

Hydrogen species motion in piezoelectrics: A quasi-elastic neutron scattering study

K. J. Alvine,^{1,a)} M. Tyagi,^{2,3,a)} C. M. Brown,² T. J. Udovic,² T. Jenkins,² and S. G. Pitman¹

¹Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

²NIST Center for Neutron Research, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, 20899, USA

³Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, 20742, USA

(Received 27 October 2011; accepted 23 January 2012; published online 5 March 2012)

Hydrogen is known to damage or degrade piezoelectric materials, at low pressure for ferroelectric random access memory applications, and at high pressure for hydrogen-powered vehicle applications. The piezoelectric degradation is in part governed by the motion of hydrogen species within the piezoelectric materials. We present here quasi-elastic neutron scattering (QENS) measurements of the local hydrogen species motion within lead zirconate titanate (PZT) and barium titanate (BTO) on samples charged by exposure to high-pressure gaseous hydrogen (≈ 17 MPa). Neutron vibrational spectroscopy (NVS) studies of the hydrogen-enhanced vibrational modes are presented as well. Results are discussed in the context of theoretically predicted interstitial hydrogen lattice sites and compared to comparable bulk diffusion studies of hydrogen diffusion in lead zirconate titanate. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.3691114>]

I. INTRODUCTION

While hydrogen has been proposed as a next-generation clean burning fuel for both stationary and vehicular power, it brings with it serious materials science challenges. Hydrogen is well-known to degrade metals through embrittlement and surface blistering.¹ Piezoelectrics, which are used as actuators to deliver high-pressure hydrogen in hydrogen internal combustion engines (HICE), are also susceptible to hydrogen damage² and subsequent device failure.³ HICE is being considered as a possible short-term replacement for fuel cells, and piezoelectric actuators allow direct injection with a 17% efficiency boost over port injection.⁴ Piezoelectric actuators are exposed to constant hydrogen pressures around 35 MPa (5000 psi) and have been shown to fail rapidly in such an environment.³ Several studies^{5–11} into low-pressure hydrogen degradation of piezoelectrics for ferroelectric random access memory (FeRAM) indicate that the ferroelectric properties are degraded by hydrogen. Recent high-pressure hydrogen studies² show that the effects in high-pressure hydrogen can be even more serious with significant Pb diffusion and surface blistering.

Here we present quasi-elastic neutron scattering (QENS) and neutron vibrational spectroscopy (NVS) studies that quantify the motion of hydrogen species in two different piezoelectric materials, lead zirconate titanate ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ with $x=0.48$, PZT), and barium titanate (BaTiO_3 , BTO). Powder samples were charged with hydrogen by gaseous exposure to high-pressure hydrogen (≈ 16.5 MPa) at 373 K, conditions relevant to the HICE injector described above. There is currently a dearth of information in the literature

about hydrogen diffusion in the piezoelectrics, which is an essential component in predicting the extent of hydrogen-induced damage in piezoelectrics for both HICE and FeRAM applications. To date, hydrogen diffusion in PZT measurements has only been reported for aqueous-charged electrode experiments rather different from the gaseous exposure route, which also induces a color change not seen in our experiments.¹² Results will be discussed in the context of theoretically predicted interstitial hydrogen locations within the perovskite lattice and with recent ^1H NMR measurements that we have undertaken.¹³ Such information may prove useful in determining methods and technology to mitigate hydrogen-induced damage in piezoelectrics.

II. EXPERIMENTAL

Lead zirconate titanate ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ with $x=0.48$ (based on energy dispersion spectroscopy (EDS)), PZT) powder was purchased from Kinetic Ceramics Inc.¹⁴ and barium titanate (BaTiO_3 , BTO) powder, 99.995% purity was purchased from Sigma Aldrich for use in both QENS and NVS experiments. Before use, both sets of powders were heated in an air furnace at 798 K for 4 h to remove residual moisture. This is also a critical processing step for the PZT sample to remove residual organic binder from the material. Samples were then stored in a vacuum desiccator for several hours prior to hydrogen annealing, and air exposure was minimized at every step to mitigate possible moisture uptake, since BTO, at least, is known to adsorb/absorb water in moisture-saturated air.¹⁵ In BTO, water nucleates and grows into 0.5 micron-sized droplets on a flat BaTiO_3 surface exposed to high humidity, with growth saturating over roughly 20 min.¹⁶ The effect is likely similar for PZT. This is important since neutron scattering is sensitive to protons

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: kyle.alvine@pnl.gov and mtyagi@nist.gov.

in different chemical states. Both PZT and BTO powder samples were then loaded into a high-pressure autoclave to charge them with high-pressure gaseous hydrogen, with portions of the sample set aside to use as an unexposed control sample. The autoclave was flushed with Ar five times to remove residual oxygen and then filled with hydrogen (Praxair, G5 > 99.99% purity) to a pressure of roughly 12 MPa. The autoclave temperature was then slowly brought up to 373 K over the course of 4 h and the final hydrogen pressure set to ≈ 16.5 MPa (2400 psi). The samples were then annealed in the high-pressure hydrogen at 373 K for 24 h. The autoclaves were then depressurized over several minutes and the hydrogen-charged powders placed in a vacuum desiccator. No discernable differences in color or powder consistency were observed after the hydrogen annealing. Subsequently, all samples, including controls, were sealed and stored under an inert atmosphere.

