

# High Pressure – High Temperature solid-state reactions: how to play with the chemistry to tune physical properties in multifunctional materials

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High Pressure/High Temperature (HP/HT) solid-state reactions constitute an effective synthesis method to metastabilize novel compounds in the field of fundamental material science. These materials are usually characterized by unusual oxidation states and coordination numbers for cations, which lead to rare crystallographic symmetries. The extreme conditions of HP/HT synthesis force strong structural distortions, which interplay with very exotic physical properties such as the coexistence of magnetism and ferroelectricity in the so called multiferroic materials. Namely, distorted double or quadruple perovskites ( $AA'BB'O_6$ ) can solely be stabilized by HP/HT solid state reaction. Their extraordinary density and tolerance factor allow to explore a wide spectrum of chemical substitutions on both A and B sites. Particularly, through a proper choice of cationic substitutes, it is possible to merge and control multiple and, in some case, complementary functionalities in a single phase.

Here we report a selection of our most interesting materials, successfully synthesized in GPa regime with a Walker-type multianvil press in the last decade, with the aim to show to the community how it is possible to move from monofunctional RT-magnets (as  $Pb_2FeMoO_6$  [1] and  $Bi_2CuMnO_6$ ), to double-functional proper multiferroics as ( $Bi_2FeMnO_6$  [2-4],  $YMn_7O_{12}$  [5,6]) and/or Ferrophotovoltaics, up to triple-functional Multiferroic Ferrophotovoltaics ( $Bi_2FeCrO_6$  [7] and  $BaFe_2O_4$  [8]), by finely tuning the composition at the A and B sites of the perovskite.

## References

- [1] F. Mezzadri et al. Structural and magnetic characterization of the double perovskite  $Pb_2FeMoO_6$ . J. Mater. Chem. C. 2016; 4, 1533-1542.
- [2] D. Delmonte et al. Thermally activated magnetization reversal in bulk  $BiFe_{0.5}Mn_{0.5}O_3$ . Phys. Rev. B. 2013; 88, 014431.
- [3] D. Delmonte et al. Field effects on spontaneous magnetization reversal of bulk  $BiFe_{0.5}Mn_{0.5}O_3$ , an effective strategy for the study of magnetic disordered systems. J. Phys.: Condens. Matter. 2015; 27, 286002.
- [4] D. Delmonte et al. Poling-Written Ferroelectricity in Bulk Multiferroic Double-Perovskite  $BiFe_{0.5}Mn_{0.5}O_3$ . Inorg. Chem. 2016; 55, 12, 6308–6314.
- [5] M. Verseils et al. Effect of chemical pressure induced by  $La^{3+}/Y^{3+}$  substitution on the magnetic ordering of  $(AMn_3)Mn_4O_{12}$  quadruple perovskites. Phys. Rev. Materials 2017; 1, 064407.
- [6] M. Verseils et al. Centrosymmetry Breaking and Ferroelectricity Driven by Short-Range Magnetic Order in the Quadruple Perovskite  $(YMn_3)Mn_4O_{12}$ . Inorg. Chem. 2019; 58, 14204–14211.
- [7] R. Nechache et al. Bandgap tuning of multiferroic oxide solar cells. Nature Photon 2015; 9, 61–67
- [8] F. Orlandi et al.  $\gamma$ - $BaFe_2O_4$ : a fresh playground for room temperature multiferroicity. Nat. Commun. 2022; 13, 7968