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High pressure synthesis and characterization of noble metal nitride IrN_x

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ABSTRACT

Novel iridium nitrides (IrN_x) have been synthesized from a double decomposition reaction between $IrCl_3$ and Li_3N powders under high pressure (5 GPa) and high temperature (1273 K) conditions. X-ray diffraction and Raman spectra analysis reveals that the as-synthesized IrN_x have a cubic crystal structure. The lattice constants of IrN_x are 4.06 Å. The x-ray photoelectron spectrum indicates the N content (x) in IrN_x is ~0.3. The first-principles calculations further suggest that iridium nitride is face-centered cubic structure, which has not ever been reported experimentally. Such structure is mechanical stable even under 10 GPa and 1273 K conditions.

1. Introduction

It is well known that the introduction of smaller atoms such as nitrogen and boron into interstitial sites in close packed transition metals (TMs) lattices leads to dramatic changes of the strength, durability, electronic and magnetic properties of the compound with respect to that of the metal [1–3]. Recently, a family of late TMs metals nitrides has been synthesized starting from their constituent elements, Pt, Ir, and Os, and nitrogen under extreme high pressure (45–50 GPa) and high temperature (above 2000 K) conditions [4–6]. These nitrides show large bulk modulus during the high pressure x-ray diffraction experiments. For example, the bulk modulus of platinum nitride (PtN_2) is 372 GPa, iridium nitride (IrN_2) is 432 GPa and osmium nitride (OsN_2) is 358 GPa, which demonstrates that the noble metals nitrides are likely to be superhard materials with low compressibility and ranking just below diamond (440 GPa).

Experimental and theoretical investigations have a consensus on the crystal structure: PtN_2 is formed in the pyrite structure and OsN_2 in the marcasite structure [7]. To date, however, the crystal structure of IrN_2 is still an open question. A variety of structure types have been considered upon searching for the structures of IrN_2, including the pyrite, fluorite, rutile, marcasite and $CoSb_2$ types [8]. Yu et al. have calculated the total energy of IrN_2 for various structure types; their results show that IrN_2 should have a monoclinic $CoSb_2$ type structure. [8] However, this result is inconsistent with the x-ray experiment data, which show that IrN_2 is hexagonal structure ($a=3.966$ Å, $c=6.958$ Å) [5]. As for IrN_x ($x\leq1$), only few theoretical works have been reported recently. Chen et al. have calculated the electronic structures of IrN. It is found that IrN should be zinc blende structure [7]. The mechanical properties of IrN have been investigated by Zhao et al., theirs results show that wurtzite structure is the most stable [9]. Up to now, there is no clear understanding on the crystal structure of IrN_x($x\leq1$).

In this study, we present the synthesis of a novel iridium nitride (IrN_x, $x<1$) at relatively moderate pressure (5–10 GPa) and temperature (1273 K). The sample was characterized by powder x-ray diffraction, Raman spectroscopy and complementary density functional theory based calculations. It is found that the obtained IrN_x crystal is face-centered cubic (*fcc*) structure, which has not ever been reported experimentally.

2. Experimental

The starting materials were powders iridium chloride (99.9%, Boren Precious Metals Co., Kunming, China) and lithium nitride

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(99.4%, Alfa Aesar, USA). The molar radio of $IrCl_3/Li_3N$ was fixed at 1:1 according to the following double decomposition reaction:

$$IrCl_3+Li_3N \rightarrow IrN+3LiCl \quad (1)$$

The raw materials powders were mixed under Ar atmosphere in a glove box, the blend was compacted to a $\phi 2\times 4$ mm pillar under a shaping pressure of 2 MPa, and the pillar was loaded into a high-pressure apparatus (walker-type, Rockland Ltd., USA) subsequently. After high pressure was applied, the sample was heated to specific temperature for 30 min and finally quenched to room temperature. The temperature was monitored by using a thermocouple (Pt–Pt Rh10%) and the pressure was given by a calibration curve that was established by determining the applied loads corresponding to the phase transformation pressures of Bi (I → II, 2.55 GPa; III → V, 7.50 GPa) and Pb (I → II, 12.50 GPa).

