Journal of Alloys and Compounds 712 (2017) 588–592

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

The new structure transition sequences of cerium around 5 GPa

Ce Ma [a], Xiao Tan [a], Zuo-yong Dou [a], Jun-ru Jiang [b], Bin Bai [a], Hong-yang Zhu [b], Peng-cheng Zhang [a, *], Qi-liang Cui [b, **]

[a] Science and Technology on Surface Physics and Chemistry Laboratory, Jiangyou, Sichuan, 621908, China
[b] State Key Laboratory of Superhard Materials, Jilin University, Changchun, Jilin, 130012, China

ARTICLE INFO

Article history:
Received 22 January 2017
Received in revised form
13 March 2017
Accepted 13 April 2017
Available online 15 April 2017

Keywords:
High pressure
Cerium
Grain growth
α-U
Pre-compression

ABSTRACT

A fascinating structure transition of cerium around 5 GPa has been studied using high-resolution synchrotron angle-dispersive powder diffraction techniques. This study indicates that the structural transition of cerium strongly depends on the process of compression. Two runs experiments with different compression conditions demonstrate two different structural transition sequences at room temperature around 5 GPa, fcc′→*C*2/*m* →bct for regular compression, fcc′→*C*2/*m* →α-U→bct for the pre-compression. These results show that pressure is not the only factor to determining structural transformation at high pressure, and the structural transformation sequences can be varied by changing the external conditions e.g. pre-compression.

1. Introduction

Cerium (Ce) a typical non-radioactive f-electron transition metal has been the subject of intense scrutiny under different pressure and temperature in recent years, as it have unique f-electron which makes it a key to understand the other lanthanide and actinide elements [1–5]. A quite extensive literatures have elucidated the unique phenomenon of the isostructural transition of γ-Ce(fcc)→α-Ce(fcc′), accompanied by about 14–20% volume collapse at 0.6–1 GPa and room temperature [4–7]. This isostructural transition is mainly caused by the dramatic variation of 4f electron, reflected in both the Hubbard-Mott transition (HM) [8] and Kondo volume collapse (KVC) [9,10] models. Above 12 GPa, cerium transforms into body-centered tetragonal structure (ε-Ce, bct) stable up to the highest experiment pressure 208 GPa [11].

In the 5–12 GPa pressure, the pressure phase diagram of Ce is ambiguity for the transformation products may be α′-Ce (α-U structure) or α′-Ce(*C*2/*m*), which are considered to be related to the trajectory of pressure-temperature [12], the initial heat-treatment state, even the sample primal preparation condition [13,14]. There seems to be a definite conclusions [13], that these structural transition productions of cerium are arisen from different sample preparation and production. However the phase stability of cerium [15,16] still remains controversies at room temperature around 5 GPa. The comparison experiments in different compression process have never done before. In fact, the α-U structure has been observed at room temperature in only, and all, studies performed on a very slow compression similar to our holding pressure compression, in Ref. [16] (The measurement time of each pressure is 30 min), in Ref. [17] (Five samples transform into α-U structure in the case of slow rate of pressure increase. The only one transform into *C*2/*m* when the pressure was raised in one quick step from its atmospheric value to 90 or 96 kbar). With the development of synchrotron source and 2D detector, the measurement efficiency is greatly improved, therefore the holding pressure time is greatly reduced in each pressure condition. Hence all the latest studies show a pure *C*2/*m* intermediate phase without any signal of α′-Ce in recent years [5,13,18]. We speculate that the compression process is effective in the structural transformation in cerium around 5 GPa.

In this letter, we will show a structural transition path of α-U structure around 5 GPa in a pre-compression sample, which clearly reveal the phase transformation sequence of fcc′→*C*2/*m*→α-U→bct. However in a regular compression, the well-known structural transformation sequence of fcc′→*C*2/*m*→bct are found. This implies different transformation products are influenced by different compression process, which is helpful for the research on

* Corresponding author.
** Corresponding author.
E-mail addresses: zpc113@sohu.com (P.-c. Zhang), cql@jlu.edu.cn (Q.-l. Cui).

http://dx.doi.org/10.1016/j.jallcom.2017.04.144
0925-8388/

the transformation of cerium. Meanwhile the reason for this structural transformation in pre-compression sample around 5 GPa has been discussed in this study.

