High-energy isochoric synthesis of elusive iodoplumbic acid


[1] Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland, [2] Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC, H3H 0B8 Canada; [3] Department of Materials Engineering, McGill University, 801 Sherbrooke St. West, Montreal, QC, H3A 0C5 Canada

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The energy required to induce a chemical reaction can be provided to a reactant system through light, heat, or electric potential. It is however also possible to activate reactions using mechanical force. Mechanical energy, supplied by techniques like ball-milling, causes friction, stress, and strain and often results in breaking a crystal symmetry. This process can lead to the destabilization of the chemical bonds making compounds prone to react.

It is important however that the mechanical energy can be as well supplied in a form of continuous and hydrostatic pressure on compression in a diamond anvil cell (DAC). Here, we demonstrate the high-energy isochoric synthesis for obtaining two hydronium forms of the proposed but yet never demonstrated iodoplumbic acid HPbI₃ (Figure 1). The proposed HPbI₃ for many years was anticipated to be the simplest member of APbI₃ class of compounds (where A represents a cation counterbalancing the polyanionic sheet) and the progenitor of the wide class of hybrid as well as inorganic lead(II) perovskites [2]. Depending on the pressure range, the reaction of PbI₂ and aqueous concentrated hydriodic acid performed in a DAC and held between 0.11 and 1.20 GPa yielded in the synthesis of two hydrated hydronium salts with composition [H₃O][PbI₃] * nH₂O (n = 3, 4) in form of single crystals (Figure 1).[4] Both compounds are composed of polymeric one-dimensional PbI₃- anions, which are so far the best match for the elusive HPbI₃. This high-energy synthesis from this same system above 2 GPa gave rise to the so far first known polymorph of β-PbI₂. Unlike the form α, crystallizing at standard conditions as yellow single crystals in the hexagonal P6-3mc space group which structure is based on 2-dimensional sheets, phase β exhibits an unprecedented PbI₂ structure. The pink single crystals of monoclinic (space group C2/m) phase β are based on six- and seven-coordinated Pb²⁺ cations connected into a 3-dimensional structure (Figure 1).

This work highlights the potential of pressure-induced synthesis as a simple and straightforward means to discover new unprecedented materials, even from systems that have been extensively studied, over a long time.

Figure 1. Two forms of hydrated iodoplumbic acid obtained in the reaction of PbI₂ with concentrated HI aqueous solution and new polymorph of PbI₂.