A. SEM and XRD

Hydrogen-annealed and unexposed control samples were previously characterized¹³ with scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), and X-ray diffraction (XRD). From XRD at room temperature, both the PZT and BTO were in the tetragonal phase with lattice parameters: $a = 4.0$ Å, $c = 4.03$ Å for BTO and $a = 4.05$ Å, $c = 4.11$ Å for PZT. No differences in lattice parameters were detectable between the control and hydrogen-annealed samples within experimental uncertainty. Particle size was measured with SEM to be, on average, 0.5 μm for all samples, with the smallest observed particle size approximately 100 nm. EDS detected only Pb, Zr, Ti, and O for the PZT samples, and trace levels (<1 at %) of Ni, Al, and Si in the BTO samples, possibly originating from the SEM sample holders, which are comprised of Ni and Al. No significant differences between the hydrogen-annealed and control samples were observable with EDS or SEM.

B. QENS studies

Hydrogen has a relatively large cross section for neutron scattering, which allows for high sensitivity even for small amounts of hydrogen in the system, as is the case in our systems where we expect only a few atomic percent of hydrogen.² For low-energy or “cold” neutrons, which have energies comparable to kT (where k is the Boltzmann constant), energy transfers with diffusing protons can amount to an appreciable and measurable energy gain or loss of the neutron’s kinetic energy. This change in energy leads to a broadening of the elastic peak (energy transfer $\hbar\omega = 0$) centered at zero and is referred to as quasi-elastic neutron scattering or QENS. This line broadening can be modeled in our system with a scattering function given by

$$S(Q, \omega) = R(Q, \omega) \otimes (\delta(Q, \omega) + B(Q, \omega) + L(Q, \omega)),$$

$$L(Q, \omega) = \frac{2}{\pi} \frac{\Lambda(Q)}{4\omega^2 + \Lambda^2(Q)},$$

where Q is the momentum transfer and ω is the frequency. In the above equation, $R(Q, \omega)$ is the instrumental resolution

function, $\delta(Q, \omega)$ is a delta function representing the elastic peak, $B(Q, \omega)$ is a background due to atomic vibrations, and $L(Q, \omega)$ is a Lorentzian function that measures the quasi-elastic broadening with peak width $\Lambda(Q)$. For long-range translational diffusion, the peak width is related to the diffusion constant D by: $\Lambda(Q) \sim \hbar D Q^2$ for small Q ,¹⁷ where $\hbar$ is the Planck’s constant over 2π . We will use this simple Fickian diffusion model to determine approximate diffusion constants for hydrogenated species in PZT and BTO.

Both the Disk Chopper Spectrometer (DCS)¹⁸ and High-Flux Backscattering Spectrometer (HFBS)¹⁹ at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), Gaithersburg, MD were employed to measure the diffusion of hydrogen species within the PZT and BTO powder samples. Samples were transferred from inert gas packaging into Al-foil-wrapped annular configurations inside a He dry box with the relative humidity kept below 25% to prevent significant moisture uptake. Samples were then sealed in aluminum sample cans under the He atmosphere. Both hydrogen-annealed and control samples were measured with QENS. All data was fit using the DAVE software developed at the NIST.²⁰ All error bars shown in this paper denote $\pm 1\sigma$.

C. DCS measurements

QENS measurements were taken at a wavelength of 6 Å with DCS for both PZT powder exposed to high-pressure hydrogen gas, and the PZT control sample. For this wavelength, the instrument resolution is about 64 μeV and the accessible Q -range is 0.10–1.9 Å^{−1}. Hydrogen-annealed samples were measured at 37, 250, 300, 350, and 380 K. Control samples were measured at 250 K and 300 K. Data from 37 K, where all hydrogen species motion should be quenched, was used as a resolution function for fitting of the QENS spectra taken at higher temperatures. PZT has a Bragg peak at $Q = 1.53$ Å^{−1}, with full width at half-maximum of 0.04 Å^{−1} corresponding to the PZT tetragonal lattice spacing of 4.1 Å. To avoid complications from this coherent scattering, we have disregarded QENS spectra from 1.475 to 1.6 Å^{−1}. Due to the relatively low quasi-elastic signal in these measurements stemming from the low hydrogen absorption concentrations, we were obligated to integrate over relatively large Q ranges in order to improve fitting quality. Data were integrated over the following regions: 0.0–0.49 Å^{−1}, 0.49–0.98 Å^{−1}, 0.98–1.475 Å^{−1}, and 1.6–2.0 Å^{−1} for all data sets, including the control and the 37 K data that served as a resolution function. QENS data were fit with a combination of a delta function, a linear background, and a Lorentzian function, all convoluted with the resolution function measured at 37 K, shown in Fig. 1(a). PZT hydrogen-annealed samples showed a small amount of quasi-elastic (QE) broadening, while PZT control samples showed no QE broadening as compared to the resolution function and could be fit with a delta function and background (convoluted with the resolution function) only, shown in Fig. 1(b). The full-width at half-maximum (FWHM) data from the hydrogen-annealed PZT samples showed Q dependence for all temperatures. The relatively

