Synthesis of a polar ordered oxynitride perovskite

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For decades, numerous attempts have been made to produce polar oxynitride perovskites, where some of the oxygen is replaced by nitrogen, but a polar ordered oxynitride has never been demonstrated. Caracas and Cohen [Appl. Phys. Lett. **91**, 092902 (2007)] studied possible ordered polar oxynitrides within density-functional theory (DFT) and found a few candidates that were predicted to be insulating and at least metastable. $YSiO_2N$ stood out with huge predicted polarization and nonlinear optic coefficients. In this study, we demonstrate the synthesis of perovskite-structured $YSiO_2N$ by using a combination of a diamond-anvil cell and *in situ* laser-heating techniques. Subsequent *in situ* x-ray diffraction, second-harmonic generation, and Raman-scattering measurements confirm that it is polar and a strong nonlinear optical material, with structure and properties similar to those predicted by DFT.

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I. INTRODUCTION

Oxide perovskites are common materials that contain cations from a majority of the elements of the Periodic Table, and polar perovskites are interesting and useful active materials with applications that include nonlinear optics, ferroelectric memories, piezoelectric transducers, and actuators. For decades, numerous attempts have been made to produce polar oxynitride perovskites, where some of the oxygen is replaced by nitrogen, but a polar ordered oxynitride has never been demonstrated. Oxynitrides have been extensively studied for their improved electronic properties [1–5]. Among the wide variety of synthesized oxynitrides, $CaTaO_2N$ and $LaTaON_2$ have been proposed for nontoxic pigments [6] and $BaTaO_2N$ as a high dielectric [7] and catalyst for photoelectrolysis of water [8]. $EuNbO_2N$ and $EuWON_2$ show intrinsic colossal magnetoresistance [9,10]. Anion ordering could produce polar oxynitrides, but making such materials in the lab has been unsuccessful until now. $SrTaO_2N$ bulk [7] does show high dielectric properties, and epitaxial thin films have been reported to have possible ferroelectricity. However, whether it is intrinsic is still unclear [11]. Recently, $MnTaO_2N$ was reported to have a polar structure with helical spin ordering without anion ordering [12].

Anion ordering in insulating oxynitrides would provide polar, electrically active materials [3,13]. Thus, considerable efforts have been exerted to synthesize oxynitrides with ordered anions [10,14–19]. Oxynitrides are usually synthesized using ammonolysis [20–23], which generally yields nonordered, nonpolar, centrosymmetric materials. Caracas and Cohen predicted a new class of stable polar oxynitride perovskites of ordered structure, including yttrium silicon oxynitride, $YSiO_2N$ [3,5], using a materials-by-design approach. They searched through many nontransition element-bearing ABO_2N compositions using density-functional theory and considered those that were insulating and stable via energy minimization in a possibly distorted perovskite structure. Phonons were then computed using density-functional perturbation theory (DFPT) for those that met the abovementioned criteria. Among the few that had stable phonon modes, $YSiO_2N$ demonstrated superior properties. It was predicted to be stable in a simple five-atom-cell polar structure with symmetry $P4mm$ (Fig. 1). DFPT also predicted that $YSiO_2N$ has a giant effective spontaneous polarization of $130\,\mathrm{mC/cm^2}$ and a very large nonlinear optic coefficient.

II. EXPERIMENTS

The high pressure-temperature experiments for the synthesis and *in situ* and *ex situ* x-ray diffraction measurements were conducted at the High Pressure Collaborative Access Team's (HPCAT) monochromatic angle-dispersive x-ray diffraction station 16-ID-B, sector 16 of Advanced Photon Source (APS), Argonne, Illinois, USA, and at the light source Petra III at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany. Finely ground yttrium nitride (YN) and amorphous silica powders were loaded into a diamond-anvil cell (DAC) with a steel gasket and ruby as the pressure standard. Simultaneous high P-T conditions were achieved using the online laser-heated DAC system [24]. Temperatures were determined by fitting the Planck radiation function to the thermal radiation collected from the heated sample. For *ex situ* x-ray diffraction measurements, a 30-keV x-ray beam was focused to 7–5 μm in horizontal and vertical directions, and diffraction patterns were recorded with a MAR charge-coupled device (CCD) detector or on a Perkin-Elmer detector.

