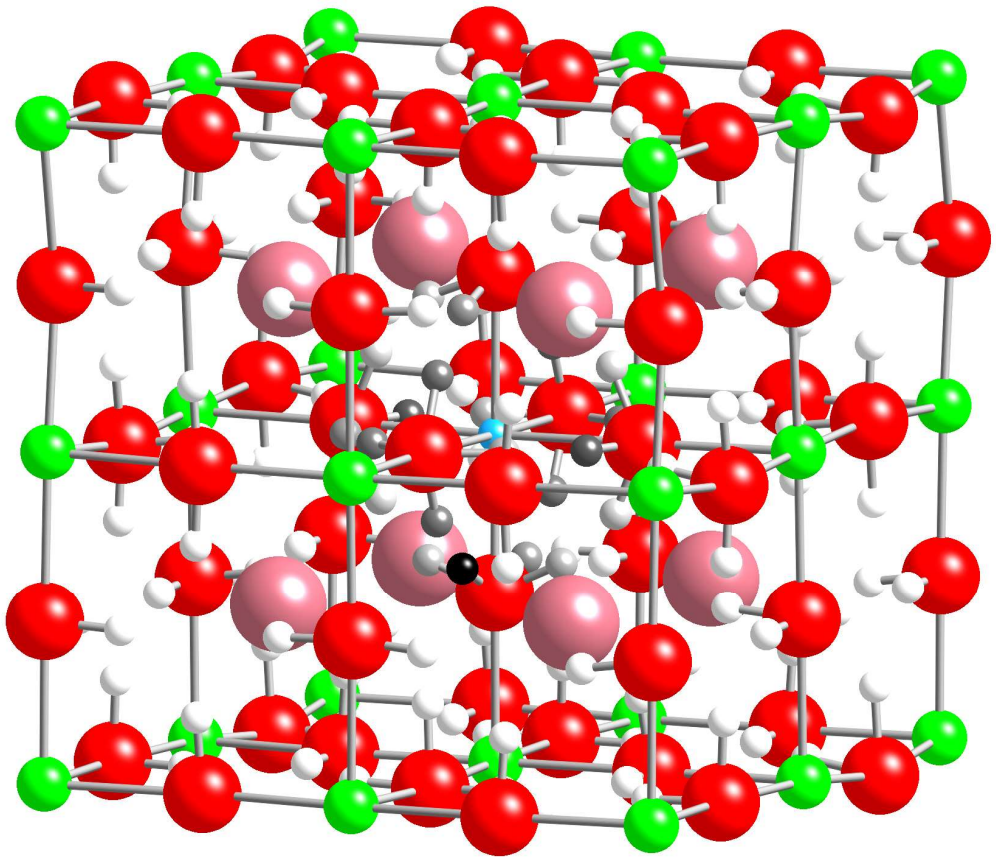
(1271-1419 ps)

Showing the whole trajectory site probabilities yields the Boltzmann distribution

