Extreme conditions synthesis, processing and characterization of metal-nitrides and alloys of mechanical and optoelectronic importance

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Abstract. High density nitrides and group IV alloys are of growing importance for both ceramic and optoelectronic applications. We present here new data and processes in our ongoing preparation of alkaline earth and transition metal nitrides as well as group IV alloys, here, up to 25 GPa and 2300 K. We employ large volume and laser-heated diamond anvil cell techniques for synthesis, processing tools including focused ion beam, and synchrotron X-ray diffraction, transmission electron microscopy and scanning electron microscopy for characterization.

1. Introduction
For many years, spurred to a considerable extent by the need to understand our planet’s interior structure, we have made significant inroads into the crystal chemistry of oxides at high densities [1,2]. The more recent realization that the confining environment of a high pressure vessel can be employed to create a rich nitride landscape has given rise to a remarkable new crystal chemistry ranging from cubic spinel structures [3] to polymerized single bonded nitrogen [4] and noble nitrides containing single bonded di-nitrogen units [5]. Moreover further efforts [6] showing that some of the simpler synthetic procedures afforded by the laser-heated diamond anvil cell, i.e. use of elemental starting ingredients, can be approached using large volume presses in their albeit narrower P-T range as well, by employing azides, is leading to a more systematic use of these techniques for developing the emerging new nitride landscape. Similarly, we employ in concert, laser-heated diamond anvil cell and large volume presses for synthesis of new alloys with a particular emphasis on group IV alloys which are also important for mechanical as well as optoelectronic applications [7] in addition to their considerable fundamental interest in both the solid and liquid state [8]. Indeed the recent report that pressure can be used to make unreactive elements of this group reactive leading to recovery of a new optoelectronically important alloy [9] prompts us to an increased focus on the high pressure and temperature crystal chemistry of this group.

In this study, we investigate the effect of high pressure and temperature on the reactivity of Mg with Fe in the presence of nitrogen. The significance of this area is both fundamental and applied. Fundamentally, without nitrogen, more than 1 million atmospheres are required to incorporate about 10 at% Mg in Fe [10]. Technologically Mg is light and strong and is thus a desirable alloying component, and Fe itself is central to most everyday metal-based constructions. Nitridation of iron itself has long been of industrial importance for steel hardening. With respect to group IV alloys we focus here on the Ge-Si system whose ambient diamond structured compositions are of widespread technological application [7] particularly in heterojunction bipolar devices. The approach here is to

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employ pressure and temperature to prepare high density GeSi modifications which can be transformed to novel forms upon recovery. In the context of our complementary multianvil and diamond anvil methods we also present focussed ion beam techniques for nanoprocessing of recovered products.

2. Experimental techniques

The starting materials for the syntheses were magnesium powder (99.8%) or foil (99.1%) (Aldrich), iron powder (99.5%) (Alpha), iron nitride powder (Alpha), sodium azide powder (99.99+) (Aldrich), germanium pieces (99.999%) (Alpha) and silicon pieces (99.999%) (Alpha). All mixes described below were ground or pressed together to micron or submicron levels, excepting the azide which was added separately. For the multianvil runs using a Sumitomo press in Bayreuth approximate mixtures of 70 at% iron and 30 at% magnesium were intimately mixed together filling about two thirds of a lidded MgO capsule, with the bottom third of the capsule being filled with sodium azide. Pressure and temperature were applied via a hydraulic press and a LaCrO3 heater respectively. The magnesium and iron containing samples were pressurized to 15 GPa and heated to 1800 K for 1 minute and cooled to room temperature in about 20 minutes. For the MAX 80 measurements at HASYLAB a cylindrical BN container was employed filled with an iron nitride/magnesium powder mix with an atomic ratio of Fe:Mg:N = 2:0.8:1 and a second adjacent cylindrical BN filled with NaCl was employed for pressure measurement. Pressure and temperature were applied via a hydraulic press and a graphite heater respectively. The magnesium and iron containing samples were pressurized up to 5.3 GPa and heated to 1500 K for 1-3 minutes and quenched to room temperature. For the laser-heated diamond cell studies pressed pellets from powder mixes of iron/magnesium or iron nitride/magnesium with atomic ratios of Fe:Mg = 3:1 or Fe:Mg:N = 3:1:0.9 respectively were placed on 3 micron polished Al2O3 plates contained in a 140 micron diameter laser-drilled tungsten hole in a nitrogen or argon pressure medium which was loaded using a 3 kbar gas loader at MPI Mainz. Laser-heating was performed using a fiber-pumped 110 Watt ytterbium-glass, single-mode continuous wave 1070 nm laser [11]. The samples were pressurized to 25 GPa and heated to 2300 K for 1-2 minutes and quenched. For the Ge-Si experiments, about 80 at% Ge was intimately mixed with 20 at% Si and placed in a lidded Al2O3 capsule and heated at high pressure using the Sumitomo press as well. In an experiment presented here, the Ge-Si mixture was pressurized to 15 GPa and heated at this pressure for 2 minutes followed by temperature quenching to room temperature in about 20 minutes. All samples were recovered for further analysis. Recovery involved cutting the capsules, polishing and coating for scanning electron microscopy [Philips XL30CP, with an energy dispersive X-ray analyser Oxford instruments EDX detector – SiLi crystal with PGT spirit analysis software for chemical analysis]. Voltages of between 10 – 20 kV were employed for SEM measurements and a 300 kV acceleration voltage for transmission electron microscopy [Philips CM30, Transmission Electron Microscope (TEM), equipped with a Gatan SS CCD camera and with Digital Micrograph software for acquisition of electron diffraction patterns and bright-field imaging]. Greater detail into the synthetic, processing and characterization protocols has been documented in previous studies [6] [11][12].