Due to LiCl can dissolve easily in water; the product was rinsed with distilled water for 5 times to remove LiCl and dried in an oven at 373 K overnight for further characterization. Phase compositions of obtained samples were identified by x-ray diffraction (XRD, Cu K_α radiation, Rigaku D/MAX-IIIA, Japan) and x-ray photoelectron spectroscopy (XPS, ESCALab MK-II, VG Scientific Ltd., UK). Binding energies were calculated with reference to C1s peak at 284.5 eV with a precision of ± 0.1 eV. Raman spectroscopy was conducted on a Renishaw InVia Raman spectrometer with a CCD detector using an excitation wavelength of 532 nm.

3. Results and discussion

The XRD patterns of the raw materials ($IrCl_3$ and Li_3N) are shown in Fig. 1, from which lithium nitrides are composed by two phases, Li_3N and β-Li_3N. Fig. 2(a) shows the XRD patterns of the samples synthesized at 5 GPa and 1273 K. No diffraction peaks of LiCl can be found in Fig. 2(a), meaning that LiCl is removed completely. The obviously strong diffraction peaks at $2\theta=40.7^\circ$, 47.3°, 69.2°, 83.4° and 88.0° belong to pure metal iridium (JCPDS, No. 87-0715) diffraction, which reveals1that iridium is one of the major components in the sample, and this is due to $IrCl_3$ decomposes rapidly under high temperature. Except for the iridium diffraction peaks, it is also found that there are four weak peaks in Fig. 2(a) at $2\theta=38.26^\circ$, 44.51°, 64.83° and 77.82°. These peaks can be seen clearly from the inset graph in Fig. 2(a), which is magnified the original graph for 15 times. It seems that some 'new' iridium nitrogen compounds have been synthesized during the high-pressure sintering process and result in the appearance of new diffraction peaks. According to the XRD characteristic of cubic structure crystal, we attempt to index these peaks as cubic structure. The four peaks accord well with (111), (200), (220) and (311) crystal planes diffractions, respectively. The lattice constant (a) is calculated by using Bragg formulation of x-ray diffraction for cubic crystal system:

$$a=\frac{n\lambda}{2\sin\theta}\sqrt{h^2+k^2+l^2} \quad (2)$$

where λ is the wavelength of x-ray, θ is the Bragg diffraction angle, and (h, k, l) is the crystal plane Miller indices. The calculated results show a lattice constant of $a=4.07$ Å, which is larger than that of the parent metal iridium (3.839 Å). Therefore, it can be sure that iridium nitrides (IrN_x) has been synthesized at 5 GPa and 1273 K. The as-prepared IrN_x should have a cubic structure and the lattice constant is 4.07 Å.

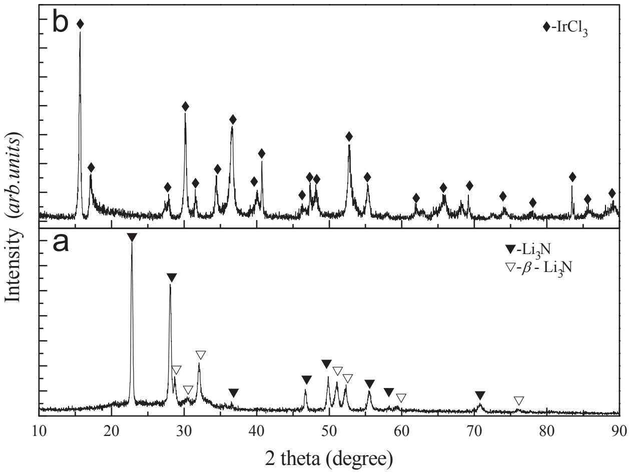

Fig. 1. XRD patterns of raw materials. (a) Li_3N; and (b) $IrCl_3$.

Higher pressure experiments are performed to test the phase stability of the IrN_x crystals. Fig. 2(b) shows the XRD patterns of the samples synthesized at 10 GPa and 1273 K. In addition to the strong iridium diffraction peaks, five diffraction peaks at $2\theta=38.41^\circ$, 44.65°, 64.99°, 78.06° and 82.23° can also be observed in Fig. 2(b), and the corresponding ratios of diffraction intensity are 1:0.55:0.2:0.16:0.05, respectively. The diffraction peak at $2\theta=82.23^\circ$ is weak and difficult to be distinguished, but it is clear in the inset graph, which has been magnified for 5 times from the original graph. Considering that the as-prepared IrN_x belongs to cubic crystal system, these peaks should belong to (111), (200), (220), (311) and (222) planes diffraction, respectively. The lattice constant of IrN_x is calculated to be 4.06 Å. Compared the IrN_x synthesized at 10 GPa with that of synthesized at 5 GPa, the lattice constant is reduced from 4.07 to 4.06 Å. From the above results, it is believed cubic IrN_x is mechanically stable even under 10 GPa and 1273 K conditions.

