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Densification of $MnSO_4$ ceramics by Cool-SPS: evidences for a complex sintering mechanism and magnetoelectric coupling

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Abstract

Dense ceramics of $MnSO_4$ composition have been successfully densified at 400 °C in only 5 min under a uniaxial pressure of 400 MPa, using Spark Plasma Sintering technique. Since the stable form of $MnSO_4$ in ambient atmosphere is its hydrate $MnSO_4{\cdot}H_2O$, crystallizing in a different space group, dehydration is required to reach a purely anhydrous phase. *In situ* dehydration during Spark Plasma Sintering allows to lower both sintering temperature and time. Applied pressure strongly influences dehydration step and therefore is a key parameter to tune densification, so far as to obtain a dense $MnSO_4{\cdot}H_2O$ ceramic. The presence of a reversible phase transition to a β-$MnSO_4$ high temperature form seems to influence the dehydration temperature under pressure, and likely drives the sintering mechanisms. The high densification obtained, beyond 95 % of theoretical density, added to the preservation of the structural and physical properties of $MnSO_4$ after sintering allowed to perform reliable and reproducible measurements showing a dielectric anomaly associated to the magnetic transition, and the hysteretic behaviour of capacitance versus magnetic field, which is a clue for an intrinsic magnetoelectric coupling in $MnSO_4$.

Keywords: Spark Plasma Sintering; Ceramics; Magnetoelectric; Low temperature