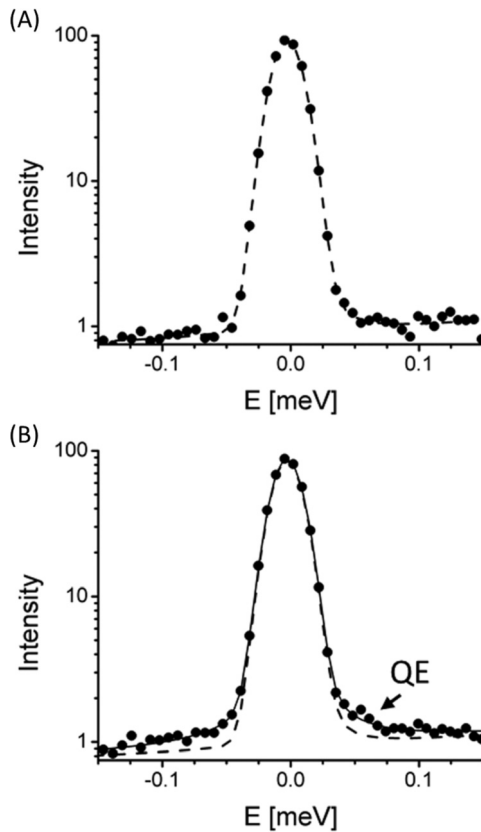


FIG. 1. QENS from DCS for PZT at 300 K integrated over $Q=0.98-1.475 \text{ \AA}^{-1}$. (A) DCS data (filled circles) from PZT control (no hydrogen). Data shows no quasi-elastic (QE) broadening and is fit (dashed line) with the resolution function plus background only. (B) DCS data (filled circles) from hydrogen annealed PZT shows quasi-elastic broadening above the resolution function plus background (dashed line). The fit including quasi-elastic broadening is shown with a solid line. Note that these fits use a smoothed resolution and are plotted on a semi-log plot for additional clarity. Standard error bars are smaller than the data symbols.

strong Q dependence shown by these samples is an indication of long-range diffusive or diffusive-like processes rather than more localized motions. Therefore, we have fit the FWHM as a function of Q with a simple long-range diffusion model $\Lambda \approx \hbar D Q^2$ as shown in Fig. 2. This model yields better fits than jump diffusion or Chudley-Elliott models.^{17,21} The diffusion constants for the different temperatures are listed in Table I.

D. HFBS measurements

“Fixed window scans” (FWS) of the elastic intensity as a function of temperature for both hydrogen-charged PZT and BTO were measured on the HFBS instrument with the Doppler drive turned off. For samples with no translational diffusion, the intensity decays as $I(Q) \approx e^{-Q^2 \langle u^2 \rangle / 3}$, where $\langle u^2 \rangle$ is the mean-square-displacement (MSD). Thus, the MSD can be extracted from the FWS as a function of temperature and is plotted in Fig. 3(a) for both materials. Standard error bars are on the order of the scatter in the data and have been omitted for clarity. A linear fit holds for low temperatures up to approximately 200 K for both PZT and BTO, indicating harmonic vibration in this region.²² For higher temperatures, the MSD increases significantly more strongly