$Y/BaZrO_3$



$Al/BaZrO_3$

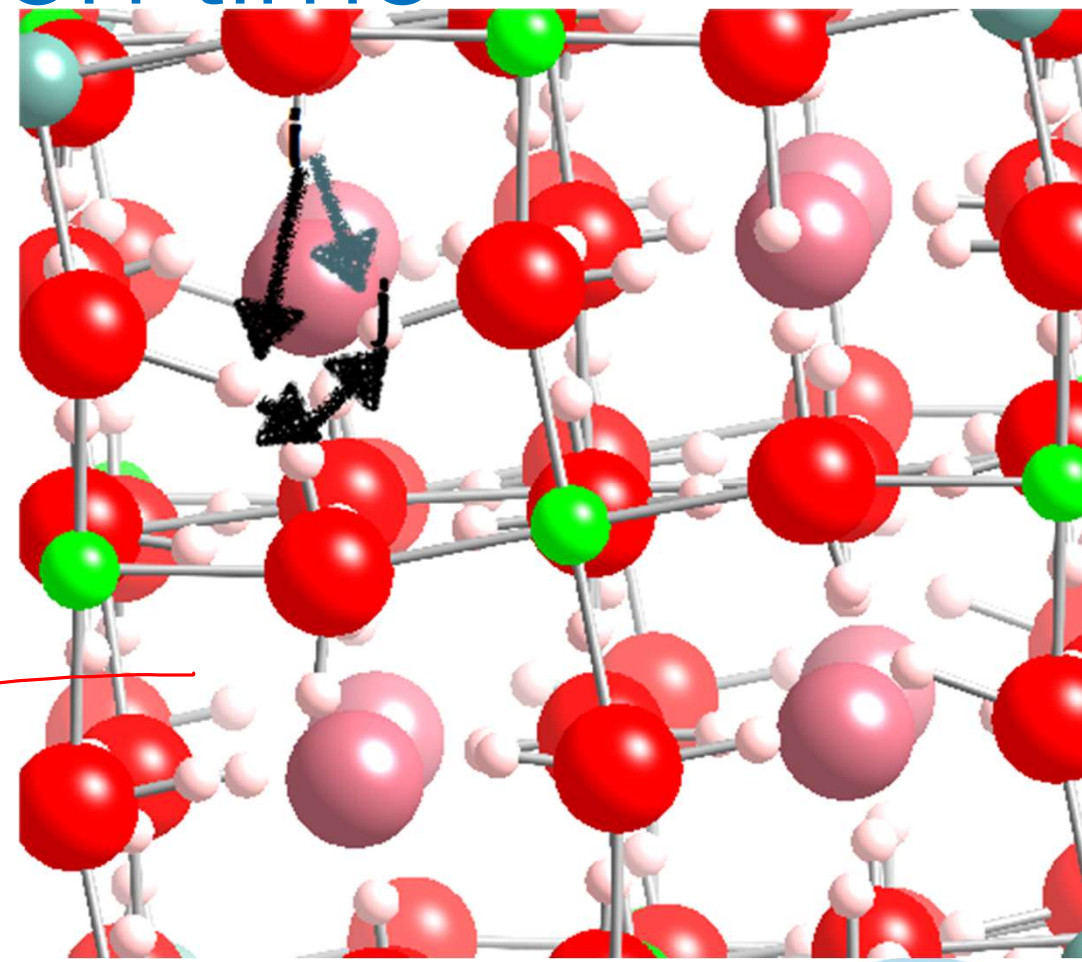


Towards centrality measures based on time

Mean first passage number of steps to go from i to j. (Grinstead and Snell)

$$m_{ij} = \overset{1 \cdot p_{ij}}{p_{ij}} + \sum_{l \neq j} p_{il}\left(1 + m_{lj}\right)$$

$$m_{ij} = p_{ij}\left(\frac{1}{k_{ij}}\right) + \sum_{l \neq j} p_{il}\left(\frac{1}{k_{il}} + m_{lj}\right)$$



Mean first passage time to go from i to j.