2. Experiment details

The Diamond Anvil Cells (DAC) with 500 μm anvil in diameter were used to provide the hydrostatic pressure. A T301 steel sheet served as the gasket with a chamber of ~200 μm in diameter and ~80 μm in thickness for packing the sample. The samples with a tiny ruby chip for the measurement of the pressure [19] were placed inside the sample chamber filled with quasi-hydrostatic pressure medium high purity silicon oil. The synchrotron angle-dispersive X-ray diffraction (ADXD) measurements were carried out at the 4W2 High-Pressure Station at Beijing Synchrotron Radiation Facility (BSRF) with the X-ray wavelength 0.6199 Å. X-ray beam size of 26X8 μm^2 was employed in all the x-ray exposures. The Bragg diffraction rings were recorded using a MAR345 image plate with a 100 μm pixel, and the XRD patterns were integrated from the images with FIT2D software. Structural results were obtained by full Rietveld refinement using Reflex module in the Materials Studio software.

Cerium slices (~100 μm) were cut from the ingot of 99.9% purity purchased from Alfa Aesar Company. During processing and transport, the Cerium was immersed in high purity silicon oil in order to avoid oxidizing. There was no any other processing such as heat-treatment or grinding before our experiments. To investigate the relationship between phase transformation sequences and compression process around 5 GPa, two runs experiments were carried out. The first run is a regular compression at room temperature from ambient pressure to 29.71 GPa without any pressure holding. The second run is a special pre-compression at room temperature from 1.43 to 31.47 GPa, that cerium slice was sealed in DAC at 1.5 GPa holding for ~72 h, and pressure drop down to 1.43 GPa before the synchrotron X-ray diffraction experiments.

3. Results and discussions

The representative diffraction spectrums of regular compression are shown in Fig. 1. The refined structures of each phase are shown in Fig. 2. The refined lattice parameters of fcc structure (ϒ- Ce, $Fm\bar{3}$ m) at 0.63 GPa are a = 5.0890(1) Å, volume = 32.95 $Å^3$/atom. The refined lattice parameters of fcc′ (α-Ce, $Fm\bar{3}$ m) at 2.76 GPa are a = 4.7050(1) Å, volume = 26.04 $Å^3$/atom. The fcc→fcc′ isostructural transition happen at 0.85 GPa, accompanied by a 14.6% volume collapse. The fcc′ have totally transformed into *C*2/*m* at 6.74 GPa. The refined lattice parameters of *C*2/*m* structure (α′-Ce, *C*2/*m*) at 8.29 GPa are a = 5.8148(10) Å, b = 3.1465(5) Å, c = 5.6203(11) Å, β = 113.160(23)°, volume = 23.64 $Å^3$/atom consist with the early work [13]. The freely refined coordinates of cerium in the 4(i) positions of *C*2/*m* are (0.2178(2),0,0.2380(5)) different from the value (0.2800,0,0.2516) [13]. At 12.87 GPa the *C*2/*m* begin to transform into bct, this transition finish at about 16.04 GPa. The refined lattice parameters of bct structure (ε-Ce, *I*4/*mmm*) at 19.38 GPa are a = b = 2.8980(2) Å, c = 4.8494 (8) Å, volume = 20.36 $Å^3$/atom. It recover to γ-Ce after the pressure return to ambient pressure. The directly fcc′→*C*2/*m* structural transition is observed without any signal of α-U structure, consistent with the early work [13,18,20]. Therefore *C*2/*m* is stable structure at 5–12 GPa in this structural transformation series.