for BTO than for PZT. QENS measurements were subsequently taken with the HFBS instrument on the hydrogen-charged BTO samples at 250 K and 300 K. Due to the low QE signal measured in the BTO samples, it was decided that it would be impractical to measure QENS on the PZT samples with the HFBS instrument due to the even lower QE signal indicated by the FWS. It is also interesting to see that the PZT data shows a very small and continuous increase in the MSD even above 200 K. We also note that these calculated MSD data sets lack the much steeper rise exhibited in confined-water experiments where the MSD increases more than tenfold from 200 to 250 K, suggesting the absence of water.²³ This is confirmed for PZT with NVS discussed in the following section. After annealing the BTO to 350 K and holding it there for several hours, subsequent FWS showed significantly less QE signal, indicating that a significant amount of hydrogen had been driven off at the higher temperatures. MSD data from one of these FWS is shown in Fig. 3(a). A fresh, unannealed portion of the hydrogen-exposed BTO sample was then used for QENS measurements on HFBS. A very low signal (even after >12 h of data collection per temperature), attributed to low levels of hydrogen in the BTO system, necessitated the averaging of data over multiple detectors at the sacrifice of Q resolution. A vanadium sample at low temperatures provided a resolution function for the analysis. The HFBS instrument offers high resolution of around $0.8 \mu\text{eV}$ to measure slow processes and the data are recorded for 16 different Q values between $0.25 \text{ \AA}^{-1}$ and $1.75 \text{ \AA}^{-1}$. Data was fit²⁰ using a background, delta function, and Lorentzian function, all convoluted with the resolution function as with the DCS data. See Fig. 3(b) for an example of the QE fitting at $T=300 \text{ K}$ and $Q=0.7459 \text{ \AA}^{-1}$. In addition, data from 1.52 to $1.7 \text{ \AA}^{-1}$ was excluded to avoid potential complication from the BTO Bragg peak from the tetragonal lattice parameter of roughly $4 \text{ \AA}$. Data (out of backscattering) from low Q detectors 1-4 were also excluded due to difficulty in achieving reliable fits with the vanadium resolution function. The FWHM from the BTO data at 250 K shows Q dependence (Fig. 4(a)) and is fit with a simple jump diffusion model as follows:

$$\Lambda(Q) = \frac{\hbar D Q^2}{1 + D \tau Q^2},$$

where τ is the residence jump time and is related to the jump length by $L = \sqrt{n D \tau}$, where $n=2, 4$, and 6 for diffusion in 1, 2, and 3 dimensions, respectively. Fit parameters are listed in Table II. Interestingly, the QENS data for BTO at 300 K does not show Q dependence and is fit by a constant FWHM of $4.89 \pm 0.14 \mu\text{eV}$, suggesting rotational diffusion. This may be partially explained by the existence of an orthorhombic to tetragonal phase transition as temperature increases at 278 K.²⁴ The rotational period from this fit is given in Table II. Further discussion of this point in regards to the elastic incoherent structure factor (EISF) is given in a later section.

E. NVS measurements

Vibrational density of states spectra were also measured for the PZT samples by NVS using the filter-analyzer

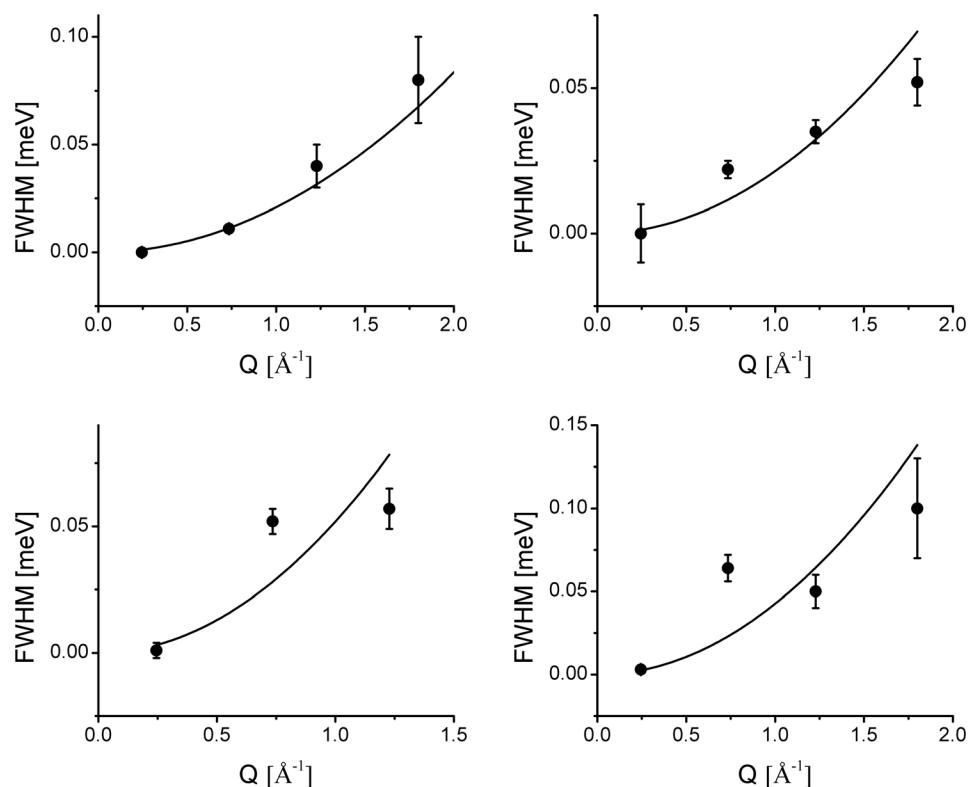


FIG. 2. Plots of Q vs FWHM for 250, 300, 350, and 380 K (clockwise from top left) for the DCS PZT data. Solid lines are parabolic fits to the data for long-range diffusion.