3. Results and discussion

For nitrides, the reaction product recovered from 15 GPa using the Sumitomo press reveals two principal reaction chemistries, namely an iron rich Fe-Mg-Na-N phase and a sodium-free Fe-Mg-N phase [13]. Electron diffraction patterns indicate hexagonal and cubic symmetries for the two respective chemistries (Figure 1). One in-situ X-ray diffraction is also currently being analyzed and is being augmented with further experiments using Al2O3 capsules rather than BN, in order to more directly correlate with the work using the Sumitomo press and ensure no interaction with BN (Figure 2). Higher pressures and temperatures in the pure Mg-Fe-N system are accessed using laser-heated diamond anvil cell methods, the additional advantage being that a nitrogen pressure medium can also serve as a pure nitrogen source for the reaction at high densities (Figure 3). The syntheses from these ongoing studies are being analyzed and extended. With regards are ongoing work in the GeSi system [13] initial electron diffraction patterns of sample recovered from 15 GPa after melting in a large volume press suggests a tetragonal phase (Figure 4). Because recovered samples can contain more than one phase it is often desirable to be able to nano-section the region of interest out selectively for further analysis. We thus briefly illustrate here in the context of our multianvil syntheses, an image of a sample thin section prepared with the focused ion beam method for electron microscopy analysis. A
particular additional advance here is that the thicker side of the thin section can be welded to the rim of a TEM grid so that there is little or no danger of losing the sample (Figure 5).

![Microdiffraction zone-axis spot patterns of the sodium containing (a) and sodium free Fe-Mg-N (b) crystal phases.](image1)

Figure 1. Microdiffraction zone-axis spot patterns of the sodium containing (a) and sodium free Fe-Mg-N (b) crystal phases.

![A boron-epoxy cube recovered from 5.3 GPa. The pre-indents are formed by six tungsten carbide anvils compressing on each side of the cube (a). Energy dispersive X-ray diffraction of the loaded Fe-Mg-N powder at various pressures and temperatures (b).](image2)

Figure 2. A boron-epoxy cube recovered from 5.3 GPa. The pre-indents are formed by six tungsten carbide anvils compressing on each side of the cube (a). Energy dispersive X-ray diffraction of the loaded Fe-Mg-N powder at various pressures and temperatures (b).

![FeMg pressed pellet viewed through the diamond and sitting on an Al₂O₃ plate before heating in a nitrogen pressure medium (a) and after heating (b), with the distinct recrystallized nitrogen from the melt surrounding the laser-heated sample at 23 GPa and 2300 K clearly visible.](image3)

Figure 3. FeMg pressed pellet viewed through the diamond and sitting on an Al₂O₃ plate before heating in a nitrogen pressure medium (a) and after heating (b), with the distinct recrystallized nitrogen from the melt surrounding the laser-heated sample at 23 GPa and 2300 K clearly visible.
4. Conclusions
This ongoing work demonstrates the ability to employ nitrogen to facilitate new reactions between elements and give rise to novel crystal structures. Further, with respect to group IV alloys, our data indicate that we can use high pressures to prepare materials that can then be recovered in new modifications. A more general point illustrated here is the utility of employing multiple synthetic techniques in order to probe new material landscapes.

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