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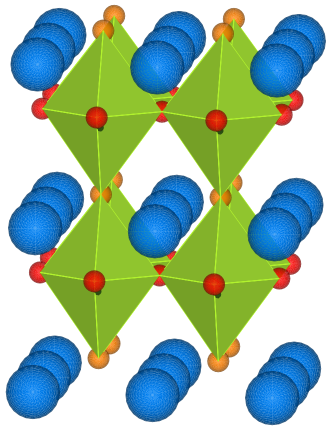

FIG. 1. *P*4*mm* polar structure of the ordered oxynitride perovskite ($YSiO_2N$) predicted by Caracas and Cohen [3]. Blue spheres represent yttrium (Y), green spheres inside the octahedra represent silicon (Si), and red and gold spheres represent oxygen and nitrogen, respectively.

Details on the laser heating system and sample preparations can be found in the Supplemental Material [25].

Raman-spectroscopy studies were carried out using a 532-nm laser as the excitation source in a backscattering geometry. The sample in the DAC was placed in a microscopic stage in our Raman setup: a Mitutoyo 20× objective with a numerical aperture of 0.28. Our microscopic Raman system, with a spatial resolution of 1.14 mm, was used for both incident light focusing and collection of scattered light; subsequently, scattered light was sent to a monochromatic spectrometer (Princeton Instrument: Acton SP2300 spectrometer) via a confocal optical pass, and spectra were recorded with a CCD detector.

For the second-harmonic generation (SHG) measurements a near IR (1064 nm, Nd:YAG), 8–20-ns pulsed laser with a 1–20-kHz repetition rate was used to excite the SHG signal; a dedicated spectrograph equipped with a CCD detector synchronized with the laser was used for the SHG signal acquisitions. The acquisition time was approximately 1 s. All measurements were performed at room temperature. More details are given in the Supplemental Material [25].

III. RESULTS

A. Synthesis and structural characterizations

We used the synthesis method outlined by Caracas and Cohen, using YN and SiO_2 as reactants: $YN + SiO_2 \rightarrow YSiO_2N$ [3,5]. We finely ground parent yttrium nitride and amorphous silica (SiO_2) in an argon atmosphere, which is necessary because of the reactive nature of YN with air and moisture. We loaded the powders in a DAC in a stack geometry of $SiO_2/YN/SiO_2$ to enhance the diffusion process of starting materials. The sample was compressed to high pressure and then heated using the double-sided laser heating method [24]. The resultant sample with the x-ray spot size of 4 μm was then studied *in situ* and *ex situ* using optical microscopy as well as synchrotron x-ray diffraction at the APS beam line 16-ID-B and at the light source Petra III at DESY, Hamburg, Germany. A new phase formed at pressures as low as 4 GPa and above 1500 K along with other minor phases. We analyzed the reaction products using synchrotron x-ray diffraction and micro-Raman spectroscopy.

The sample of $YSiO_2N$ was synthesized by reacting a mixture of cubic YN and SiO_2 glass. From our earlier *in situ* laser heating experiments conducted at HPCAT of APS, we realized that an excess of one of the two components is preferable to laser heating a 1:1 mixture. Second, we wanted to minimize the interference of a more complex coesite (monoclinic) in comparison to a tetragonal stishovite phase in the diffraction pattern and accordingly chose a synthesis pressure higher than 10 GPa. Since the current experiment involved *ex situ* synthesis, we decided to obtain diffraction patterns from a grid encompassing the whole sample chamber both before and after the heating cycle. The laser heating was performed with a 1.06-mm Nd:YLF fiber laser focused to a 30-μm heating spot. To minimize the effects of performing *ex situ* synthesis, we rastered the whole sample chamber with the heating beam. Although the initial pressure was estimated to be 13 GPa, the pressure after synthesis dropped to 10 GPa, which could be attributed to release of stresses at high temperatures. The diffraction pattern from the quenched sample showed regions of unreacted YN as well as a highly crystalline and textured pattern of $YSiO_2N$. Stishovite and minor amounts of coesite were also observed with much less texture since they were synthesized from a micrograined, glassy starting material. This is shown by the cake pattern [Fig. 2(a)]. The predominant phases are labeled accordingly in this two-dimensional (2D) pattern as well as in the diffraction pattern [Fig. 2(b)] obtained from an integration of some of the azimuthal scans in this pattern. The starting material YN is highly granular (about 20 μm); the pattern becomes more granular after laser heating, as well as highly textured. Given this innate poor quality of the diffraction patterns both for the starting material and the synthesized material, we found that any attempt to refine the patterns to extract structural information is fraught with difficulties and likely to give us a wrong assessment (whether about compositional disorder or the structure itself). In fact, we do not see the strong [111] peak in the integrated powder pattern, but we do observe a few strong spots in the 2D image indicating that the synthesized sample is probably oriented preferentially along the (111) direction.