Towards centrality measures based on time

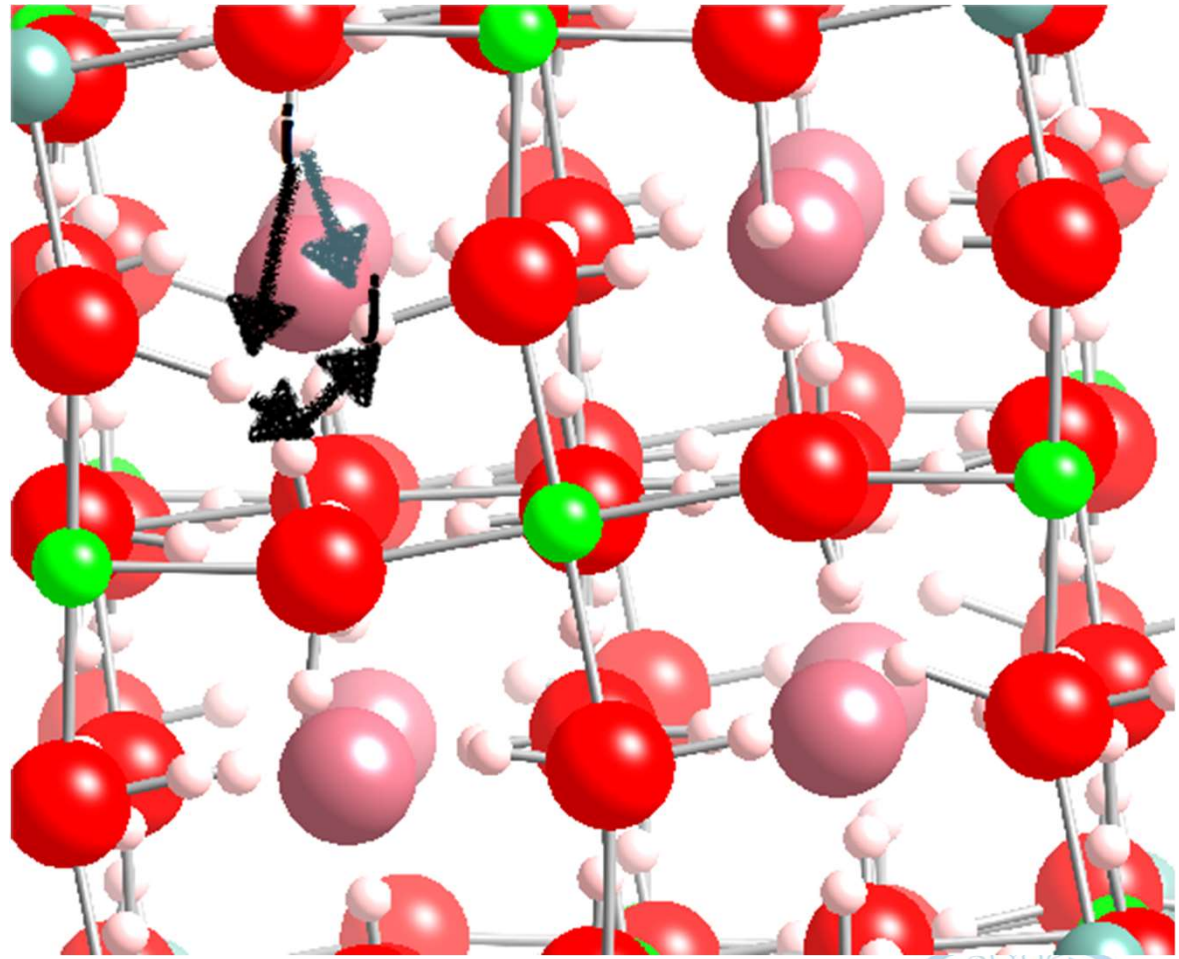
Round trip time to go from i to j and back to i

