Compressibility of α-Ca_3N_2 to 137 Kb Using Synchrotron Radiation and a Diamond Anvil Cell

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Abstract-α-Ca_3N_2 as an opaque, red-brown crystalline powder lying in the cubic Ia3 space group, was placed into a specially designed glove box under nitrogen atmosphere, along with powdered fcc Au, and carefully loaded within the β-brass gasket of a conventional high pressure diamond anvil cell (DAC). The powdered samples were then sealed under nitrogen atmosphere to a pressure of 8.4 Kb and taken to Cornell High Energy Synchrotron Source where conventional Debeye-Scherrer diffraction photographs were recorded at 8.4, 91 and 137 Kb. The pressure of the sample was monitored by using the equation of state of Au, and no phase change from the Ia3 structure was observed in the sample of powdered α-Ca_3N_2 up to a pressure of 137 Kb, although the red-brown powder was observed to undergo a slight band gap broadening as the opaque powder became a slightly yellow-like tinged transparent phase above 8.4 Kb. A compressibility curve and a bulk modulus for α-Ca_3N_2 are derived from the data presented herein.

1. Introduction

α-Ca_3N_2 belongs to the series of curious alkaline earth nitride salts that are constrained by their stoichiometry of 3-to-2 divalent alkaline earth cations to trivalent nitride anions, to form odd cubic crystals containing cation vacancies ordered along their <111> axes, in a 2x2x2 supercell of an anti-fluorite arrangement, that nonetheless exists in a high space group symmetry of Ia3 [1]. In the high pressure study conducted for, and described in this communication, using a conventional diamond anvil cell (DAC) [2], the nature of these cation vacancies was probed as a function of pressure to a maximum pressure, as measured by the equation of state of Au [3], of 137 Kb. Although no phase transition was observed in the α-Ca_3N_2 salt to 137 Kb, a compression of the unit cell was observed in diffraction photographs taken of the sample at several pressures, by conventional Debeye-Scherrer powder methods [4]. The compression of the nitride unit cell with pressure is thereby traced in a compressibility curve of the volume of the Ia3 unit cell versus pressure, for the data given below, and a bulk modulus is reported from the derivative of this compressibility curve (its slope).

2. Experimental

Powdered red-brown, opaque α-Ca_3N_2 was loaded into a conventional diamond anvil high pressure cell along with Au powder, that served as a pressure calibrant, within a carefully drilled brass gasket hole used in the study. The tables of data given below therefore consist of nitride, Au and brass Bragg reflections, given at 3 different pressures of 8.4 Kb, 91 Kb and 137 Kb, as determined from the equation of state of Au in the study. A calibration of the energy of the synchrotron x-ray source used in the study, using a powdered Pt standard at room pressure in the same Debeye-Scherrer geometry as was used in the experiment, showed that, to better than 0.005 Å agreement, with Pt (200), (111) and (311) Bragg reflections recorded, that the monochromatic synchrotron x-ray beam had a wavelength of 0.72382 Å. The dataset associated with this Pt powder diffraction recording is shown for reference as Table 1 below:

Table 1

The nitride and Au powders were ground together under a nitrogen atmosphere, in a specially designed glove-box that was useful for cryogenic applications and applications involving inert conditions such as are used with nitride salts. The glove-box design was created by M.J. Bucknum and will be described fully in a separate publication. At the seal-off pressure the volume of the unit cell of Au in the DAC was determined to be V/V_0 = 0.9952, which yielded a pressure from the literature equation of state (EOS) of Au of 8.4 Kb. At this pressure the nitride (411), (321), (222), (721) and (444) Bragg reflections were recorded. From a least squares regression analysis of these reflections, a least squares determination of the lattice parameter, **a**, of this anti-fluorite supercell, containing <111> ordered cation vacancies, in the cubic Ia3 space group, will be determined. The raw data from the Debeye-Scherrer photograph at 8.4 Kb is given below in Table 2:

Table 2

At the first pressure above the seal-off pressure, the volume of the unit cell of Au was given by V/V_0 = 0.9526, from the Au (200) and (111) reflections, from which, using Au's EOS, one could determine a pressure of 91 Kb inside the DAC. At this second pressure in the study, the nitride (322), (311) and (221) Bragg reflections were recorded in the dataset. From a least squares regression analysis of these reflections, a least squares determination of the lattice parameter, **a**, of this anti-fluorite supercell, containing <111> ordered cation vacancies, in the cubic Ia3 space group, will be determined. The raw data from the Debeye-Scherrer photograph at 91 Kb is given below in Table 3:

Table 3

It should as well be noted that the nitride salt transformed from a red-brown opaque powder into a yellow-tinged transparent phase above 8.4 Kb in this study. It is thus apparent that as no structural phase transition was observed at 91 Kb, that evidently the calcium nitride salt underwent a band gap opening and broadening under pressure in the study. From private discussion with Grigori Vajenine, PhD on this subject, he assured me that nitride salts are known to undergo band broadening and band gap opening with pressure initially in a pressure study. It is only later on at much higher pressures that one can expect band gap closure.

