High pressure crystal structure of PrN

Hyunchae Cynn¹, Magnus Lipp¹, William Evans¹, Yasuo Ohishi²

¹Lawrence Livermore National Laboratory, Livermore, CA, USA, 94550, USA
²SPring-8/JASRI, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

E-mail: cynn1@llnl.gov

Abstract. Compression of PrN yields a phase transformation to a tetragonal structure with ~8.8 % volume collapse at ~40 GPa at ambient temperature. A refinement reveals a distorted CsCl-like structure for the high pressure phase PrN(II), which is different from the high pressure phases seen among other lanthanide monopnictides. The space group of the new structure is P4/nmm (#129) with Pr in the 2c(0,1/2,0.3546) and N in the 2a(0,0,0) positions. PrN(II) persists to 85 GPa.

1. Introduction

Simple compounds of lanthanides and transition metals seem to display similar crystal structure behavior at high pressures as well as novel physical properties like magnetic and electronic properties. [1,2] Lanthanide nitrides are known to be narrow gap semiconductors. They are also known as refractory material.

Laser heating assisted direct chemical reactions among the elements loaded inside a sample chamber of a diamond anvil cell (DAC) have been recognized as a viable route to synthesize novel compounds. [3] In 2002, Cynn et al. [4] rekindled the idea that certain metals and metal compounds can have high values for stiffness, and suggested synthesizing novel metal compounds of osmium, iridium, and other stiff elemental metals to form novel carbides and nitrides. We have seen successful attempts in synthesizing transition metal nitrides using a laser heated DAC; a zinc-blende type PtN was reported to form above 45-50 GPa and 2,000 K [5] and the crystal structure has been later revised to a pyrite-type PtN₂, although both compounds were synthesized under similar conditions [6]. IrN₂ synthesized at similar conditions as the Pt nitrides is different from the pyrite-type. The effort led by T. Yagi at Tokyo University was successful in forming lanthanide nitrides with higher content of nitrogen by laser heating at a supercritical condition of nitrogen. [7] Niwa et al. [8] reported diffraction lines of Pr nitride(s) without assigning a crystal structure to the nitride(s) formed by laser heating at 30 GPa. A recent study of OsN₂ suggested an orthorhombic (Pnmn) marcasite structure for a new osmium nitride. [9]

There have been continuous efforts to understand systematic trends shown in high pressure crystal structures of lanthanide compounds of Group VA elements. At ambient conditions, the NaCl type (B1) structure is the ground state phase for lanthanide monopnictides. [10] At high pressure their structural changes have been progressively studied by Shimomura at SPring-8 [11] and by Benedict. [12] The high pressure structure was identified as a tetragonal cell for LaSb and CeSb. [13] Later, LaP [11], LaAs [11], CeSb [10], CeBi, PrP [10], and NdP [10] were determined to show the same high pressure structure. So, except CeP transforming from B1(I) to B1(II) at ~5 GPa and CeAs transforming from B1 to B2, most of the lanthanide monopnictides appear to show a transition from cubic to P4/mmm...
2. Experiments

Synchrotron angle dispersive x-ray diffraction (ADX) was used to study compression behavior and crystal structures of PrN using a diamond anvil cell (DAC) at the BL10XU of SPring-8, Japan. X-ray diffraction intensity was recorded using an image plate (Rigaku). Fit2D [14] was used to collapse the intensity as a function of diffraction angle. The input parameters to collapse measured images were determined by measuring an image of LaB$_6$ placed at the rotation axis of sample stage. Tilt angle and rotation angle of the image plate were simultaneously determined as well as the distance from the image plate to the sample aligned at the rotation axis. Wavelength of x-ray beam was 0.4618 Å and the exposure time to record an x-ray diffraction image was about five minutes.

Samples of nominal purity of 99.98 % were purchased from Alfa Aesar or synthesized by nitridation with Pr. Two high-pressure samples were prepared using 200 μm culet and 300 μm culet size anvils. A piston-cylinder type DAC was modified in order to adapt a gas membrane since a precise control of pressure was desired to minimize anvil failures. The sample has been compressed to ~85 GPa using 200 μm culet anvils and ~50 GPa with the larger anvils. Samples were decompressed after a phase transformation was measured in order to record hysteresis. Argon and copper powder were loaded together with the sample for the runs using 200 μm culet anvils and no pressure medium was loaded for the runs using 300 μm culet anvils. The sample was contained in a Rhenium gasket. A membrane was used to remotely control sample pressure by varying He gas pressure. Pressure was determined using a reduced shock Hugoniot of copper fit to a 3rd order Birch-Murnaghan equation-of-state (EOS). [15] Pressure was also occasionally checked using an Ar EOS fit using pressure-volume data. [16]

![Figure 1. Angle-dispersive x-ray diffraction patterns of PrN at high pressure. X2 indicates that the diffraction intensity has been multiplied by 2. The patterns were shifted vertically to highlight the changes in the patterns.](image)
3. Results

Collapsed x-ray diffraction intensity is plotted as a function of pressure in Fig. 1. The x-ray diffraction patterns measured from 23 GPa successively to 48 GPa are stacked to show gradual changes from a low-pressure phase to a high-pressure phase. The two low 2θ peaks below 10° at 23 GPa represent the (111) and (200) peaks for the low-pressure phase of PrN. As pressure increases, the positions of the two peaks move to higher 2θ and their intensity gradually decreases.