$$R_{\mathrm{ij}} = m_{ij} + m_{ji}$$

Average round trip time to go from i to any j and back

$$R_i = \frac{1}{N}\sum_j R_{ij}$$

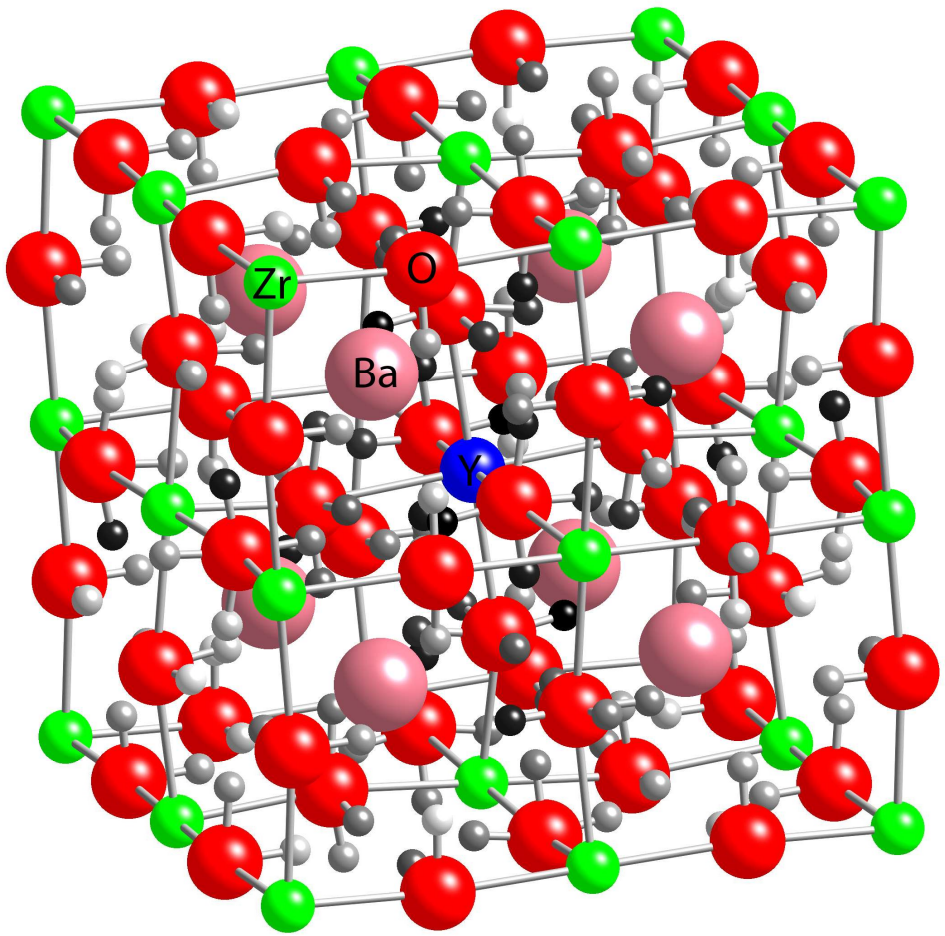
Centrality of i $\frac{1}{R_i}$



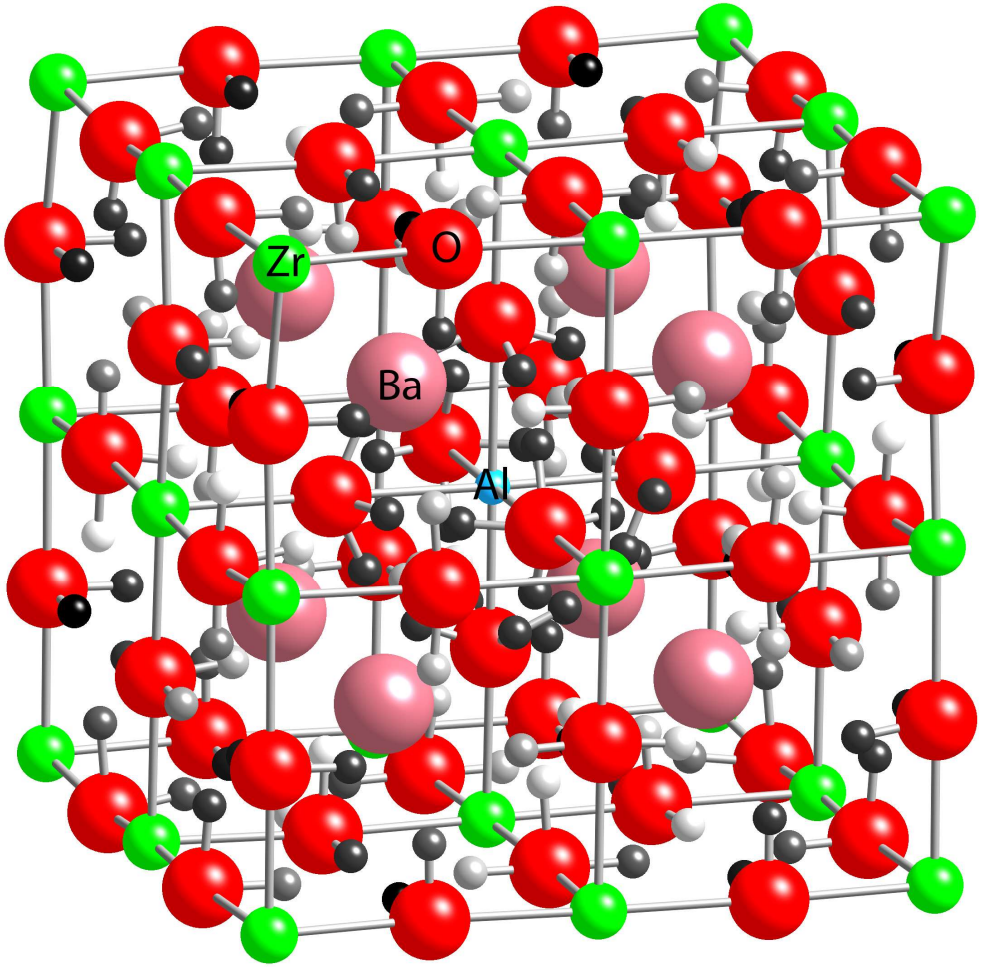
Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories

