High pressure synthesis and characterization of predicted oxynitride perovskite: Yttrium Silicon Oxynitride ($YSiO_2N$)

Rajasekarakumar Vadapoo,[1] Muhtar Ahart,[1] M. Somayazulu,[1] and R. E. Cohen[1,2]

[1]Geophysical laboratory, Carnegie institution of Washington, Washington, DC 20015 USA
[2]Department of Earth Sciences, University College London, WC1E 6BT, London, UK

New stable polar oxynitride perovskites were predicted from first principle calculations.[1] These structures were derived by replacing an oxygen atom by nitrogen in the perovskite structure and also the cations of divalent and trivalent as shown in figure 1. Among the combination of oxynitrides, Yttrium Silicon Oxynitride ($YSiO_2N$) and Yttrium Germanium Oxynitride ($YGeO_2N$) were found to be dynamically stable polar insulators. $YSiO_2N$ was predicted to have a giant effective spontaneous polarization of 130 μC/cm^2, which is one of the largest polarization predicted so far. It has the polar structures with P4mm symmetry as shown in figure 1. The predicted large spontaneous polarization and the nonlinear optical properties of this material have the potential for the futuristic piezoelectric, nonlinear dielectric, high energy x-ray and neutron generator applications.[2, 3]

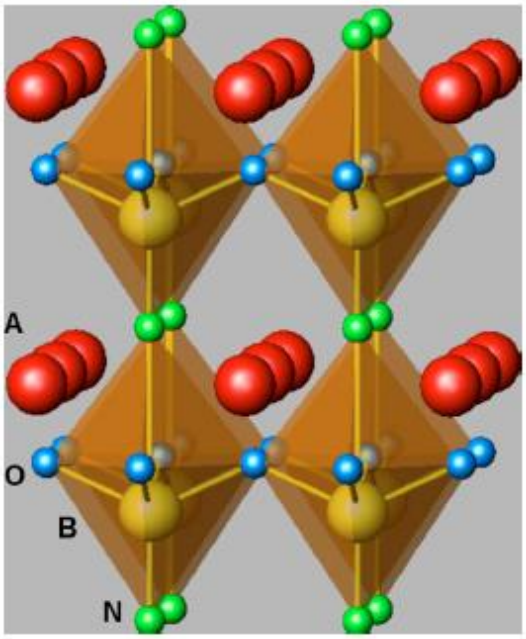

Figure 1. P4mm polar structure of the ordered ABO_2N oxynitride perovskites.[1] Here, A represent Yttrium (Y) and B represent Silicon (Si) atoms.

The theoretical prediction of these improved properties of oxynitride perovskites motivated us to synthesize these novel materials. We prepared the $YSiO_2N$ starting from a mixture of Yttrium nitride (YN) and amorphous Silicon dioxide (SiO_2). We prepared the $YSiO_2N$ sample under high pressure (12GPa) and high temperature (1200 ^{o} C) by using a combination of diamond anvil cell and laser heating technique. Note that YN must be handled in a glove box as it reacts with air and water.

We characterized the run products by x-ray diffraction and Raman spectroscopy for their phase and structural properties. The x-ray diffraction experiments were carried out at sector 16 (0.41 Å) at the Advanced Photon Source, Argonne National laboratory. The x-ray diffraction pattern shows the phase formation of $YSiO_2N$ and matches with the diffraction pattern (shown in red lines at the bottom of the scale) derived from

