Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis of Ln nitrides (Ln = Ce, Pr, Gd, Lu) in high pressure and temperature

Ken Niwa^a, Masashi Hasegawa^{a,*}, Takehiko Yagi^b

^a Dept. Mater. Sci., Nagoya University, Nagoya, Aichi 464-8603, Japan
^b Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

ARTICLE INFO

Article history: Received 10 July 2008 Received in revised form 8 October 2008 Accepted 14 October 2008 Available online 3 December 2008

PACS: 81.05.Zx 81.05.Je 81.40.Vw 62.50.+P 61.66.Fn

Keywords: Lanthanide nitride high pressure and high temperature synthesis Diamond anvil cell

1. Introduction

The combination of the diamond anvil cell and YAG laser heating (LASER-DAC) is a useful technique for the synthesis of metal nitrides in a supercritical nitrogen fluid. The synthesis and crystal growth of metal nitrides of simple metal, transition metal and rare earth metal using the LASER-DAC system [1-7] have been reported. For example, we have grown colorless transparent fine crystals of GaN in the wurtzite-type structure from molten gallium and fluid nitrogen at about 10 GPa and high temperature [1]. We have also reported the systematic study of the syntheses and stability of transition-metal nitrides at high pressures (about 10 GPa) and high temperatures (about 1800K) using LASER-DAC [2-4]. Nitrides such as TiN, VN, CrN, Mn₃N₂, Fe₂N, Co₂N and Ni₃N have been easily and quickly synthesized by a simple direct nitriding reaction between metal and fluid nitrogen. There are also several reports on the synthesis of transition-metal nitrides using LASER-DAC by other groups. For example, Zerr et al. reported the synthesis of the new Th_3P_4 -type, Zr_3N_4 and Hf_3N_4 nitrides at 18 GPa and ~3000 K [5]. Gregoryans et al. reported the first

ABSTRACT

We have synthesized Ln nitrides (Ln = Ce, Pr, Gd, Lu) in a supercritical nitrogen fluid at high pressure (about 30 GPa) and high temperature (about 2000 K) using the diamond anvil cell and YAG laser heating system. New Ce and Pr nitrides have been synthesized, while the well-known NaCl-type GdN and LuN have been obtained. It is found that the structures of the new Ce and Pr nitrides are different from those of the new La nitrides reported recently.

© 2008 Elsevier B.V. All rights reserved.

Pt nitride, PtN (ZnS-type) synthesized at 45 GPa and \sim 2000 K [6].

Recently, we have also succeeded in synthesizing two new lanthanum nitrides in a supercritical nitrogen fluid at high pressure (about 30 GPa) and high temperature (about 2000 K) using the LASER-DAC heating system [7]. These nitrides were found to be stable down to 5 GPa and \sim 300 K in a nitrogen atmosphere. One of the new lanthanum nitrides is a cubic P lattice-type phase. The calculated lattice parameter is a = 11.979 Å at 5 GPa, 300 K. The other nitride is a trigonal P lattice-type. The calculated lattice parameters are a = 3.889 Å and c = 6.691 Å at 5 GPa, 300 K. The most likely phase of the former new La nitride is $Pa\bar{3}$ La₂N_{3+ δ}, the structure of which may be similar to the $Ia\bar{3}$ Mn₂O₃-type (Ia80). The phase of the latter nitride is $P\bar{3}m1$ La₂N_{3+ δ}, the structure of which is the same as the $P\bar{3}m1$ La₂O₃-type (*hP*5). Since La nitrides are usually synthesized as the NaCl-type structure under ambient pressure, they are novel La nitrides which are different from NaCl-type nitrides. Other Lanthanide nitrides are also usually synthesized as the NaCltype structure under ambient pressure. Accordingly, it is expected that novel Ln ones can be obtained by the LASER-DAC as well as the La nitrides. This manuscript reports the synthesis of other Ln nitrides (Ln = Ce, Pr, Gd, Lu) in a supercritical nitrogen fluid at about 30 GPa by the LASER-DAC in comparison with the novel La nitrides.





^{*} Corresponding author. Fax: +81 52 789 3370. E-mail address: hasegawa@numse.nagoya-u.ac.jp (M. Hasegawa).

^{0925-8388/\$ –} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2008.10.064

2. Syntheses and experimental procedure

The LASER–DAC systems installed at Photon Factory, the National Laboratory for High Energy Physics (KEK) in Tsukuba and at the SPring8, was used for synthesizing samples. The YAG laser (100 W CW multimode) was used for sample heating. Samples in a lever-type DAC were irradiated by the laser beam from one side of the DAC. The sample was observed during heating using a CCD camera. The culet size of the diamond anvil was 450 μ m in diameter. A rhenium gasket was used and the gasket hole was about 200 μ m in diameter. The LASER–DAC system used in this study was described in detail elsewhere [8].