That said, our diffraction data are consistent with the synthesized polar structure of $YSiO_2N$ (space group *P*4*mm*), with lattice parameters $a = 3.234(5)$ Å and $c = 4.339(5)$ Å (Table I), which match well with the theoretical prediction and prove the formation of predicted ordered $YSiO_2N$ structure [3,5]. The high c/a ratio of 1.34 is strong evidence for O/N ordering. Theory shows that disordered $YSiO_2N$ would likely be cubic perovskite (or transform to another phase), since it is the strong N-Si covalent bond that causes the distortion. Partially ordered $YSiO_2N$ would have c/a ratios between 1 and 1.34. The Raman frequencies would also change significantly for disordered O and N.

From other runs, we synthesized this new polar phase of $YSiO_2N$ at 12 GPa and 1200 K [26,27]. Raman spectra of the above synthesized material measured at 3 GPa at ambient temperature are consistent with the theoretically predicted Raman spectra [Fig. 3(a)]. Most of the major Raman modes clearly match with the theoretically predicted modes

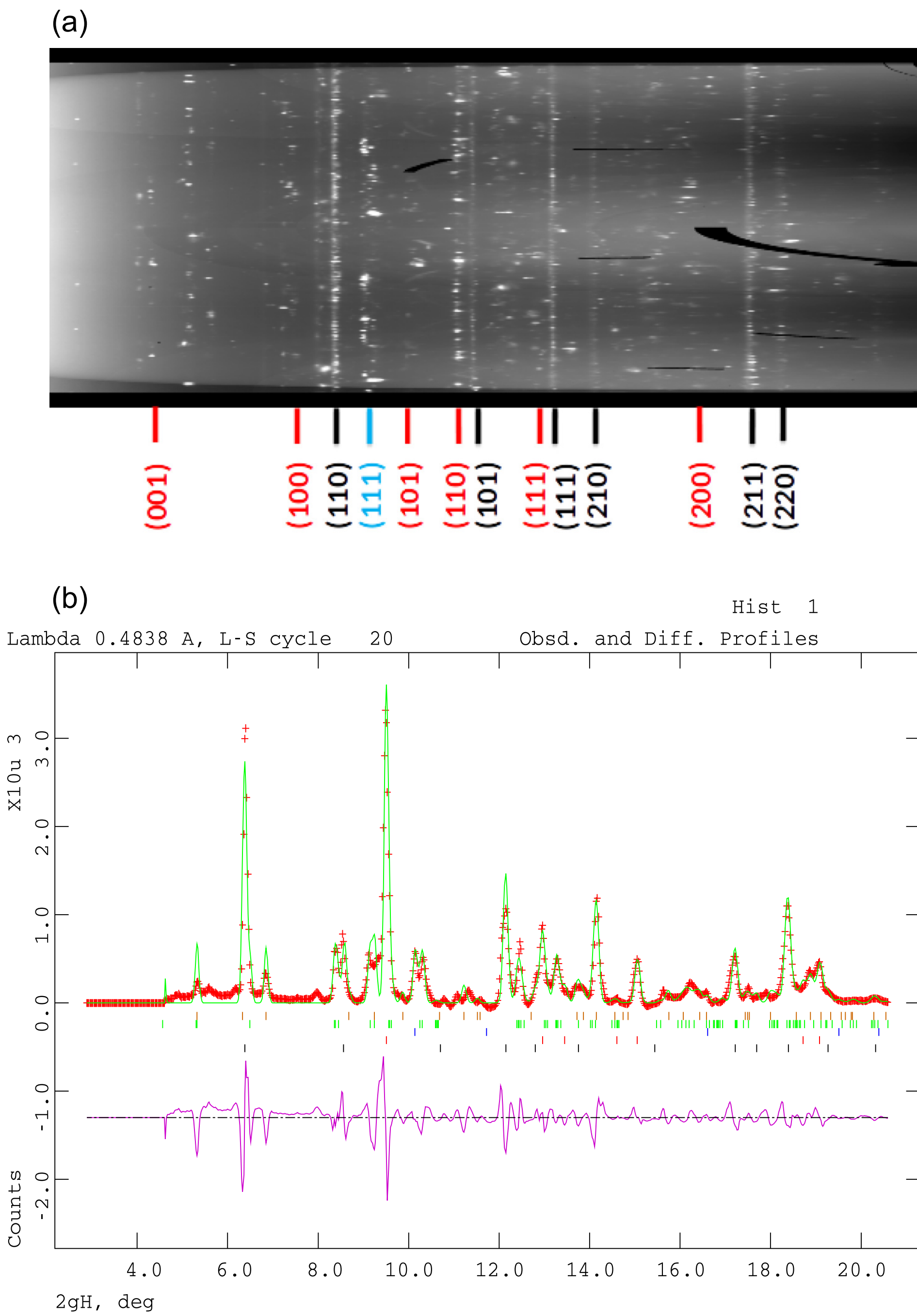

FIG. 2. X-ray diffraction image and pattern (x-ray wavelength 0.4838 Å) of a sample synthesized at 13 GPa and above 1500 K and then quenched to ambient temperature and measured at 10 GPa. (a) Image of the diffraction lines (white vertical lines) with corresponding prominent indexed diffraction peaks marked with color vertical bars for $YSiO_2N$ (red), stishovite (black), and yttrium nitride (blue). Along with these major contributions of the three phases, trace amounts of hexagonal $YSiO_2N$ and coesite were also detected and added to the phases fitted in the diffraction analysis. (b) In the pattern, marks represent the diffraction data, and the solid fitting curve represents the total simulated pattern using Le Bail fitting. The vertical bars from bottom to top show the corresponding diffractions for the new ordered phase of $YSiO_2N$ (black vertical lines), stishovite, which is a high-pressure phase of SiO_2 (red vertical lines), unreacted yttrium nitride (blue vertical lines), coesite, another high-pressure phase of SiO_2 (green vertical lines), and hexagonal $YSiO_2N$ (brown vertical lines) [30,31]. The difference between the observed and simulated pattern is shown in the lower part near the horizontal axis. The synthesized polar $YSiO_2N$ has the structural parameters of the $P4mm$ structure as predicted [3].

