Review on Cold Sintering of (K,Na)NbO_3 Ceramics

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The microstructure plays a dominant role in driving the electromechanical performance of polycrystalline piezoelectric materials. Below critical grain size, both the piezoelectric and dielectric properties are known to exhibit a rapid decline.[1] Above a certain grain size, the properties are found to be saturated.[2] Typically, the relationship between grain size and domain size is expressed as follows: Domain size α (Grain size)^m, m > ½ for grain size <1 μm.[3] Controlling grain size and shape is essential to achieve higher densification and theoretically predicted piezoelectric response.

Among lead-free materials, KNN ($K_{0.5}Na_{0.5}NbO_3$)-based compositions have gained attention due to their high ferroelectric-paraelectric transition temperature and intermediate ferroelectric-ferroelectric phase transition temperature. Traditional methods of densification and grain growth involve prolonged high-temperature soaking, which can make ceramics susceptible to alkali volatilization ultimately leading to poor electrical performance.

To mitigate alkali volatilization, cold sintering methods have been developed. These methods involve processing green compacts with external fluids to enhance intergranular wettability.[4,5] Unlike conventional sintering, cold sintering comprises of three stages: wetting of the green compact and partial dissolution of the ceramic composition, a dissolution-precipitation process, and subsequent grain growth through recrystallization.[4] One of the challenges in cold sintering is the excessive dissolution of ions, with alkali ions dissolving more rapidly in lower pH solvents, while 'B' site ions dissolve more readily in higher pH solvents.[5] The dissolution kinetics generally follows the sequence [K] > [Na] > [Nb] after a few hours of stabilization, regardless of temperature.[6] To maintain an appropriate pH balance and to regulate the dissolution of ions, typically deionized (DI) water is the primary choice as an external liquid phase for the cold sintering process. However, an excess of DI water can lead to the formation of a secondary phase ($K_4Nb_6O_{17}$) and result in poor densification.[7]

This review primarily focuses on the effect of the external liquid phase on the overall microstructure and phase formation of unmodified KNN composition along with the trends in the dissolution of ions as a function of pH of the solvents used. The study also explores the optimization of sintering conditions for achieving a saturated piezoelectric response as a function of grain size and distribution.

Reference:

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