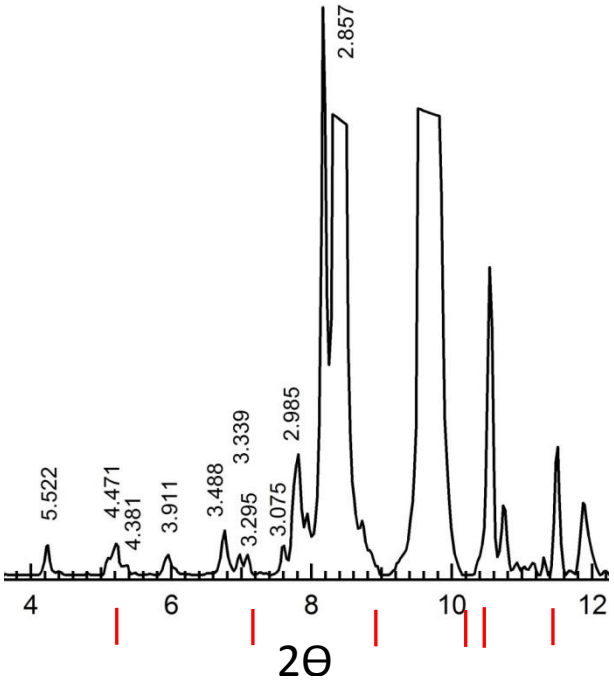

Figure 2. X-Ray diffraction pattern of the high pressure synthesized $YSiO_2N$ compared with the theoritical predicted patterns at the bottom of the scale (in red).

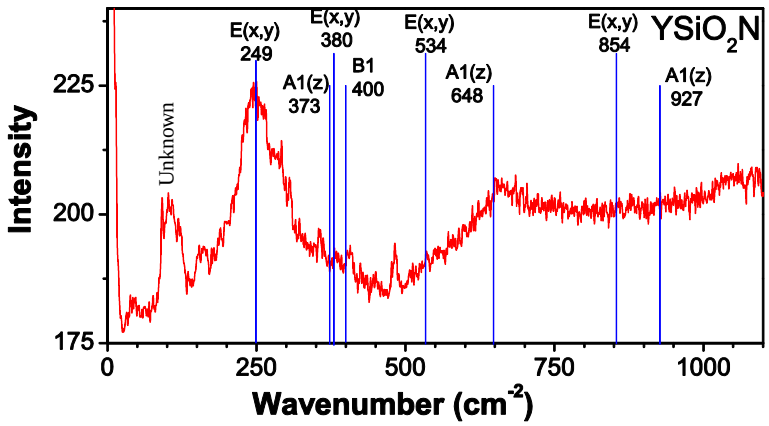

Figure 3. Raman spectra of the $YSiO_2N$ synthesized at high pressure along with the theoretically predicted modes shown with blue reference lines.

the first principle predicted lattice parameters and atomic positions as shown in figure 2. The predicted structure for $YSiO_2N$ in P4mm space group with the lattice parameters of a = 3.228 Å, c = 4.435 Å and with the Wyckoff positions of 1b (0.5 0.5 z), 1a (0 0 z), 2(0.5 0 z) and 1a (0 0 z) for the Y, Si, O, and N atoms respectively.[1] From figure 2, it is clear that the sample is not a single phase oxynitride perovskite, and the sample is not yet well crystallized. The dominant broad peaks at 2Θ correspond to 8.4 and 9.7 match the starting material YN. In addition, a new unassigned dominant peak at d = 2.857 Å is also observed. This indicates the co-existence of other unknown phases. Further effort is in progress to optimize the formation of pure oxynitride phase.

Experiment	Theory[1]
357	A1(z) 373
652	648
Weak 927	927
402	B1 400
246	E(x,y) 249
381	380
Weak 535	534
Weak 859	854

Table 1. The experimental and theoretical Raman modes observed for $YSiO_2N$.

Raman spectroscopy confirms the phase formation of $YSiO_2N$. The comparison of Raman spectra for the synthesized structure with the Raman active modes predicted by theoretical calculations can be seen from figure 3 and table 1. We can observe that most of the theoretically predicted modes are in agreement with the experimentally observed Raman modes. While the predominant 246 cm^{-1} is in excellent agreement some modes show a small shift. Moreover, we observed a strong unassigned peak at 105 cm^{-1} and emergent peaks like at 161 cm^{-1}. Also, the peaks at 534, 854 and 927 cm^{-1} are extremely weak. These evident the formation of oxynitride perovskite along with the coexistence of other phases as confirmed by X-ray diffraction results.

In summary, we have successfully synthesized the stable oxynitride perovskite of $YSiO_2N$ by high energy-high pressure method. The structural characterization confirms the formation of the first principle predicted oxynitride perovskite phase. However unpredicted mixed and, or high pressure induced phases also coexist.

Acknowledgements

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