MS086.O01

Novel nitrogen-rich iron nitrides synthesized at high-pressure high-temperature conditions

Maxim Bykov[1], Elena Bykova[2], Georgios Aprilis[1], Konstantin Glazyrin[2], Egor Koemets[1], Irina Chuvashova[1], Hanns-Peter Liermann[2], Natalia Dubrovinskaia[3], Leonid Dubrovinsky[1]

[1]Bayerisches Geoinstitut, University Of Bayreuth, Bayreuth, Germany, [2]PetraIII, DESY, Hamburg, Germany, [3]Material Physics and Technology at Extreme Conditions, Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany

E-mail: maxim.bykov@uni-bayreuth.de

Since the invention of a diamond anvil cell, a huge progress has been made in the field of high-pressure research, and, in particular, in methods of accurate structural characterization, particularly single-crystal X-ray diffraction (XRD). In the last few years, high-pressure single-crystal diffraction studies become possible up to pressures exceeding one megabar. However, a route to novel compounds and phenomena often lies through high-pressure - high-temperature conditions. Up to now, only powder XRD experiments combined with laser-heating system were feasible. We have developed the double-sided laser-heating system, which allows simultaneous laser-heating and single-crystal XRD data collection. Using this system installed at the synchrotron beamline P02.2 (Petra III, DESY, Hamburg, Germany) we have synthesized and characterized crystal structures of four novel iron nitrides Fe3N2, FeN, FeN2 and FeN4.

Iron nitrides have a very complex phase diagram, and can exist in many different phases such as α''-Fe16N2, γ'-Fe4N, ε-Fe3N, ζ-Fe2N, and FeN [1]. Among them, the most nitrogen-rich compound FeN has only been synthesized in the form of thin films with ZnS and NaCl structure types. To our knowledge no experimental studies have so far dealt with the iron nitrides with N:Fe ratio > 1. At the same time several theoretical calculations have predicted spinel-type Fe3N4 and iron pernitride FeN2 [2]. We have studied the chemical reactions between Fe and N2 in a diamond anvil cell in the pressure range up to 135 GPa and temperatures up to ~2700 K. We found that higher pressure favors formation of iron nitrides with higher nitrogen content (Fe3N2 → FeN4). Remarkably, the most nitrogen-rich compound FeN4 contains polymeric nitrogen chains. Such transition metal nitrides are usually considered as possible ultra-hard low-compressible high-energy materials. Various theoretical works propose several possible tetranitrides MN4 (M = Re, Ru, Os, Cr, W and Hf) [3] featuring polymeric nitrogen chains, however no such compounds have been experimentally confirmed so far, and structure we discovered have not been predicted. Our study shows an experimental route to these nitrides. In this contribution the details of the experiments, data analysis, crystal structures of iron nitrides and relations between them will be discussed.

[1] Ching, W. Y., et al. (2002), Appl. Phys. Lett. 80, 2904

[2] Wessel, M., et al. (2011) Chem. - A Eur. J. 17, 2598-2603.

[3] Kvashnin, A.G., et al. (2017) J. Phys. Chem. Lett. 8, 755-764.

Keywords: High-pressure crystallography, iron nitrides, polymeric nitrogen