Rachel Krueger, F. G. Haibach, **Dana L Fry,** and Maria A Gomez "Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories,"J. Chem. Phys. **142**, 143110 (2015).

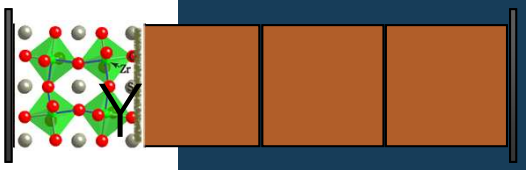
Y/$BaZrO_3$



Al/$BaZrO_3$



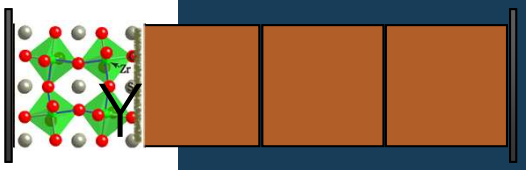
Barriers to proton conduction



	Limiting Barrier in Long range paths (graph theory) (eV)	Barrier Range to Escape dopant Trap (eV)	Long Range Limiting Barrier to Kinetic Monte Carlo 1 proton (eV)	Long Range Kinetic Monte Carlo 4 protons (eV)	Experiment (eV) H.G. Bohn, T. Schober, J. Am. Ceram. Soc. 83 (2000) 768.
$Y/BaZrO_3$	0.32	same	0.39	0.43	0.43 for 10% doping
$Al/BaZrO_3$	0.40	0.7-0.9	0.81	0.88	

In $Y/BaZrO_3$, the percent of limiting barriers that are intra-octahedral transfers, rotations, and inter-octahedral transfers changes from 87% , 11%, and 2% in the single proton case to 90%, 0%, and 10% in the four proton case.