The representative diffraction spectrums of pre-compression are shown in Figs. 3 and 4. *C*2/*m* begin to appear at 4.64 GPa. Then fcc′, *C*2/*m* and α-U structure are coexisting at 4.92 GPa, consistent with Gu's results, who considered the coexisting pressure is from 5 to 8 GPa or higher pressure [16]. However, at 5.40 GPa all the diffraction peaks representing fcc′ or *C*2/*m* have disappeared followed with the emergence of numerous new diffraction peaks which are recognized as the characteristic of pure α-U structure, shown in Fig. 4. The refined lattice parameters of α-U structure (α′-Ce, *Cmcm*) at 8.85 GPa are a = 3.0137(3) Å, b = 5.9258 (15) Å, c = 5.1320(11) Å, volume = 22.91 $Å^3$/atom, the 4(c) positions of *Cmcm* is 0.1141(12) shown in Fig. 5. The R_{wp} is bigger than 10% which is caused by the diffraction spots of α-U structure, shown in Fig. 6.

The original diffraction images of pre-compression sample are clearly shown in Fig. 6. Repetitive experiment can be seen in supplementary material [21]. The pure fcc′ is observed below 4.06 GPa, the first three diffraction strong peak (except the innermost one, the signal of Ce-H) can be identified by the continuous diffraction rings which shows the random orientation of the crystal planes. At 4.64 GPa there are three new weak continuous rings, which are identified as the diffraction peak of *C*2/*m* structure. The integrated diffraction rings of *C*2/*m* still exist at 4.92 GPa, explained as the huge random orientation of *C*2/*m* crystal planes. Meanwhile, there are abundant spots identified as α-U structure at 4.92 GPa, which shows the grain size of α-U structure is the same or even bigger than the X-ray beam size. Recrystallization and grain growth during the fcc′→fcc′+*C*2/*m*→α-U transformation is observed at high temperature and high pressure Repetitive experiment [16]. These spots still exist at 5.4 GPa (the red circle in Fig. 6), meanwhile some new spots begin to appear, accompanied by the disappearance of the continuous diffraction rings. It indicates the pure α-U structure emerge, accompanied by the vanishment of fcc′ and *C*2/*m*. The fcc′(4.06 GPa) → fcc′+*C*2/*m* (4.64 GPa) → fcc′ + *C*2/*m* +α-U (4.92 GPa) → α-U (5.4 GPa) structure transition is clearly observed, which is the evidence that α-U structure is stable phase and *C*2/*m* is metastability phase in this structural transformation sequence.

Experimental results in two runs experiments show that both of *C*2/*m* and α-U structure are possible stable phase around 5 GPa. Therefore pressure is not the only factor to identify the stability of Ce around 5 GPa at room temperature. Comparison with the early work [12,13,16], once α-U structure emerge at certain pressure, the formation of pure α-U structure is inevitable as the increasing of pressure. We speculate the increasing of pressure can promote the structural transition from *C*2/*m* to α-U structure, when these two phases are coexistence. However numerous experiments

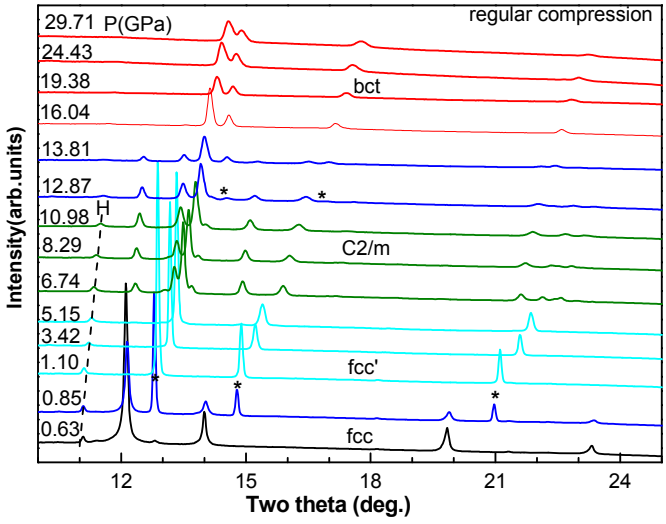

Fig. 1. X-ray diffraction patterns of Cerium in regular compression. The asterisk (*) denotes the occurrence of the new peaks of the transformation of cerium. The epactal peak "H" at low angle is the strongest line of CeH [13,16].