neutron spectrometer (FANS) at the NCNR.²⁵ With this technique, a monochromatic thermal neutron beam inelastically scatters from the sample. A low-pass Bragg cutoff filter detects all scattered neutrons below the cutoff energy. The incident energy is scanned to measure the intensity as a function of the energy transfer. The vibrational spectra for both PZT hydrogen-annealed and control samples are shown in Fig. 5(a). The peaks have been labeled by comparison with Ref. 26 for Raman studies of PZT. These are the E and A_1 normal vibrations for a tetragonal system.²⁷ “LO” and “TO” refer to longitudinal and transverse optical modes, respectively. The numbering such as $E(3LO)$ simply serves to distinguish between different modes. These vibrational spectra refer to the Zr/Ti – O vibrations in the tetragonal system. The hydrogen-annealed system has increased intensity in several, but not all measured peaks. Since the hydrogen in this system is predicted to form OH^- groups,²⁸ the increase in signal comes from the increase in scattering due to the presence of the hydrogen bound to the oxygen. Figure 5(b) shows the predicted locations of hydrogen in the perovskite system according to Park²⁸ with the numbers indicating

increasing energy. The increased signal in certain peaks is akin to a “riding” mode where the hydrogen moves with the oxygen and the resulting vibration benefits in an intensity increase due to the large hydrogen cross-section. Peaks that are not enhanced likely relate to Zr/Ti – O vibrations along the vertical direction of the tetragonal unit-cell centerline where the hydrogen is less likely to reside due to energy considerations. To eliminate the potential of scattering due to the presence of additional water in the PZT system, we note that the librational mode for water occurs at approximately 550 cm^{-1} .²⁹ While there is a peak in the FANS data at this location, the peak is not enhanced relative to the control sample.

III. DISCUSSION

We have measured hydrogen species dynamics in both PZT and BTO. In PZT we note an increase in the long-range hydrogen species diffusion constant between 250 K and 380 K, with an activation energy of $3 \pm 2\text{ meV}$. The diffusion constants are in the range of $3 \times 10^{-10}\text{ m}^2/\text{s}$ to $8 \times 10^{-10}\text{ m}^2/\text{s}$. While these values are approximately 14%–36% of the values of bulk water translational diffusion ($2.2 \times 10^{-9}\text{ m}^2/\text{s}$) they are similar to values for water surface diffusion of $2.4 \times 10^{-10}\text{ m}^2/\text{s}$ to $8.5 \times 10^{-10}\text{ m}^2/\text{s}$ at 298 K. Neutron scattering cannot distinguish between different hydrogen species and cannot definitively address whether this is atomic hydrogen diffusion or water diffusion on the PZT grains.³⁰ However, only PZT exposed to high-pressure hydrogen showed measurable QE broadening, compared to the non-hydrogenated material, and this is an indication that the hydrogen measured is not due to surface

TABLE I. Calculated diffusion constants for PZT from DCS measurements for long-range diffusion.

T [K]	$D [\times 10^{-10}\text{ m}^2/\text{s}]$
250	3.2 ± 0.3
300	3.2 ± 0.6
350	8 ± 3
380	6 ± 3

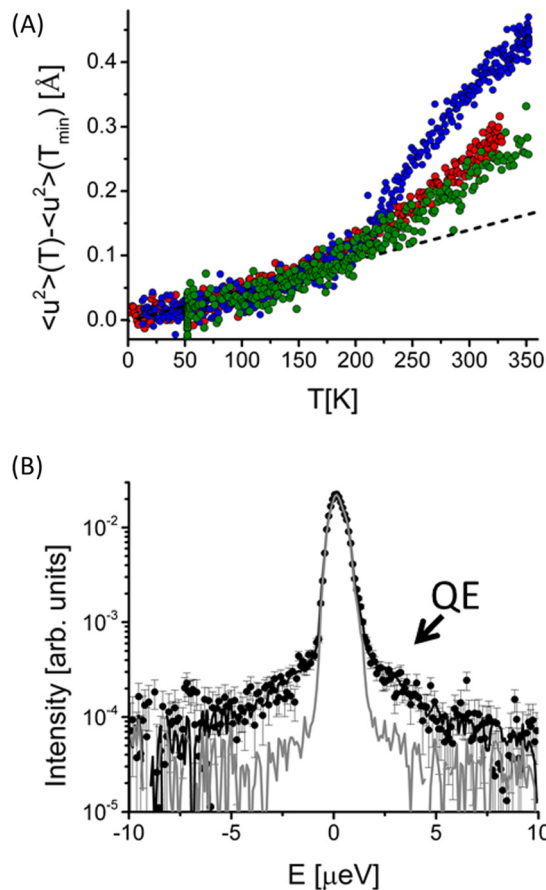


FIG. 3. (Color online) (A) Mean-square-displacement extracted from fixed window scans on the HFBS instrument for PZT (red) and BTO (blue). The mean-square displacement data for the BTO is larger than for the PZT above 220 K. BTO data after annealing above 350 K is also presented (green) and shows similar behavior to the PZT, but shifted to slightly lower values. The dashed line is a linear fit to the low-temperature data. (B) Example of QENS data and fitting for BTO at 300 K, $Q = 0.7459 \text{ \AA}^{-1}$. Solid black line is a fit to the data and the gray line is a fit only of the elastic and background contributions.

water as the materials have been handled in a similar fashion, but it cannot be totally ruled out.