Fig. 3 shows the XPS spectra of the samples synthesized at 10 GPa and 1273 K, in which a positive evidence of the formation of iridium nitrogen compounds is obtained from a binding energy shift compared with that of the elemental Ir. Specifically, the Ir $4f_{7/2}$ binding energy for IrN_x is 61.5 eV versus 60.3 eV for elemental Ir. Nitrogen binding energies (N1s) display a shifted component indicates the formation of nitride. The binding energies of N1s (398.0 eV) is somewhat larger than the typical value for other transition metal nitrides, i.e., TiN (396.7 eV), Si_3N_4 (397.7 eV), and suggests some covalent bonding exists. By comparing the shifted components of each element together with the appropriate sensitivity factors, the x value was obtained to be ~0.3 for IrN_x.

To further explore the structure of IrN_x, we performed first-principles calculations using the VASP code with the projector augmented wave (PAW) potentials and generalized gradient approximation (GGA) [10,11]. Before calculations are carried out, we first speculated that N atoms occupy interstitial sites in the metal Ir with a face-centered cubic structure because its five peaks in XRD patterns are similar with metal Ir. The lattice constant of IrN_x is determined to be 4.07 Å, which is larger than pure metal Ir of 3.84 Å. Taking N composition from XPS measurement into consideration; it should be a reasonable structure that N atoms are interstitial in the lattice of metal Ir and results in the expansion of the lattice. We checked the total energies for tetrahedral and octahedral configurations of N. The total energy difference is less than 1 meV, indicating the two configurations are almost equal. To simulate the IrN_x, therefore, we constructed a face-centered cubic structure of metal Ir, and the N atom is placed on octahedral and tetrahedral interstitial sites in disorder corresponding to the N content of $x=0.25$, close to experimental value for XPS data. The cutoff energy for the plane-wave basis set is 500 eV. For the Brillouin zone integration, an $8\times 8\times 8$ k-point mesh was used. All atoms are allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.01 eV/Å.

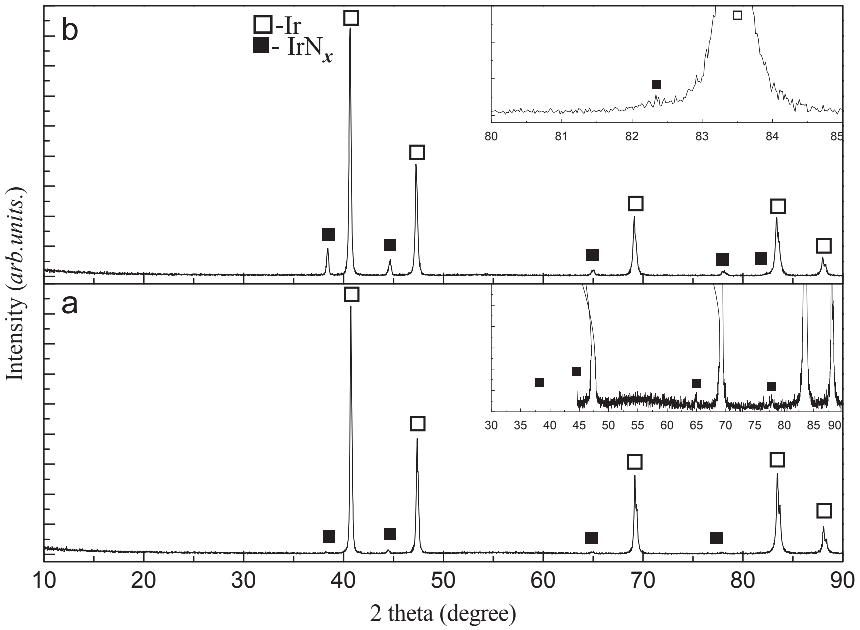

Fig. 2. XRD patterns of the samples synthesized under high pressure and high temperature conditions.(a) 5 GPa, 1273 K; and (b) 10 GPa, 1273 K.