Barriers to proton conduction



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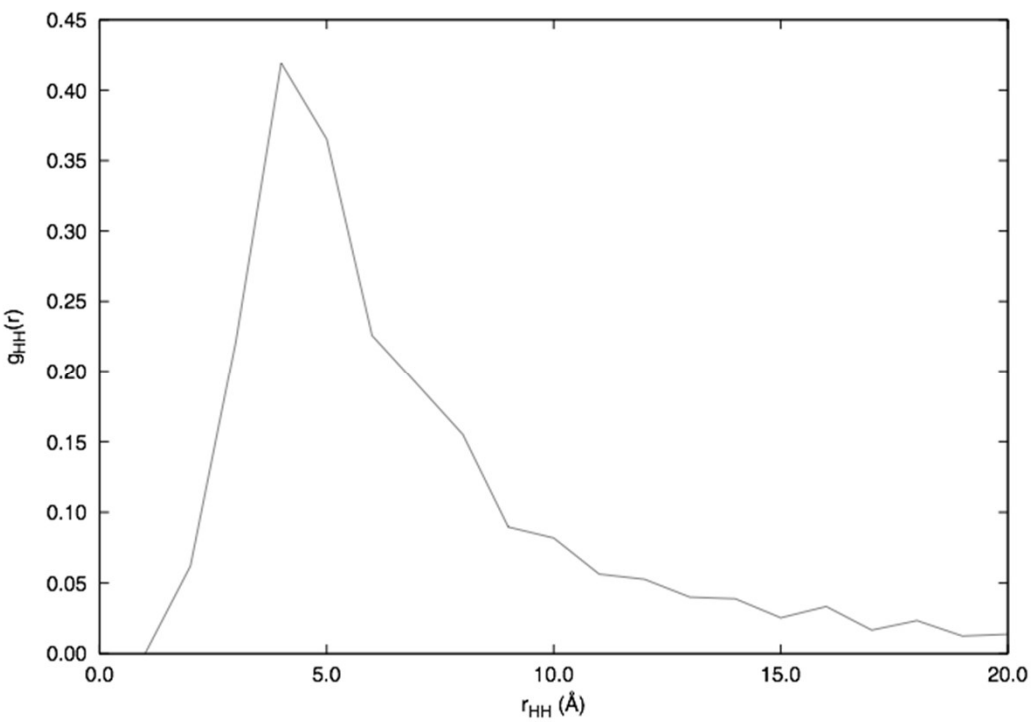
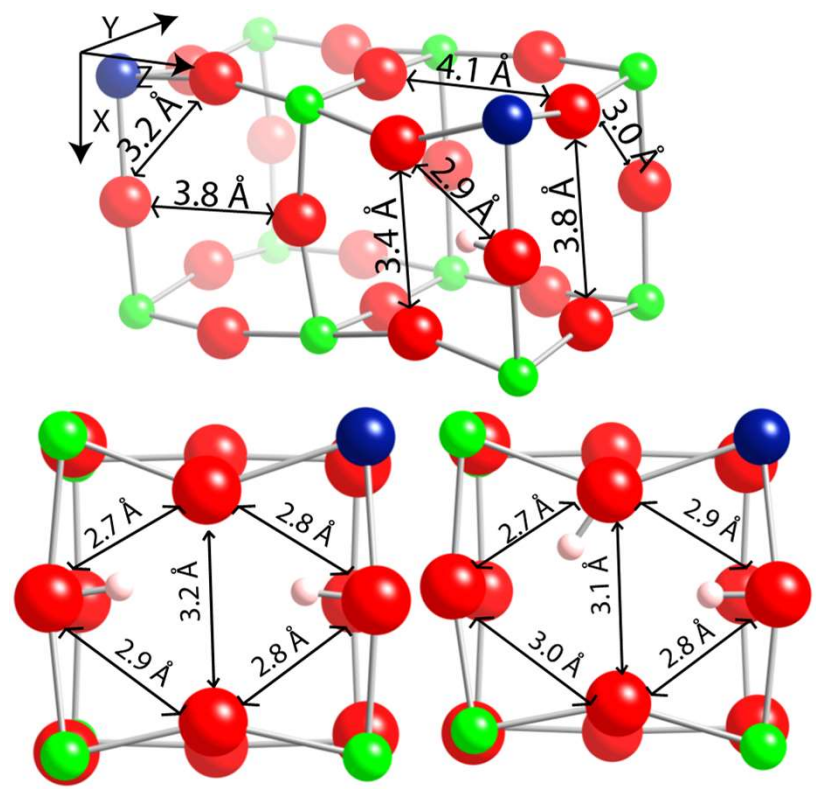
$Y/SrZrO_3$	0.43	same	0.57	0.69	0.43 for 5% doping
$Al/SrZrO_3$	0.60	0.7-0.8	0.73	0.84	0.97 for 5% doping

Experimental numbers from : H.G. Bohn, T. Schober, J. Am. Ceram. Soc. 83 (2000) 768.
Y. Liu, M. Yoshino, K. Tatsumi, I. Tanaka, M. Morinaga, H. Adachi, Mater. Trans. 46 (2005) 1106
T. Yajima, H. Suzuki, T. Yogo, and H. Iwahara, Solid State Ionics 51 (1992) 101.