Synthesis pressure was about 30 GPa, which was measured before and after laser heating using the ruby fluorescence technique at room temperature. Starting materials were solid Ln metal (about $100 \times 100 \times 10 \,\mu\text{m}^3$) and gaseous nitrogen. To prevent the starting Ln metal from coming into contact with the diamond anvil, which worked as a big heat sink, a thin NaCl plate was placed between the Ln metal and the anvil. The nitrogen was loaded at room temperature using an apparatus modified from that described before [9]. The assembled diamond anvil cell was enclosed in the casing and attached to the gear mechanism and then placed at the bottom of the high-pressure vessel. The vessel was then purged several times (usually five times) with the appropriate high-pressure pure nitrogen gas (99.99995%) from the gas bomb by using valves. The piston was set to the bottom position to minimize the volume of the vessel. The pressure in the bomb was usually about 13 MPa, and so the dilution factor by this purge process was more than about 10⁶. After purging, the vessel was filled with a large amount of pure nitrogen gas again by loading into the sample chamber at about 150 MPa. It was then compressed further by the DAC up to about 30 GPa. During this pressure increase, the nitrogen solidifies at about 3 GPa. The sample was heated by the laser for about 30 min and then quenched to room temperature by decreasing the laser power quickly. The sample temperature during the laser heating was monitored spectroradiometrically and the temperature at the heating spot was maintained at about 2000 ± 50 K.

High-resolution angle dispersive X-ray diffraction experiments were carried out using synchrotron radiation at the Photon Factory in Tsukuba and at the SPring-8. A monochromatized X-ray was collimated to a thin beam ($30 \,\mu$ m $\times 30 \,\mu$ m) and used to irradiate the sample. The diffracted X-ray was detected by an imaging plate (IP). In order to obtain high resolution and accuracy, the IP detector was placed about 310 mm from the sample. The X-ray intensities recorded on the IP were measured by a laser-scanning reader and converted into two-dimensional digital intensity data. These data were then integrated along the polar axis which coincided with the Debye rings observed on the IP, and the powder diffraction intensities were obtained as a function of the 2θ angle. Typical exposure times were about 20 min. Details of the data analysis were described elsewhere [8].

3. Results and discussion

Fig. 1 shows the results of the X-ray diffraction pattern when synthesizing Ce nitride. The pattern at about 30 GPa and room temperature before heating is identified by the combination of tetragonal (*tl*2) Ce metal [10] and solid nitrogen since the starting materials, Ce metal and nitrogen, do not react at this stage and the NaCl thermal insulator was not used in this experiment. Fig. 1(b) shows the X-ray diffraction pattern at about 30 GPa and room temperature after heating at 30 GPa and 2000 K. It is clear that the pattern is completely different from that in Fig. 1(a), indicating that the Ce metal has reacted with the nitrogen. It was clearly



Fig. 1. X-ray diffraction patterns at room temperature (RT) when synthesizing Ce nitride. (a) At about 30 GPa before laser-heating; (b) at about 30 GPa after laser-heating at about 30 GPa, 2000 K; (c) after recovered to 0.1 MPa (ambient pressure).

observed through the monitor of the LASER-DAC system that the solid nitrogen melted during the laser heating. Fig. 2 shows the photograph of the sample chamber before and after laser-heating at about 30 GPa. The boundary between the melted and unmelted solid nitrogen is observed in the figure (b). Therefore, the nitriding reaction occurred between Ce metal and supercritical nitrogen fluid. The X-ray diffraction pattern just after the decompression was also measured at 0.1 MPa and room temperature in an atmosphere of the nitrogen gas, as shown in Fig. 1(c). The Ce nitride(s) pattern remains almost the same as that at 30 GPa although the diffraction intensity was changed because of the sample movement during the decompression. After measurement at 0.1 MPa and 300 K, the X-ray diffraction pattern was measured again in air. The pattern was a broad halo, indicating that the synthesized nitrides got glassy due to the decompression or oxidation. This is the same result of the new La nitrides reported before [7].