represented by blue lines [3,5]. The predominant line observed at 246 cm^{-1} is in good agreement with the predicted mode, whereas some modes show a small shift (Table II). We also observed a strong peak at 105 cm^{-1} and emergent peaks such as at 161 and 356 cm^{-1} that are assigned to the coesite [26]. The agreement of the observed major Raman modes with the theoretically predicted ones further proves the formation of the oxynitride perovskite of $YSiO_2N$.

TABLE I. Lattice parameters observed for the synthesized material at 13 GPa after quenching from above 1500 K. Theoretically predicted cell parameters of $YSiO_2N$ [3,5] and experimentally reported values for stishovite at 9.6 GPa [29].

	Lattice parameter (Å)			
	Observed @ 10 GPa		Previous studies	
Material	*a*	*c*	*a*	*c*
Polar $YSiO_2N$	3.234(5)	4.339(5)	3.228	4.435
Stishovite	4.128(1)	2.510(2)	4.129	2.649

TABLE II. Raman modes observed for the synthesized polar $YSiO_2N$ compared with the theoretically predicted modes along with their symmetry [3,5].

	Theory [3,4]	
Experiment	Symmetry	Modes (cm^{-1})
357	$A1(z)$	373
		415
652		648
		750, 927,1058
	B1	400
246	$E(x,y)$	249
285		281
381		380
402		402
		534, 721, 854, 930

B. Second-harmonic generation

Conventional x-ray diffraction or Raman spectroscopy cannot prove lack of inversion symmetry. We tested the synthesized material for inversion symmetry using optical second-harmonic generation. We observed a very strong SHG signal [Fig. 3(b)], clearly demonstrating that the synthesized material was indeed polar. For a crystal of thickness (l), the second-harmonic intensity (I) is given by $I \propto I_{\rm in}^2 f(n) d_{\rm eff}^2 \Delta l^2 \sin^2(\pi l/2\Delta l)$, where $I_{\rm in}$, $f(n)$, $d_{\rm eff}$, and Δl are the incident light intensity, the function of refraction indices, the effective nonlinear coefficient, and the coherence length, respectively [28]. Calculating the nonlinear optical coefficients could be a cumbersome process because of the very small size of the sample and the dependency of $f(n)$ and $d_{\rm eff}$ with pressure. However, it should be noted that the SHG intensity observed in $YSiO_2N$ at 11 GPa is comparable with our earlier studies on $PbTiO_3$ at 5 GPa for the similar incident signal. The synthesized $YSiO_2N$ shows robustness of polarity against the pressure.

