

MS20-P3 Mg₂Fe₂O₅ a novel breakdown product of MgFe₂O₄ at high pressureTiziana BOFFA BALLARAN¹, UENVER-THIELE Laura², WOODLAND B. Alan²

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Since the recent discovery of the novel oxide Fe₄O₅ resulting as a breakdown product of siderite or magnetite [1,2], investigations on the possible substitutions of Mg and Cr for Fe²⁺ and Fe³⁺ and their implication for the Earth's mantle have been undertaken [3]. Fe₄O₅ crystallises in the *Cmcm* space group and has a structure similar to that of SrTi₂O₅ and CaFe₃O₅, consisting of layers of edge-sharing FeO₆ octahedra and layers of trigonal prisms alternating along the *c*-axis. In the present study the structure of a novel Mg₂Fe₂O₅ oxide, synthesized at 15 GPa and 1550 °C from a mixture of MgFe₂O₄ and MgO, has been determined by means of single-crystal X-ray diffraction. This compound is isostructural with Fe₄O₅ and it can be considered as the other end-member of a binary system between these two oxides involving the complete substitution of Fe²⁺ for Mg. The Mg and Fe³⁺ cations are disordered among the three crystallographic sites of the Mg₂Fe₂O₅ structure, although preference of Mg for the trigonal prism coordination is observed. Substitution of Mg into the Fe₄O₅ structure reduces the octahedral distortion of both octahedral sites. It also has been reported that FeCr₂O₄ dissociates into Fe₂Cr₂O₅ and Cr₂O₃ at high pressure [4]. However, such compound appears to be isostructural with Mg₂Al₂O₅, having space group *Pbam* and a different stacking of the octahedral units that, in this case, form long chains surrounding the trigonal prisms. This is quite puzzling given that samples belonging to the Fe-Cr solid solution with up to 50% of the Fe₂Cr₂O₅ component [3] appear instead to crystallise in the *Cmcm* space group. A possible explanation of such difference may reside in the different Jahn-Teller distortions of the two compounds, since in Fe₂Cr₂O₅ only Cr³⁺ is present while in Mg₂Fe₂O₅ the transition cation is exclusively Fe³⁺. M₄O₅ phases can now be considered a new addition to the phase relations of a number of simple oxide systems at pressures and temperatures at which the spinel-structured phase becomes unstable. These phases may form complex solid solutions; moreover, our results indicate that cation order-disorder phenomena may help to stabilize the M₄O₅ phase, particularly at higher temperatures.

References:

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Keywords: Mg₂Fe₂O₅, Fe₄O₅, high-pressure, crystal structure**MS20-P4** High pressure synthesis and characterization of hydrogenated nitrogen-rich carbonaceous polymerKamil F. Dziubek^{1,2}, Margherita Citroni^{1,3}, Samuele Fanetti¹, Carla Bazzicalupi³, Marco Pagliai^{1,3}, Mohamed Mezouar⁴, Roberto Bini^{1,3}

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High pressure synthesis and recovery of new materials based on the C-N-H system have gained remarkable interest fueled by their potential use as high energy density materials, layered graphitic structures for nanoelectronics, metal-free photocatalysts or intermediates for the production of superhard carbon nitrides. Due to its highly symmetric molecule with C and N atoms alternating in an aromatic ring and equal contents of all three elements, 1,3,5-triazine (*s*-triazine, C₃N₃H₃) is a promising candidate for the synthesis of novel extended compounds.

We have thoroughly studied pressure and temperature induced reaction in solid *s*-triazine and characterized its phase diagram and *P-T* stability boundaries of the crystalline molecular phases by the means of IR spectroscopy. The reaction kinetics was analyzed as well. Powder diffraction patterns measured as a function of pressure allowed us to obtain atomic coordinates for the high pressure phase II of *s*-triazine and to confirm the previously described low temperature crystal form of *C2/c* space group symmetry, existing at atmospheric pressure below 198.07 K. Following the pressure evolution of short C...N contacts we determined the critical minimum distance, which marks the threshold of the chemical reaction. In addition, the stable amorphous product of the reaction was recovered to ambient conditions and analyzed by IR spectroscopy and pair distribution function analysis. Depending on the reaction conditions different products are formed.

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Keywords: high pressure chemistry, synthesis, functional materials