Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2018

Local structure and vibrational dynamics in indium-doped barium zirconate (Supporting Information)

Laura Mazzei,[a] Adrien Perrichon,[b] Alessandro Mancini,[c] Göran Wahnström,[a] Lorenzo Malavasi,[c] Stewart F. Parker,[d] Lars Börjesson [a] and Maths Karlsson*[b]

[a]*Department of Physics and* [b]*Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. E-mail: maths.karlsson@chalmers.se; Tel. +46 733873207.* [c]*Department of Chemistry, University of Pavia & INSTM, 27100 Pavia, Italy.* [d]*ISIS facility, STFC Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, United Kingdom.*

1 *Ab initio* molecular dynamics simulations

1.1 Structural models

Table S1 regroups all 6 possible inequivalent arrangements of 4 Zr and 4 In atoms over the 8 *B* sites of the 2×2×2 supercell of our structural models of 50In/BZO. We also show the three O atom environments (first shell of neighbors), by counting the number of symmetric Zr-O-Zr patterns, and the number of asymmetric Zr-O-In patterns (SP and AP, respectively). Note that the number of SP for Zr-O-Zr and In-O-In is identical for a 50%-50% composition. Assuming that the distribution of Zr and In atoms on the *B* site is random, the ratio SP/AP would tend to 0.5 for a high enough number of atoms.

Included in the table is also the information about a stacking plane (if any), generated by the periodic boundary conditions. Since there is no experimental evidence of superstructures (stacking planes), nor of heterogeneous composition domains (segregation), we selected the model marked as "III" in Table S1, as it does not contain any stacking plane and has a SP/AP ratio of 0.5.

1.2 Vibrational density of states

Fig. S1(a) shows the VDOS calculated from the trajectories based on structural models with experimental cell parameters (20 kBar of compressive residual pressure on the trajectories), and with cell parameters adjusted to give a residual pressure of 0 kBar. Spectra are summed over the same four structural models (16 trajectories) for both cases. The two VDOS are in good qualitative agreement, with similar peak shapes and frequencies. The effect of the 20 kBar of compressive pressure is limited to a small broadening of the spectra, and a slight red-shift of the ν(O-H) band and a blue-shift of the δ(O-H) band, of the order of 2 meV, respectively.

From the AIMD trajectories we analyzed, for each proton in each configuration, the distribution of the hydrogen bond length $d_{\mathrm{O\cdot\cdot H}}$ extracted from the simulations. The average hydrogen bond lengths $\bar{d}_{\mathrm{O\cdot\cdot H}}$ and the FWHM of the hydrogen bond length distribution are summarized in Table S2. Fig. S1(b) shows the filtered VDOS (VDOS$_f$) as a cumulative sum.