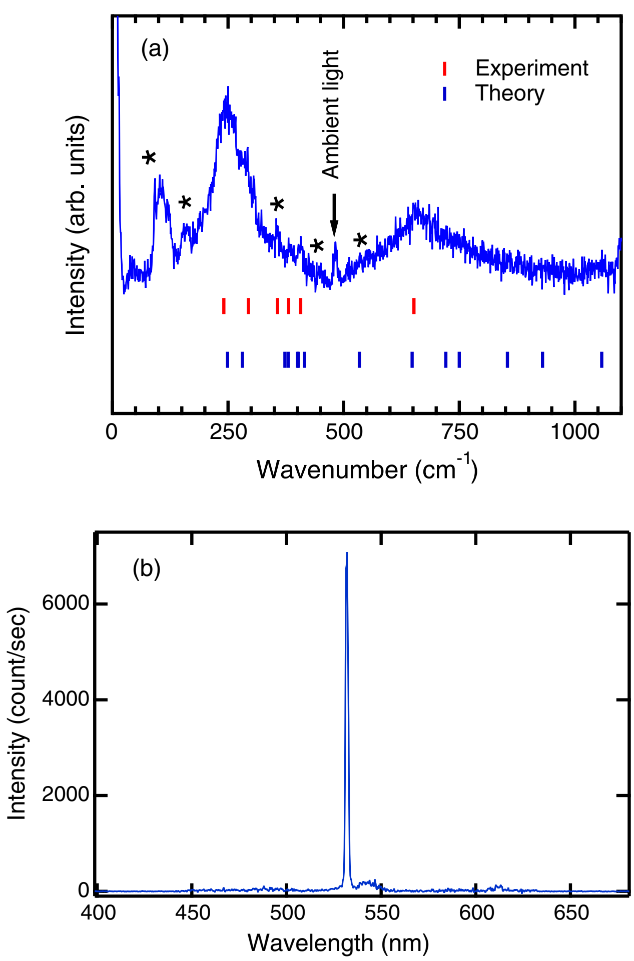

FIG. 3. The new phase of $YSiO_2N$ synthesized at 12 GPa and 1200 K. (a) Raman spectra measured at 3-GPa pressure at ambient temperature. The vertical bars from top to bottom show the observed experimental modes (red vertical bars) of the polar structure and the corresponding theoretically predicted Raman modes (blue vertical bars) [3]. The brown star symbols correspond to the coesite [26], the high-pressure phase of SiO_2 formed along with the synthesised mixture. (b) Observation of strong optical second-harmonic generation measured at 11 GPa and ambient temperature, excited by a near-IR 1064-nm pulsed laser.

IV. CONCLUSIONS

We have successfully synthesized the unique class of polar ordered perovskite oxynitride predicted by the systematic chemical approach of the first-principles method. The polar ordered $YSiO_2N$ has been achieved by high pressure-temperature methods. Our methodology and results provide an alternative way to synthesize new type of materials which can be predicted with computational calculation but cannot be synthesized by traditional high-temperature solid-state reaction methods. Our results are consistent with synthesis of an anion ordered perovskite oxynitride, possibly useful for nonlinear optic applications.

