

Discovery of pressure-induced transition of aurophilic gold iodide

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The expansion of high-pressure (HP) research due to the development of diamond-anvil cells and associated characterization techniques has led to many important breakthroughs during the last decade. This has recently driven the discovery of new materials or new phases of known materials with unique properties. Among inorganic compounds a vast majority of HP studies have been focused on nitrides and oxides. In contrast with those inorganic compounds, few efforts have been devoted to study the behavior under compression of aurophilic compounds, like gold iodide (AuI).

The most important feature of the AuI is the enticing interaction between closed-shell Au⁺ centers. [1, 2] It is the general trend of metal (M) aggregates to reproduce the topology of their metallic fcc-structures. This interaction is commonly referred as aurophilic bonding and in general it has a strength between 29 and 46 KJ/mol, similar to that of the hydrogen bonding. The similarity in strength between hydrogen bonding and aurophilic interaction has proven to be a convenient tool in the field of polymer and supramolecular chemistry. To date, the study of the aurophilicity under high pressure has been very limited. On the other hand, the interest on the HP behavior of metal iodides has been recently stimulated by the giant barocaloric effect of silver iodide (AgI) [3,4] induced by pressure-driven structural changes. Such effect is associated to a decrease of the superionic transition temperature at high pressure. This phenomenon can be extremely useful for developing environmentally friendly cooling devices. Such breakthrough has shown the need of information of the influence of pressure in the crystal structures of AgI and other noble-metal iodides, like AuI. Surprisingly, AuI has never been studied at HP. The scarce information on AuI concerns both high pressure and ambient conditions.

The effects of pressure on the crystal structure of aurophilic tetragonal gold iodide have been studied by means of powder x-ray diffraction up to 13.5 GPa at MSPD beamline in ALBA synchrotron. We found evidence of the onset of a structural first-order transition at 1.5 GPa with an associated 5% volume collapse. The low- and high-pressure phases coexist from this pressure up to 3.3 GPa. At 3.8 GPa the phase transformation is completed and the high-pressure polymorph remains stable up to 10.7 GPa. Rietveld refinement of the high-

pressure phase reveals a monoclinic crystal structure. The high-pressure polymorph is more densely packed than the layered structure of aurophilic gold iodide, involving the formation of I-I bonds and a three dimensional arrangement. We determined the axial and bulk compressibility of both phases of gold iodide. The tetragonal phase is extremely compressible with a bulk modulus of 18.1(8) GPa and its response to pressure is anisotropic. On the other hand, the monoclinic phase shows a smaller compressibility with a bulk modulus 31.8(1.5) GPa. Our work reveals the shortest pressure-induced Au-Au aurophilic distance, 2.823 Å at 4.9 GPa, in a 3D fully inorganic gold(I) structure.

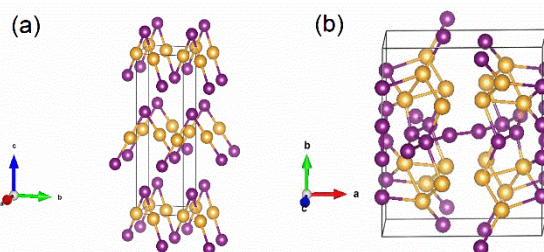


Figure 1. (a) Ambient pressure phase and (b) new discovered phase at high-pressure of AuI.

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