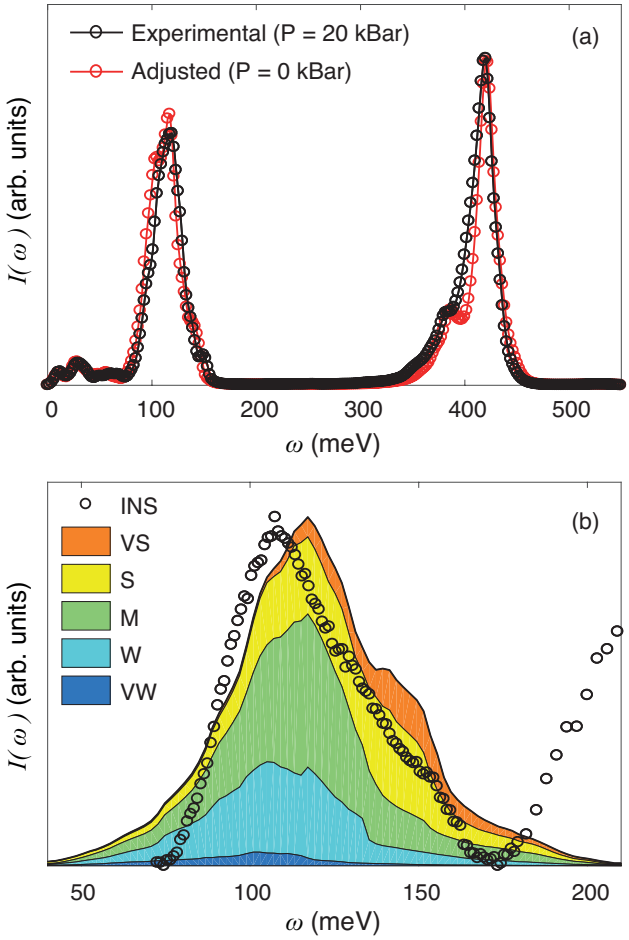


Fig. S1 (a) Comparison of the VDOS calculated from trajectories with a 20 kBar of compressive residual pressure (experimental cell parameters, black) and with 0 kBar (adjusted cell parameters, red). (b) Cumulative VDOS$_f$ in the δ(O-H) energy region for trajectories filtered according to the hydrogen bond length grouping: very strong (*VS*), strong (*S*), medium (*M*), weak (*W*), and very weak (*VW*). The spectra are normalized and background corrected. The INS spectrum (black markers) is also reported for comparison.

Table S1 Inequivalent configurations of the 4 Zr and 4 In atoms on the 8 available *B* sites in the 2×2×2 supercell of 50In/BZO. ZrO_6 and InO_6 octahedra are shown in grey and blue color, respectively. The number of SP and AP, as well as the stacking plane (if any), are indicated for each configuration.

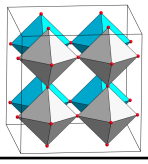
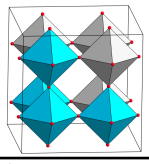
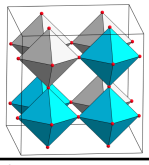
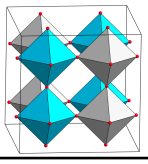
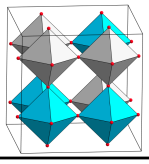
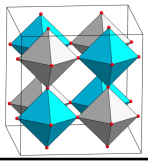
Model	"I"	"II"	"III"	"IV"	"V"	"VI"
						
Number of SP	8	6	6	4	4	0
Number of AP	8	12	12	16	16	24
Stacking plane	(100)	(222)	none	(110)	none	(111)

Table S2 Average hydrogen bond length $\bar{d}_{O\cdot\cdot H}$, for each proton and model, and associated FWHM, calculated from the Gaussian fit of the hydrogen bond length distribution for each proton and model, as obtained from the AIMD simulations. The symbols $^{\circ}$, $^{\otimes}$ and $^{\times}$ label hydrogen atoms in a Zr-O(H)-Zr, Zr-O(H)-In and In-O(H)-In configuration, respectively.

	$\bar{d}_{O\cdot\cdot H}$ [Å]				FWHM [Å]			
Configuration	H1	H2	H3	H4	H1	H2	H3	H4
Uncorrelated (I)	1.92°	1.89°	$2.00^{\times}$	$2.13^{\times}$	0.33	0.38	0.32	0.20
Uncorrelated (II)	$2.06^{\times}$	$2.00^{\otimes}$	1.69°	$2.08^{\otimes}$	0.29	0.28	0.27	0.25
Uncorrelated (III)	$1.81^{\otimes}$	$1.92^{\times}$	$1.94^{\times}$	$1.81^{\otimes}$	0.25	0.32	0.39	0.21
Uncorrelated (IV)	$2.06^{\times}$	$1.87^{\otimes}$	$2.04^{\otimes}$	$1.91^{\otimes}$	0.29	0.27	0.29	0.23
Uncorrelated (V)	$1.78^{\times}$	$2.00^{\times}$	$1.93^{\otimes}$	$1.95^{\otimes}$	0.21	0.27	0.27	0.31
Uncorrelated (VI)	$2.06^{\times}$	$1.94^{\times}$	$1.97^{\otimes}$	$1.92^{\otimes}$	0.22	0.24	0.37	0.23
Correlated (*P*-type, I)	1.91°	$2.00^{\otimes}$	1.96°	$2.06^{\times}$	0.29	0.23	0.25	0.20
Correlated (*R*-type, I)	1.81°	$2.15^{\otimes}$	$1.97^{\otimes}$	$1.74^{\times}$	0.33	0.39	0.27	0.21
Correlated (*R*-type, II)	1.99°	1.74°	$2.03^{\otimes}$	$1.70^{\otimes}$	0.18	0.26	0.31	0.19
Correlated (*R*-type, III)	1.80°	$2.07^{\otimes}$	1.86°	$1.85^{\otimes}$	0.20	0.20	0.21	0.25