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[1] A. Fuertes, J. Mater. Chem. **22**, 3293 (2012).
[2] S. G. Ebbinghaus, H.-P. Abicht, R. Dronskowski, T. Muller, A. Reller, and A. Weidenkaff, Prog. Solid State Chem. **37**, 173 (2009).
[3] R. Caracas and R. E. Cohen, Appl. Phys. Lett. **91**, 092902 (2007).
[4] J. P. Attfield, Cryst. Growth Des. **13**, 4623 (2013).
[5] R. E. Cohen and R. Caracas, Oxynitride Perovskites, U.S. Patent No. 8,287,831 (October 16, 2012); U.S. Patent No. 8,721,915 B2, Ordered Oxynitride Perovskites (May, 2014).
[6] M. Jansen and H. P. Letschert, Nature (London) **404**, 980 (2000).
[7] Y.-I. Kim, P. M. Woodward, K. Z. Baba-Kishi, and C. W. Tai, Chem. Mater. **16**, 1267 (2004).
[8] M. Higashi, R. Abe, T. Takata, and K. Domen, Chem. Mater. **21**, 1543 (2009).
[9] A. B. Jorge, J. Oró-Solé, A. M. Bea, N. Mufti, T. T. M. Palstra, J. A. Rodgers, J. P. Attfield, and A. Fuertes, J. Am. Chem. Soc. **130**, 12572 (2008).
[10] M. Yang, J. Oró-Solé, A. Kusmartseva, A. Fuertes, and J. P. Attfield, J. Am. Chem. Soc. **132**, 4822 (2010).
[11] D. Oka, Y. Hirose, H. Kamisaka, T. Fukumura, K. Sasa, S. Ishii, H. Matsuzaki, Y. Sato, Y. Ikuhara, and T. Hasegawa, Sci. Rep. **4**, 4987 (2014).
[12] C. Tassel, Y. Kuno, Y. Goto, T. Yamamoto, C. M. Brown, J. Hester, K. Fujita, M. Higashi, R. Abe, K. Tanaka, Y. Kobayashi, and H. Kageyama, Angew. Chem. **54**, 516 (2015).
[13] K. Page, M. W. Stoltzfus, Y.-I. Kim, T. Proffen, P. M. Woodward, A. K. Cheetham, and R. Seshadri, Chem. Mater. **19**, 4037 (2007).
[14] F. Tessier and R. Marchand, J. Solid State Chem. **171**, 143 (2003).
[15] R. L. Withers, Y. Liu, P. Woodward, and Y.-I. Kim, Appl. Phys. Lett. **92**, 102907 (2008).
[16] B. Ravel, Y.-I. Kim, P. M. Woodward, and C. M. Fang, Phys. Rev. B **73**, 184121 (2006).
[17] H. Wolff and R. Dronskowski, J. Comput. Chem. **29**, 2260 (2008).
[18] S. J. Clarke, C. W. Michie, and M. J. Rosseinsky, J. Solid State Chem. **146**, 399 (1999).
[19] E. Günther, R. Hagenmayer, and M. Jansen, Z. Anorg. Allg. Chem. **626**, 1519 (2000).
[20] S. J. Clarke, P. R. Chalker, J. Holman, C. W. Michie, M. Puyet, and M. J. Rosseinsky, J. Am. Chem. Soc. **124**, 3337 (2002).
[21] F. Cheviré, F. Tessier, and R. Marchand, Eur. J. Inorg. Chem. **2006**, 1223 (2006).
[22] C. A. Andersen, K. Keil, and B. Mason, Science **146**, 256 (1964).
[23] S. J. Clarke, B. P. Guinot, W. Michie C, M. J. C. Calmont, and M. J. Rosseinsky, Chem. Mater. **14**, 288 (2002).
[24] Y. Meng, R. Hrubiak, E. Rod, R. Boehler, and G. Shen, Rev. Sci. Instrum. **86**, 072201 (2015).
[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.95.214120 for sample loading configurations, experimental setup diagrams, equation of state of $YSiO_2N$, and additional x-ray diffraction patterns and analyses.
[26] R. J. Hemley, in *High-Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono (Terra Scientific Publishing Company, Tokyo/American Geophysical Union, Washington, DC, 1987).
[27] R. J. Angel, J. L. Mosenfelder, and C. S. J. Shaw, Phys. Earth Planet. Inter. **124**, 71 (2001).
[28] R. C. Miller, Phys. Rev. **134**, A1313 (1964).
[29] D. Andrault, R. J. Angel, J. L. Mosenfelder, and T. L. Bihan, Am. Mineral. **88**, 301 (2003).
[30] P. E. D. Morgan, P. J. Carroll, and F. F. Lange, Mater. Res. Bull. **12**, 251 (1977).
[31] L. Ouyang, H. Yao, S. Richey, Y. N. Xu, and W. Y. Ching, Phys. Rev. B **69**, 094112 (2004).