At the second pressure above the seal-off pressure, the volume of the unit cell of Au was given as $V/V_0 = 0.9343$, from this datum it was determined from Au's EOS that a pressure of 137 Kb obtained in the DAC at this state. At 137 Kb the nitride (444) and (555) reflections could be recorded in the dataset. From a least squares regression analysis of these reflections, a least squares determination of the lattice parameter, **a**, of this anti-fluorite supercell, containing <111> ordered cation vacancies, in the cubic Ia3 space group, will be determined. The raw data from the Debeye-Scherrer photograph at 137 Kb is given below in Table 4:

Table 4

3. Least Squares Refinement of Nitride Pressure Data

The nitride data will be refined using a least squares refinement procedure, to determine the lattice parameter, **a**, and cubic unit cell volume, V, as a function of pressure, as they have been measured in this work. This analysis will be forthcoming.

4. Results

A compressibility curve will be plotted from the results of Section 3, using unit cell volume, V(P), against pressure, P, in a graphical form. By calculating the slope of this V-versus-P curve, one will be able to determine the bulk modulus of the nitride salt to a maximum pressure of 137 Kb

5. Conclusions

A discussion of the principal results of this work will be provided in the future.

REFERENCES

[1] P.Y. Laurent, J. Lang, M.T. Le Bihan, *Acta Cryst.*, **B24**, 494, (1968).

[2] W.A. Bassett, A.H. Shen, M. Bucknum, I.M. Chou, *Review of Scientific Instruments*, **64(8)**, 2340, (1993).

[3] equation of state of Au reference

[4] L. Pauling, General Chemistry, Dover Publishing, Mineola, NY, 3rd edition, 1988.

Table 1: Powdered Platinum Data used in X-ray Energy Calibration in Synchrotron High Pressure Study at 1 atmosphere

intensity	bragg angle	l 0.72382	d-spacing	hkl	material	d-spacing exp	d-spacing lit
90	5.85625	3.5469825	3x1.183	3x311	Pt	3.547	3.547
90	7.34375	2.8313535	fayalite reflection				
30	8.1175	2.5630305	fayalite reflection				
20	8.355	2.4906689	fayalite reflection				
80	9.1925	2.2654441	2.265	111	Pt	2.265	2.265
40	10.6625	1.9560177	1.962	200	Pt	1.956	1.962

Table 2: Debeye-Scherrer Powder Diffraction Data for Ia3 α-Ca_3N_2 at a Pressure of 8.4 Kb

intensity	bragg angle	l 0.72382	intensity	d-spacing	hkl	material	d-spacing exp	d-spacing lit
70	2.45	8.466199	70	4x2.117	4x200	brass	2.117	2.134
5	2.8125	7.3757144	5	4x1.844	4x210	brass	1.844	1.908
100	3.2625	6.3592572	100	3x2.120	3x200	brass	2.12	2.134
70	3.775	5.4969211	70	3x1.832	3x210	brass	1.832	1.908
5	4	5.1881802	5	4x1.297	4x002	brass	1.297	1.335
5	4.4625	4.6513942	5	3x1.550	3x444	nitride	1.55	1.653
5	4.7	4.4168385	5	3x1.472	3x721	nitride	1.472	1.561
50	5.35	3.881501	50	3x1.294	3x002	brass	1.294	1.335
60	6.28125	3.3078545	60	3.307	hkl	brass	3.308	3.41
10	6.5375	3.1787272	10	3.178	222	nitride	3.178	3.31
5	7.275	2.8579642	5	2.858	321	nitride	2.858	3.07
5	8.4625	2.4592557	5	2.459	411	nitride	2.459	2.704
80	8.85625	2.3507318	80	2.355	111	gold	2.351	2.355
90	9.825	2.1208997	90	2.134	200	brass	2.121	2.134

Table 3: Debeye-Scherrer Powder Diffraction Data for Ia3 α-Ca_3N_2 at a Pressure of 91 Kb

intensity	bragg angle	l 0.72382	intensity	d-spacing	hkl	material	d-spacing exp	d-spacing lit
70	2.4875	8.3386463	70	4x2.084	4x200	brass	2.084	2.134
50	3.225	6.4331226	50	3x2.143	3x101	brass	2.143	2.265
100	3.3125	6.263373	100	3x2.088	3x200	brass	2.088	2.134
20	3.825	5.4251706	20	3x1.808	3x210	brass	1.808	1.908
5	6.375	3.2594061	5	3.259	221	nitride	3.258	3.824
15	7.1625	2.9026141	15	2.902	311	nitride	2.902	3.459
20	8.8625	2.3490873	10	2.349	322	nitride	2.349	2.783
100	8.9875	2.3166785	100	2.317	111	gold	2.317	2.355
30	10.025	2.0790074	30	2.079	200	brass	2.079	2.134
30	10.3875	2.0072103	30	2.007	200	gold	2.007	2.039

Table 4: Debeye-Scherrer Powder Diffraction Data for Ia3 α-Ca_3N_2 at a Pressure of 137 Kb

intensity	bragg angle	l 0.72382	intensity	d-spacing	hkl	material	d-spacing exp	d-spacing lit
70	2.50625	8.2763017	70	4x2.134	4x200	brass	2.069	2.134
5	2.99375	6.9295384	5	5x1.385	5x444	nitride	1.385	1.561
20	3.31875	6.2515907	20	3x2.134	3x200	brass	2.084	2.134
20	3.825	5.4251706	20	4x1.338	4x444	nitride	1.338	1.561
5	5.4375	3.8192232	5	3x1.273	3x444	nitride	1.273	1.561
10	6.3675	3.2632293	10	3x1.088	3x555	nitride	1.026	1.088
70	9.04375	2.3023881	70	2.355	111	gold	2.302	2.355
100	10.075	2.0687955	100	2.134	200	brass	2.069	2.134