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# The Influence of Alkaline Germanate Based Liquid Phase Sintering Aid on Microstructure and Phase Composition of $K_{0.5}Na_{0.5}NbO_3$ Ceramics

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Much of the current research in piezoceramics materials is oriented towards investigation of lead-free ceramics (such as alkaline niobates) as an environment-friendly alternative to commercially available lead-based ceramics. The major problems related to alkaline niobates are the synthesis and sintering. Stoichiometric $K_{0.5}Na_{0.5}NbO_3$ (KNN) densifies within an extremely narrow temperature window close to the solidus temperature at 1140°C. One way to improve the sinterability is by introducing additives with a melting point below the sintering temperature of KNN. It is known that the addition of Cu based additives lowers the sintering temperature of KNN down to 1060°C and results in a density of 97.5% of theoretical density (TD) [1]. We recently demonstrated that the addition of a (K, Na) - germanate sintering aid improves the densification of KNN ceramics as well and also preserves its piezoelectric properties [2]. The density of the modified KNN ceramics was 95.6 % of TD at 1000°C, which is more than 100°C lower than that usually required for pure KNN. However, the influence of alkaline germanates based liquid phase sintering aid on microstructure and consequently on electrical properties of KNN is not fully understood.

The aim of our work was to study the influence of (K,Na)-germanate liquid phase on the KNN microstructure and phase composition using the X-ray powder diffraction analysis (XRD), scanning (SEM) and transmission electron microscopy (TEM) methods. The compositions of KNN with the addition of 0.5, 1, 2, and 4 mass% of potassium sodium germanate were prepared. The powders were sintered at 1000°C/1100°C for 2 h/8h in air.

According to XRD analysis all samples annealed at 1000°C can be refined as a single perovskite with unit cell parameters corresponding to stoichiometric $K_{0.5}Na_{0.5}NbO_3$. Upon annealing at 1100°C the formation of two perovskites with slightly different unit cells was observed (Figure 1). Figure 2 shows the fracture surfaces of pure KNN and KNN modified with 4 mass% alkaline germanate (KNN + 4% Ge), after sintering at 1100°C for 2h. According to SEM analysis the microstructure of pure KNN consists of cuboidal shaped grains with bimodal grain size distribution ranging from a few micrometers up to 20µm. The addition of (K,Na)-germanate additive contributes to a uniform grain size distribution. In order to understand the influence of the alkaline germanates sintering aid on the mobility of the grain boundaries and phase composition of KNN, a detailed quantitative chemical analysis (EDS) by TEM and SEM microscope was performed. In this study the XRD, EDS, SEM and TEM results will be compared and discussed.

References

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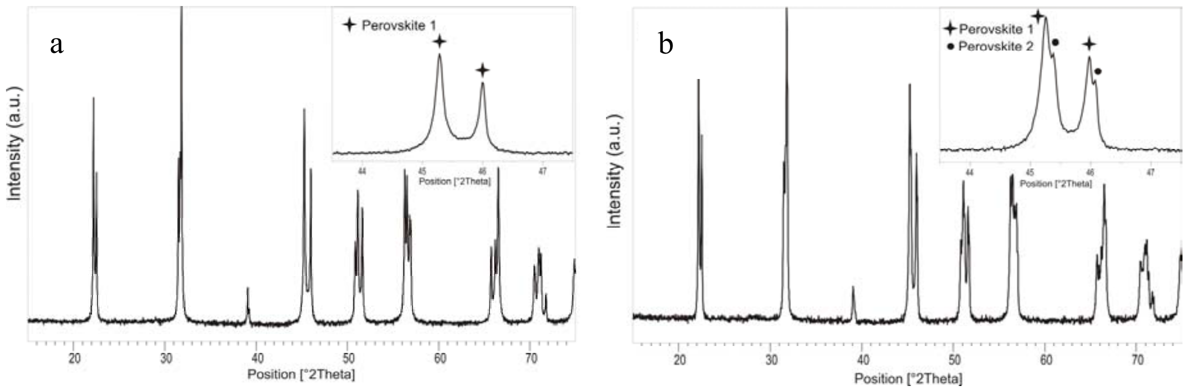


FIG. 1. XRD diagrams of KNN + 4% Ge after sintering at different temperatures for 8 hours. The sample annealed at 1000°C (a) is a single perovskite, as shown on the peaks of the (200) family (inset). The sample annealed at 1100°C (b) is a mixture of two perovskites with different unit cell parameters.

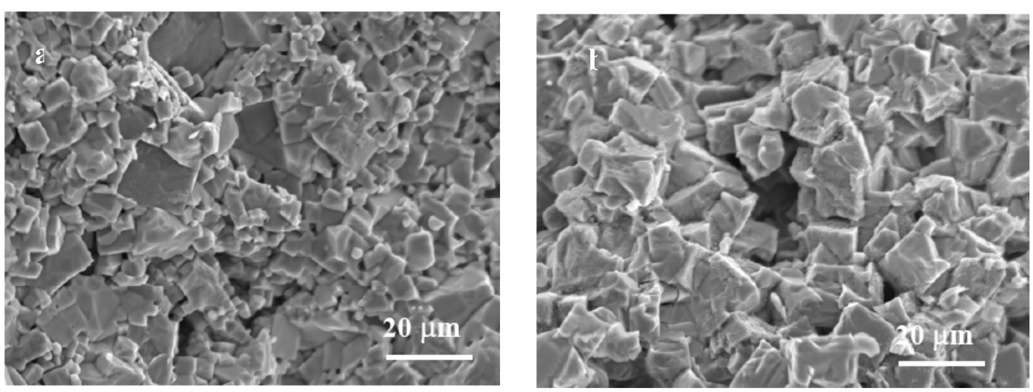


FIG. 2. SEM micrographs of fracture surfaces of pure KNN (a) and KNN + 4% Ge (b), after sintering at 1100$^{o}$C for 2 hours.

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