HFBS measurements showed dynamics in BTO that are temperature-dependent. At 250 K, the dynamics appear to be jump diffusion, while at 300 K, the dynamics appear to be rotational diffusion. This may be related to the orthorhombic to tetragonal phase transition at 278 K. In addition to the FWHM of the QE signal, we have also looked at the EISF for the two temperatures. The EISF, which is the fraction of elastic scattering as a function of Q , does not appear to approach zero within the Q range that we measure; instead approaching a value near 0.9, suggesting localized motion rather than long-range diffusion for hydrogen species in the BTO.¹⁷ This occurs for both 250 K and 300 K. For 300 K, where the FWHM data suggests rotational motion, this is expected. For 250 K, this may suggest that the jump diffusion is spatially restricted by local energetic traps or defects in the material as discussed in Ref. 17. The EISF parameter is calculated by taking the ratio of the delta function prefactor to the elastic and QE scattering (delta function plus Lorentzian). Park *et al.*²⁸ calculated the most energetically favorable hydrogen positions in a perovskite around the oxy-

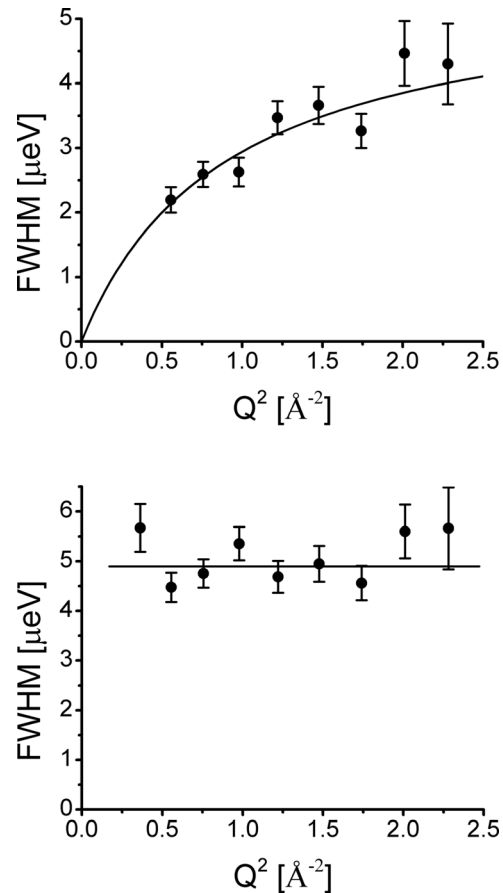


FIG. 4. Fitted FWHM as a function of Q for hydrogen annealed BTO from HFBS. Data from 250 K and 300 K are shown in the top and bottom panels, respectively. Solid lines are fits to the data using the standard jump diffusion model and rotational diffusion (Q -independent data) for 250 K and 300 K, respectively.

gen atom with an O-H bond length of approximately $0.92 \text{ \AA}$. These positions are shown schematically in Fig. 5(b). Based on these positions, the lattice parameters, and the crystal symmetry, the calculated jump lengths suggest 1 D local hydrogen hopping between adjacent oxygens within the same unit cell at 250 K.

NVS of PZT suggests that hydrogen is bonded to lattice oxygens that are situated on the faces perpendicular to the c -axis of the tetragonal unit cell, in agreement with calculations of Park *et al.*²⁸ In addition, the absence of a water band supports the theory that this motion is primarily due to atomic hydrogen motion.

Recent ^1H NMR measurements¹³ indicated much slower diffusion constants for hydrogen species in both PZT and BTO of approximately $1 \times 10^{-17} \text{ m}^2/\text{s}$. Such slow diffusion is completely outside the time scale achievable with QENS

TABLE II. Calculated diffusion constants, residence times, and possible jump diffusion lengths in BTO at 250 K. Calculated rotation period for BTO at 300 K.

T [K]	D [m^2/s]	τ_R [ns]	$L_{(1D)}$ [$\text{\AA}$]	$L_{(2D)}$ [$\text{\AA}$]	$L_{(3D)}$ [$\text{\AA}$]
250 (JD)	$9 \pm 2 \times 10^{-11}$	0.12 ± 0.02	1.5 ± 0.2	2.1 ± 0.3	2.5 ± 0.4
300 (R)	...	0.13 ± 0.04	...	...	...