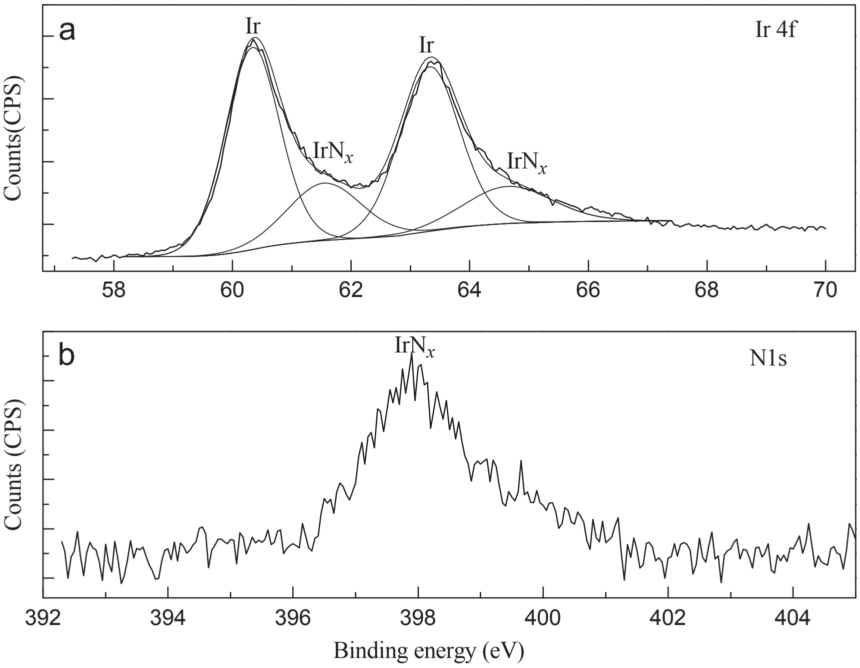

Fig. 3. XPS spectra of the samples synthesized at1273 K under10 GPa. (a) Ir4f; and (b) N1s.

The lattice constants of tetrahedral and octahedral configurations are 4.077 and 4.076 Å, respectively, in good agreement with the XRD pattern. Fig. 4 shows the simulated XRD patterns of $IrN_{0.25}$ with a face-centered cubic (*fcc*) structure. There are five strong diffraction peaks located at 38.2°, 44.4°, 54.6°, 77.6° and 81.76°, corresponding to (111), (200), (220), (311) and (222) diffraction, respectively, and the corresponding ratios of the diffraction intensity are 1:0.5:0.25:0.25:0.07, respectively. The simulated diffraction peaks and intensities are fit in well with the XRD patterns, indicating that the speculated cubic structures with N atoms occupy octahedral sites in disorder is reasonable. It is worthy of note that the crystal symmetry has not changed from face-centered cubic to simple cubic, it is due to the fact that the N atoms intercalate in the lattice of the parent metal Ir in disorder and form the Ir–N disordered solid solution phase with fcc structure.

Raman spectroscopy plays an important role in the determination of crystal structure of noble metal nitride. Fig. 5 shows the Raman spectra of the samples synthesized at 5 GPa and 10 GPa. We observe similar strong Raman scattering peaks for these two samples. As shown in Fig. 5(a) and (b), the Raman spectra can be fitted well with six Gaussian peaks at about 324, 515, 808, 912, 979, and 1082 cm^{-1}. The first-order Raman scattering is forbidden in the perfect crystal with a rock salt structure. Nevertheless the as-synthesized IrN_x ($x \approx 0.3$) is non-stoichiometric and contains many microscopic defects, i.e., nitrogen ion site vacancies. These

