Prospection of fragile ferroic phases through high pressure low temperature spark plasma sintering (SPS)

Thomas Herisson de Beauvoir, Michael Josse

For different applications, densification is a key point which condition the development of devices from functional materials. It’s the case for ferroic and multiferroic materials on which we have to deposit electrodes for the specific measurement of their dielectric properties. Looking for possibly multiferroic phases lead us to consider a wide range of materials exhibiting interesting crystal structures and compositions for potential ferroic properties. The common point of these materials is the difficulty to access high densification level (> 90% relative compactness) necessary for reliable dielectric characterizations. Spark plasma sintering (SPS) was mostly used up to now to sinter materials under high temperatures with fast ramp, applying mostly low pressures (often up to 100MPa). Yet the SPS technique offers the possibility to reach higher pressures that can be used to sinter ceramics at lower temperatures than in a classical sintering route. Starting from that point, we got interested in some materials having low decomposition temperatures (typically <700°C) preventing them from being sintered under classical conditions. We will refer to such compounds as "fragile" phases in the following. Up to now, not only did we managed to sinter fragile phases, but we also pointed out the SPS environment as a unique one implying very different stability domains for different phases. We were able to stabilize some phases at much higher temperatures than the classical stability range of the materials, from decomposition under air at 150°C to stability up to 350°C in the SPS environment for example. The conservation of the phases following sintering was confirmed by XRD, magnetic measurements, and ICP. By investigating different type of fragile ferroics, we established a proof of concept for the densification of fragile phases by low temperature SPS. We used the obtained ceramics to perform dielectric measurements within a PPMS, enabling the application of magnetic field during dielectric measurement to investigate the magnetoelectric response of our samples. Here we present the different phases we densified by SPS and the physical characterizations we performed on dense pellets. The presentation will be focused on two different fragile ferroics : an antiferromagnetic sulfate, potentially multiferroic, decomposing around 700°C, which was sintered via a metastable phase transition down to 400°C with a 93% compactness ; and a ferromagnetic carbonate, potentially multiferroic, stabilized up to 350°C in the SPS conditions while decomposing at 150°C under air. The two phases exhibit dielectric anomalies and one of them exhibit a magnetic field dependant capacitance with an hysteresis behaviour.