The well-known reported Ce nitride is of the simple NaCl-type structure [11]. No X-ray diffractions of the NaCl-type structure cannot be found in the pattern of the recovered sample (Fig. 1(c)). There is another reported Ce nitride which crystallizes the La_2O_3 -type structure [12]. This structure is the same as that of one of the new La nitrides recently reported by us [7]. Fig. 3 shows the comparison of the X-ray diffraction pattern at about 30 GPa between the Ce nitride(s) in this study and the reported La nitrides. These patterns are different from each other. Besides, the results of the TEM-EDS analysis indicated that the Ce metal was nitrided. These results indicate that one (or some) new Ce nitride(s) has (have)





Fig. 2. Photograph of the sample chamber at room temperature. The boundary between the melted and unmelted solid nitrogen is indicated by an arrow in the figure (b). (a) Before laser-heating at about 30 GPa and (b) after laser-heating at about 30 GPa, 2000 K.

been synthesized in this study. Although we have tried to analyze the X-ray diffraction pattern, it cannot be identified so far. Since we have not solved the structures and even index patterns, only 2θ angle, observed d-spacing and intensities are shown in Table 1.

Fig. 4 shows the X-ray diffraction pattern at about 30 GPa and room temperature after heating at 30 GPa and 2000 K when synthesizing Pr nitride. Many diffraction lines are observed in the pattern, accompanying with the diffractions of α -U type Pr (unreacted Pr) and NaCl (thermal insulator). This indicates that Pr nitride(s) has

Table 1

Observed 2θ angle, d-spacing and intensity of the diffraction lines of Ce nitride(s). Here, the intensity "ss", "s" and "w" which indicate "very strong", "strong" and "weak", respectively.

20	d-Spacing (Å)	Intensity	2θ	d-Spacing (Å)	Intensity				
7.454	3.281	w	12.345	1.983	S				
7.800	3.135	w	13.337	1.836	S				
8.255	2.963	S	13.658	1.793	w				
8.358	2.926	S	14.193	1.726	w				
8.468	2.888	SS	14.439	1.697	S				
8.616	2.839	S	14.537	1.686	w				
8.902	2.748	S	14.836	1.652	S				
9.382	2.608	w	15.369	1.595	w				
9.698	2.523	w	15.619	1.569	W				
9.952	2.459	w	16.014	1.531	w				
10.140	2.413	S	16.528	1.484	w				
10.349	2.365	S	16.754	1.464	w				
10.465	2.338	S	16.961	1.446	S				
10.581	2.313	w	17.085	1.436	S				
10.696	2.288	w	18.682	1.314	w				
11.096	2.206	w	18.856	1.302	w				
11.452	2.137	w	19.608	1.252	W				
11.970	2.045	S							



Fig. 3. Comparison of X-ray diffraction patterns of Ce nitride(s) in this study and La nitrides in the previous study [7] at about 30 GPa and room temperature after laser-heating at about 30 GPa, 2000 K.



Fig. 4. X-ray diffraction pattern at room temperature after laser-heating at about 30 GPa, 2000 K when synthesizing Pr nitride.

496

Table 2

Observed 2θ angle, d-spacing and intensity of the diffraction lines of Pr nitride(s). Here, the intensity "ss", "s" and "w" which indicate "very strong", "strong" and "weak", respectively.

20	d-Spacing (Å)	Intensity	20	d-Spacing (Å)	Intensity
7.307	3.231	W	11.050	2.138	S
7.811	3.023	w	11.353	2.082	W
8.009	2.948	S	11.577	2.041	W
8.106	2.913	SS	11.960	1.976	W
8.330	2.835	S	12.804	1.847	S
8.446	2.796	SS	13.131	1.801	W
8.890	2.657	w	13.441	1.760	W
9.361	2.523	w	13.912	1.700	S
9.550	2.474	w	14.132	1.674	S
9.799	2.411	S	16.292	1.453	SS
9.969	2.370	SS	18.925	1.252	W
10.275	2.299	w	19.201	1.235	S
10.810	2.186	W	19.898	1.192	S

(have) been synthesized by laser heating. The observed 2θ angle, d-spacing and intensities are described in Table 2. The well-known reported Pr nitride is of the simple NaCl-type structure [13]. There is another reported Pr nitride which crystallizes the La₂O₃-type structure as well as Ce nitride [12]. The diffraction pattern cannot be identified by these reported Pr nitrides. This indicates that one (or some) new Pr nitride(s) has (have) been synthesized in this study.

Fig. 5 shows the X-ray diffraction patterns just after laserheating Gd and Lu metals in a supercritical nitrogen fluid at 30 GPa, 2000 K. Both patterns are simple and can be identified by the wellknown NaCl-type nitrides [14,15] and unreacted pure metal phases. The cell parameters of GdN and LuN at 30 GPa were 4.739(1)Å and



Fig. 5. X-ray diffraction patterns at room temperature after laser-heating at about 30 GPa, 2000 K when synthesizing Gd and Lu nitrides. (a) Gd and (b) Lu.