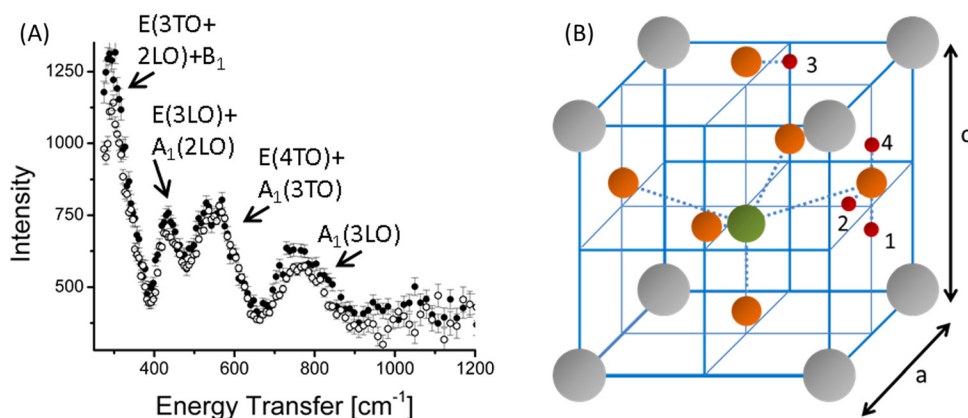


FIG. 5. (Color online) (A) PZT hydrogen-annealed (filled circles) and control (open circles) vibrational spectra from FANS measurements. Peaks are labeled according to Ref. 26. Bands typical for water are not present. (B) Possible hydrogen (smallest, red) locations in relation to the oxygen (near face centered locations, orange), Pb or Ba (gray, corners), and Zr or Ti (green, near body center location) according to Park²⁸ for the tetragonal perovskite. Sites are numbered from lowest to highest energy.

instrumentation available and would not be observed in these measurements. In the same manner, such rapid diffusion would not be discernable in most types of ^1H NMR experiments. For BTO, it is probable that the slower rates pertain to long-range translational atomic hydrogen diffusion as compared local hydrogen motion that we are likely sensing with the neutrons. In PZT, it is possible that the much faster neutron result is due to surface diffusion at the grain boundaries rather than the likely long-range translational diffusion seen with NMR.

Previous studies of hydrogen diffusion in PZT reported a value of $4.9 \times 10^{-12} \text{ m}^2/\text{s}$ based on the advancement of a color change (yellow to gray) front for bulk sintered PZT blocks charged in NaOH solutions at room temperature with a current of $50 \text{ mA}/\text{cm}^2$.¹² Our experiments are substantially different in that we are observing intrinsic diffusion with a local probe in a powder sample where the hydrogen charging is done via a gaseous approach. In addition, we see no evidence of a color change in either the PZT or BTO upon hydrogen charging, indicating that a fundamentally different process may be occurring when the PZT is in solution under an electric field. Rajopadhye *et al.*³¹ did observe a similar color change (yellow to black) in PZT annealed in a hydrogen zone furnace, but at much higher temperatures of 873 K. They attributed the color change to migration of oxygen from the bulk. Our observations of faster hydrogen diffusion through PZT may be an indication of a simpler process than what is leading to some form of phase transition (yellow to black) in their experiments.

IV. CONCLUSIONS

Our quasi-elastic neutron measurements indicate a rapid hydrogen species diffusion constant in both PZT samples exposed to high-pressure hydrogen on the order of $3 \times 10^{-10} \text{ m}^2/\text{s}$. This is more rapid than the processes observed in previous measurements on PZT where the samples were charged in an aqueous electrochemical environment rather than a gaseous one. We expect that the two routes are fundamentally different due to a distinct color change in the PZT only observed in the electrochemical measurements. Similar measurements on BTO suggest localized motion of hydrogen within the lattice. We have also observed vibrational spectroscopy that is supportive of

the theoretically predicted²⁸ OH binding for hydrogen in a PZT lattice.

ACKNOWLEDGMENTS

This research was supported under DOE Contract No. DE-AC05-76RL01830. A portion of the research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0944772.

¹Materials for the Hydrogen Economy, edited by Russell H. Jones, and George J. Thomas (CRC Press, Boca Raton, 2008).

²K. J. Alvine, V. Shuttanandan, W. D. Bennett, C. C. Bonham, D. C. Skor-ski, S. G. Pitman, M. E. Dahl, and C. H. Henager, *Appl. Phys. Lett.* **97**, 221911 (2010).

³A. M. D. Welch, S. Munshi, J. Holbery, B. Boyer, M. Younkins, and H. Jung, "Challenges in developing hydrogen direct injection technology for internal combustion engines," SAE, 2008. 2008-01-2379.

⁴S. Verhelst and T. Wallner, *Prog. Energy Combust. Sci.* **35**, 490 (2009).