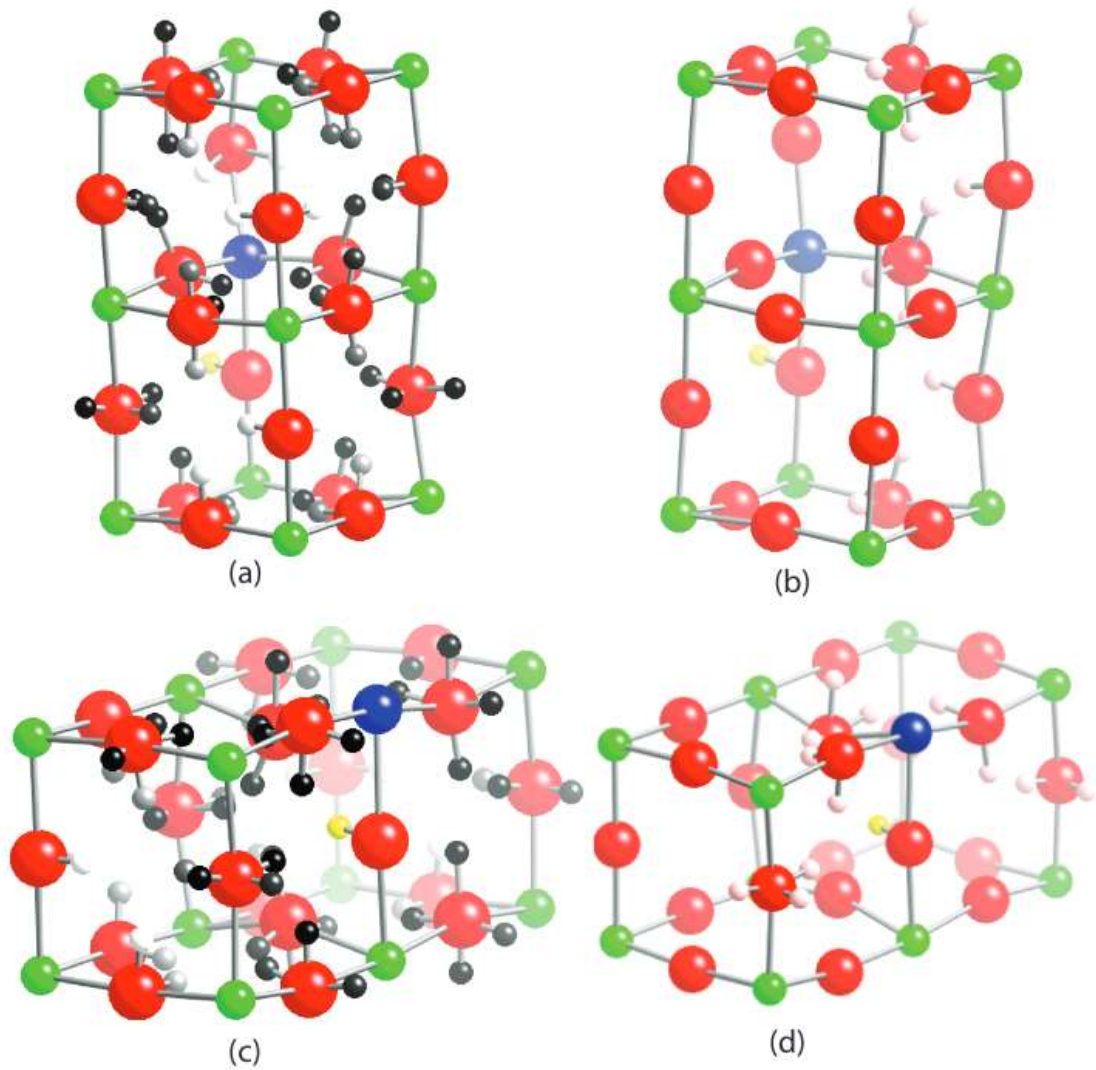
Lattice distortions stabilize a second proton binding near the first proton





Maria A. Gomez, **Dana L. Fry, Marie E. Sweet**, "Effects of the proton conduction limiting barriers and trajectories in BaZr0.875Y0.125O3 due to the presence of other protons," J. of the Korean Ceramic Society. **53**, 1, 2016.

Second proton pathways move along regions of high centrality



Conclusions

- Traditional graph theory ideas can help find long range conduction highways.
- Centrality measures using mean time to first returns rather than mean number of steps to first returns can highlight traps, access points to fast long range pathways, and long range pathways.
- Kinetic Monte Carlo both verifies the path information seen using centrality measures and also allows us to calculate limiting barriers which compare well with experiment.
- Proton conduction pathways in yttrium doped barium zirconate tend to be in regions with the dopant which include the yttrium trap. In contrast, protons moving in the aluminum doped system escape traps to fast highways away from the dopant to do long range conduction.

Collaborators and Funding

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