

Synthetic investigation on structure-property relationships in the $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ quadruple perovskite system

S Bhoi¹, M LEGENDRE², C GOUJON², M JOSSE³, M SUCHOMEL⁴

¹*Institut de Chimie de la Matière Condensée de Bordeaux, PESSAC,* ²*Institut Néel UPR 2940, 38042 Grenoble FRANCE, Grenoble,* ³*University of Bordeaux, ICMCB, UMR 5026, 33600 Pessac, FRANCE, Pessac,* ⁴*ICMCB-CNRS UMR 5026, 33600 Pessac FRANCE, Pessac, France*
sub.bhoi@icmcb.cnrs.fr

Pressure assisted synthesis is a proven route for expanding the explorable range of phase space in order to discover and stabilize new metastable ABO_3 perovskite-type structures. Recently, a new class of complex perovskites termed quadruple perovskites (QPv) have been investigated for their unusual cation ordering and interesting ferroic properties [1]. One intriguing member of this family is $\text{CaMnTi}_2\text{O}_6$, which displays ferroelectric character ($T_{\text{FC}} = 630\text{K}$) and was previously reported by High-Pressure High-Temperature (HP-HT) synthesis methods at 1200°C - 1700°C and 7 GPa [2]. A recent work [3] showed that related Ca-rich compositions in the $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ series could be achieved at much lower pressures (100 MPa) using a Spark Plasma Sintering (SPS) approach. Our present study explores the optimized P-T synthesis conditions for compositions across the $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ series under a variety of different synthetic techniques (HP-HT, SPS, etc.). Furthermore, the effect of varying synthetic parameters (Ca/Mn ratio, pressure, temperature, SPS current, etc.) on competing phase stabilities, structural distortions, and cation ordering in $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ series of QPv is discussed. Finally, connections are proposed concerning the structure-property relationship, in particular for the ferroelectric transition temperature (T_{FC}) and dielectric permittivity response.

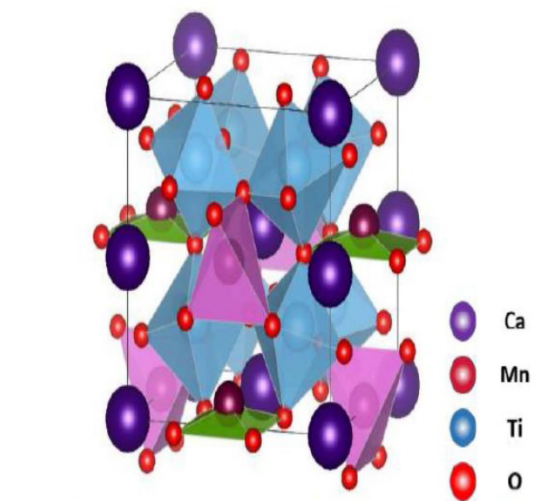


Figure 1. Schematic of $\text{CaMnTi}_2\text{O}_6$ structure. Light blue, pink and green polyhedral are for TiO_6 , tetrahedral- MnO_4 and square pyramidal- MnO_4 respectively.