⁵N. Ikarashi, *Appl. Phys. Lett.* **73**, 1955 (1998).

⁶K. Niwa, Y. Kotaka, M. Tomotani, H. Ashida, Y. Goto, and S. Otani, *Acta Mater.* **48**, 4755 (2000).

⁷M. Wu, H. Huang, W. Chu, L. Guo, L. Qiao, J. Xu, and T.-Y. Zhang, *J. Phys. Chem. C* **114**, 9955 (2010).

⁸S. Zafar, V. Kaushik, P. Laberge, P. Chu, R. E. Jones, R. L. Hance, P. Zurcher, B. E. White, D. Taylor, B. Melnick, and S. Gillespie, *J. Appl. Phys.* **82**, 4469 (1997).

⁹S. Aggarwal, S. R. Perusse, C. W. Tipton, R. Ramesh, H. D. Drew, T. Venkatesan, D. B. Romero, V. B. Podobedov, and A. Weber, *Appl. Phys. Lett.* **73**, 1973 (1998).

¹⁰J. K. Lee, Y. Park, and I. Chung, *J. Appl. Phys.* **92**, 2724 (2002).

¹¹S. Shin, U. H. Pi, D. J. Kim, B. S. Kang, T. W. Noh, and Z. G. Khim, *Appl. Surf. Sci.* **188**, 411 (2002).

¹²H. Y. Huang, W. Y. Chu, Y. J. Su, K. W. Gao, J. X. Li, and L. J. Qiao, *J. Am. Ceram. Soc.* **90**, 2062 (2007).

¹³K. J. Alvine, M. Vijayakumar, M. E. Bowden, A. L. Scherer-Kohn, S. G. Pitman, "Hydrogen Diffusion in Lead Zirconate Titanate and Barium Titanate" (unpublished).

¹⁴Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by

- the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
- ¹⁵B. Chornik, V. A. Fuenzalida, C. R. Grahmann, and R. Labbé, *Vacuum* **48**, 161 (1997).
- ¹⁶D. Y. He, L. J. Qiao, A. A. Volinsky, Y. Bai, M. Wu, and W. Y. Chu, *Appl. Phys. Lett.* **98**, 062905 (2011).
- ¹⁷R. Hempelmann, "Quasielastic neutron scattering and solid state diffusion," in *Oxford Series on Neutron Scattering in Condensed Matter* (Oxford University Press, New York, 2000).
- ¹⁸J. R. D. Copley and J. C. Cook, *Chem. Phys.* **292**, 477 (2003).
- ¹⁹A. Meyer, R. M. Dimeo, P. M. Gehring, and D. A. Neumann, *Rev. Sci. Instrum.* **74**, 2759 (2003).
- ²⁰R. T. Azuah, L. R. K. Y. Qiu, P. L. W. Tregenna-Piggott, C. M. Brown, J. R. D. Copley, and R. M. Dimeo, *J. Res. Natl. Inst. Stand. Technol.* **114**, 341 (2009).
- ²¹A. Ishikawa, H. Maekawa, T. Yamamura, Y. Kawakita, K. Shibata, and M. Kawai, *Solid State Ionics* **179**, 2345 (2008).
- ²²R. Inoue, T. Kanaya, K. Nishida, I. Tsukushi, M. T. F. Telling, B. J. Gabrys, M. Tyagi, C. Soles, and W.-I. Wu, *Phys. Rev. E* **80**, 031802 (2009).
- ²³X.-q. Chu, K.-H. Liu, M. S. Tyagi, C.-Y. Mou, and S.-H. Chen, *Phys. Rev. E* **82**, 020501 (2010).
- ²⁴G. H. Kwei, A. C. Lawless, S. J. L. Billinge, and S. W. Cheong, *J. Phys. Chem.* **97**, 2368 (1993).
- ²⁵T. J. Udovic, C. M. Brown, J. B. Leao, P. C. Brand, R. D. Jiggetts, R. Zeitoun, T. A. Pierce, I. peral, J. R. D. Copley, Q. Huang, D. A. Neumann, and R. J. Fields, *Nucl. Instrum. Methods Phys. Res. Sect.* **588A**, 406 (2008).
- ²⁶G. Burns and B. A. Scott, *Phys. Rev. Lett.* **25**, 1191 (1970).
- ²⁷K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1997).
- ²⁸C. H. Park and D. J. Chadi, *Phys. Rev. Lett.* **84**, 4717 (2000).
- ²⁹M. C. Bellissent-Funel and J. Teixeira, *J. Mol. Struct.* **250**, 213 (2000).
- ³⁰J.-P. Korb, M. Whaley Hodges, Th. Gobron, and R. G. Bryant, *Phys. Rev.* **60E**, 3097 (1999).
- ³¹N. R. Rajopadhye, S. V. Bhoraskar, S. Badrinarayan, and A. P. B. Sinha, *J. Mater. Sci.* **23**, 2631 (1988).