4.542(2) Å, respectively. Compared to the reported cell parameters at ambient pressure (4.969 Å [13] and 4.7599 Å [14]), it is found that they are compressed into about 86.75 and 86.89% in volume at 30 GPa, respectively. This suggests that they have almost the same compressibility. Kieffer et al. reported the Mn_2O_3 -type Gd and Lu nitrides of which crystal structure is different from the La₂O₃-type of the Ce and Pr nitrides [12]. These results are different from ours. They were reported to be synthesized in nitrogen gas at about 3 MPa and 1700–1800 K, accompanying with their NaCl-type phases. Since their X-ray diffraction patterns were not shown in the manuscript, the volume fraction of the Mn_2O_3 -type phase has not been clear. The different result is attributable to the different conditions of our syntheses.

It is concluded from our present and previous studies, La, Ce and Pr nitrides in a supercritical nitrogen fluid at about 30 GPa and 2000 K crystallize to the new phases different from the well-known NaCl-type one. Besides, the crystal structures of the new La nitride are different from those of the Ce and Pr ones. On the other hand, Gd and Lu nitrides crystallize to the NaCl-type phase. La, Ce and Pr ions are larger than Gd and Lu ones. For example, La trivalent ionic radius is much larger than others, and Ce and Pr ones have almost the same radius (La: 1.032 Å, Ce: 1.01 Å, Pr: 0.99 Å, Gd: 0.938 Å and Lu: 0.861 Å [15]). These suggest that the phase formation of the Lanthanide nitride in a supercritical fluid at high pressure and temperature is relevant to its ionic size.

4. Conclusions

Ln nitrides (Ln = Ce, Pr, Gd, Lu) have been synthesized in a supercritical nitrogen fluid at high pressure (about 30 GPa) and high temperature (about 2000 K) using the diamond anvil cell and YAG laser heating system. New Ce and Pr nitrides have been synthesized, while the well-known NaCl-type GdN and LuN have been obtained. Although the new phases are not identified at this stage, it is found that their structures are different from that of the new La nitrides reported recently, i.e. La_2O_3 -type, pseudo-Mn_2O_3-type [7]. Our summarized conclusion is that La, Ce and Pr nitrides crystallize to the new phases different from the well-known NaCl-type one in a supercritical nitrogen fluid at about 30 GPa and 2000 K. On the other hand, Gd and Lu ones crystallize to the NaCl-type structure phase in the same condition.

Acknowledgements

The authors are grateful to T. Ohsuna for his useful discussion. They are also grateful to N. Sata and Y. Ohishi for their experimental supports at the SPring-8. Experiments at the SPring-8 were performed with the approval of the JASRI (PROPOSAL No. 2006A1364). A part of this research was supported by Grant-in-Aid for Scientific Research on Priority Areas "Nano Materials Science for Atomic Scale Modification 474" from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the JFE 21st Century Foundation.

References

- [1] M. Hasegawa, T. Yagi, J. Cryst. Growth 217 (2000) 349.
- [2] M. Hasegawa, T. Kondo, T. Yagi, Special issue of the review of high pressure science and technology, the Japan Society of High Pressure Science and Technology, 8 (1998) 54.
- [3] M. Hasegawa, T. Yagi, Solid State Commun. 135 (2005) 294.
- [4] M. Hasegawa, T. Yagi, J. Alloys Compd. 403 (2005) 131.
- [5] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, Nature 400 (1999) 340.
- [6] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.K. Mao, R.J. Hemley, Nat. Mater. 3 (2004) 294.
- [7] M. Hasegawa, K. Niwa, T. Yagi, Solid State Commun. 141 (2007) 267.

- [8] T. Yagi, T. Kondo, T. Watanuki, O. Shimomura, T. Kikegawa, Rev. Sci. Instrum. 72 (2001) 1293.
- [2007] 1295.
 [9] T. Yagi, H. Yusa, M. Yamakata, Rev. Sci. Instrum. 67 (1996) 2981.
 [10] D.L. Decker, J. Appl. Phys. 42 (1971) 3239.
 [11] U. von Essen, W. Klemm, Z. Anorg, Allg. Chem. 317 (1962) 25.

- [12] R. Kieffer, P. Ettmayer, S.W. Pajakoff, Monatsh. Chem. 103 (1972) 1285.
 [13] P. Ettmayer, J. Waldhart, A. Vendl, Monatsh. Chem. 110 (1979) 1109.
 [14] H.P. Klesnar, P. Rogl, High Temp. High Press. 22 (1990) 453.
 [15] R.D. Shannon, Acta Cryst. A 32 (1976) 751.