Between 38 and 42 GPa, noticeable changes occur in the x-ray diffraction pattern. New diffraction peaks start appearing at lower 2θ positions, ~8.3° and ~9.6°, relative to the two peaks described previously. The intensities of the new peaks gradually increase as pressure increases. The gradual evolution of those peaks from the low-pressure phase and the new high-pressure phase are clearly shown in Fig. 2.

There is another small peak at 2θ = ~8° in the pattern measured at 48 GPa. This peak also shows similar behavior as other new peaks in intensity increase as pressure increase. It is barely recognizable in the patterns measured between 42 and 44 GPa (Fig. 1 and 2). Similar appearance and disappearance of peaks from a new high-pressure phase and the low-pressure phase are seen at 2θ higher than 10°.

The patterns displayed in Fig. 1 and 2 were measured using a non-hydrostatically compressed PrN sprinkled with copper powder. A comparison is made with the x-ray diffraction pattern of sample loaded with argon as a pressure medium in Fig. 3. The pressure determined using the argon EOS agrees well with the pressure estimated using the copper EOS for the pattern. The upper ADX shown in Fig. 3 is the same pattern shown in Fig. 1 and 2. The ADX measured at ~48 GPa non-hydrostatically shows peaks from the low-pressure phase. However, the ADX measured under argon shows negative evidence for the existence of B1 phase above 44 GPa.

Based on the new x-ray diffraction peaks from PrN(II), the crystal structure fits well with a tetragonal structural model. Rietveld refinement of PrN(II) using the Pearson VII profile-shape is shown in Fig. 4 which were set for the three phases at ~ 48 GPa. Preferred orientation was modeled only for PrN(II).

Figure 2. Angle dispersive x-ray diffraction patterns measured at high pressure. The figure 1 is expanded here in 2θ from 7° to 11° to show details in the patterns. The patterns measured between 42 GPa and 48 GPa were doubled in intensity to enhance the appearance of the new peaks.
Figure 3. Comparison of angle-dispersive x-ray diffraction patterns of PrN loaded with and without argon as pressure medium. The peaks assigned as the low pressure phase (B1) are marked in blue. The hkl’s in black denote peaks originating from the high pressure phase of PrN(II). The peaks from argon and copper are also labelled with Ar in green and Cu in red.

Figure 4. Refinement of the x-ray diffraction pattern for the three phases coexisting in a sample chamber at ~48 GPa. Rietveld refinements were performed using GSAS [17] and FullProf [18].

The space group of the new structure, PrN(II) is selected to be P4/nmm (#129) with Pr in 2c(0,1/2,0.355) and N in 2a(0,0,0). Residual error was estimated to be 11 %. The lattice parameter of Cu is refined as a=3.372 Å. The lattice parameter of the coexisting rock salt structure of PrN(I) is refined as a=4.781 Å. The lattice parameters of PrN(II) at ~ 48 GPa are refined as a=4.052 Å and
c=3.001 Å with z=2. The PrN(II) structure persists to 85 GPa. The refined structure is similar to the high pressure phase of BaO. [19,20] The c/a ratio of PrN(II) at 48 GPa is 0.741 and slightly larger than that of BaO. The structure transformation of PrN is determined to be at ~ 40 GPa and on decompression of non-hydrostatically compressed PrN to 50 GPa, shows a significant hysteresis. PrN(II) was identified down to 16 GPa coexisting with PrN(I).

Figure 5. EOS of the low- and high-pressure phases of PrN. Pressure and volume data are fit to a 3rd order Birch-Murnaghan equation.

The pressure and volume of PrN(I) and PrN(II) are fit to a 3rd order Birch-Murnaghan EOS as shown in Fig. 5. Due to a significant scatter in the data, attributed to the non-hydrostatic conditions, all the data were used for the fit. The best fit parameters were obtained when the first pressure derivative \( B'_0 \) was assumed to be 2.4(0.4). It appears to better constrain the extrapolated volume for PrN(II) and also for PrN(I) at ambient conditions. The initial volume, \( V_o \) of the rock salt structure PrN(I) is determined as 68.5(0.2) Å\(^3\) (reduced to z=2), which agrees very well with the published value, ICDD database, PDF-2 #18-1077. However, 67.70 Å\(^3\) was reported by Ettmayer et al. [21] This value is 1% smaller than the present fit value. \( B'_0 \) is estimated as 149(3) GPa. EOS parameters for PrN(II) are \( V_o=62.4(0.3) \ \text{Å}^3 \) (z=2) and \( B'_0=158(3) \ \text{GPa} \). Based on the EOS fits, the volume collapse at 40 GPa is estimated to be ~ 8.8 % from the B1 structure to the P4/nmm structure.

4. Conclusion
A new high pressure structure transformation of PrN is measured using angle-dispersive x-ray diffraction at SPring-8. The refined structure is a distorted CsCl-like structure similar to the high pressure phase of BaO. The refined structure appears different from the P4/mmm measured in other lanthanide monopnictides..

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