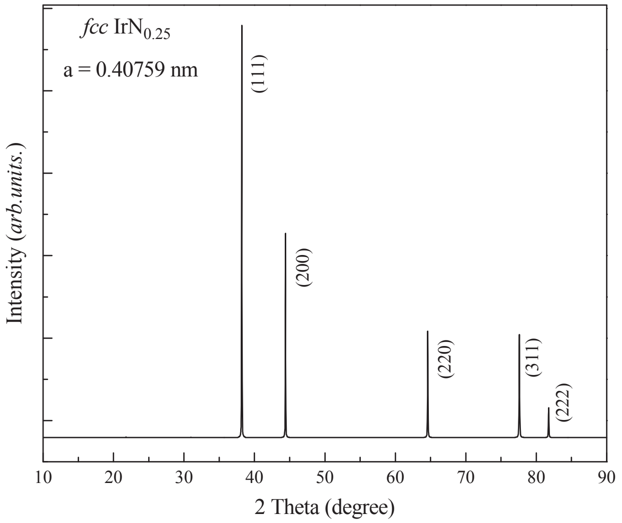

Fig. 4. Simulated XRD patterns of the $IrN_{0.25}$.

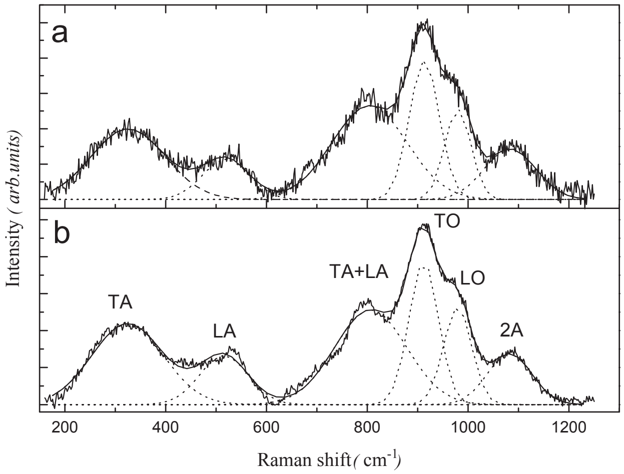

Fig. 5. Raman spectra of the sample synthesized at 1273 K under: (a) 5 GPa; and (b) 10 GPa.

defects induced distortion on the structure and first-order Raman scattering could be observed.

Like in the transition metal nitrides, i.e., TiN_x [12], ZrN_x [13] or HfN_x [14], the vibrations in acoustic mode are mainly due to the vibrations of metal atoms, while the lighter non-metal ions dominate the optical vibrations. As shown in Fig. 5(b), the Raman peaks at 324, 515, 808, and 1082 cm^{-1} could be assigned to transverse acoustic (TA), longitudinal acoustic (LA), first-order transverse and longitudinal acoustic (TA+LA) and second-order acoustic (2A) modes of the cubic IrN_x, respectively. The Raman peaks at 912 and 979 cm^{-1} could be assigned to transverse optical (TO) and longitudinal optical (LO) modes of the cubic IrN_x. The analyses of Raman spectra agree well with the XRD results, which shows further evidence that the as-prepared iridium nitrides should be face-center cubic structure. The observed Raman scattering in the cubic phase is induced by the existence of defects in the structure, like interstitial N vacancy defects.

The synthesis of IrN_x(x≈0.3) with *fcc* structure does not favor the theoretic predictions of Chen et al. [7] and Zhao et al. [9]. The reasons for the disagreement between the predictions and experimental results need further investigation. The synthesis of non-stoichiometric iridium nitrides is of assistance to enriching the Ir–N binary alloy phase diagrams.

Several high pressure metastable phases synthesized by the double decomposition reactions have been reported. For example, the rock salt structure TaN has been synthesized by the reaction of $TaCl_5$ with $LiNH_2$ at less than 1 atm [15]; ReN_2 with MoS_2 structure has been synthesized from a reaction between $ReCl_5$ and Li_3N under 7.7 GPa [16]. Therefore, the present double decomposition reaction under high pressure and high temperature may open a window in the synthesis of the other noble metal nitride, i.e., PtN_x, OsN_x or RuN_x.

4. Conclusions

Novel iridium nitrides have been synthesized under high pressure (5 GPa) and high temperature (1273 K) conditions. The as-synthesized IrN_x (x≈0.3) crystal has a *fcc* structure; such structure is different from any of the structures for iridium nitride ever predicted by theoretical calculations. This work is useful for both enriching the Ir–N phase diagram and synthesizing other novel noble metal nitrides.

Acknowledgments

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