

Pb(Zn,Mg)_{1/3}Nb_{2/3}O₃-PbTiO₃ Relaxor Ferroelectric System : (I) Stabilization of Perovskite Phase and Densification Behavior

(Pb(Zn,Mg)_{1/3}Nb_{2/3}O₃-PbTiO₃ 완화형 강유전체 : (I) Perovskite 상의 안정화와 소결 특성)

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Single crystal of perovskite $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.1\text{PbTiO}_3$ (PZN-0.1PT) is a relaxor-type ferroelectric material and has the largest electromechanical coupling coefficient ($k_p \sim 0.92$) among all ferroelectric materials, together with excellent electrostrictive and dielectric properties near its morphotropic phase boundary (MPB). However, due to thermodynamic instability, it is virtually impossible to prepare pure PZN or PZN-0.1PT polycrystalline ceramics with perovskite structure.

In view of this, we have focused on the stabilization of perovskite phase in the (PZN-0.1PT)-based ferroelectric material by the addition of PMN, which is comparable to the perovskite PZN in its dielectric properties. For this purpose, 0.9(PZN-PMN)-0.1PT composite ferroelectrics were fabricated using the columbite precursor method. Phase relations and microchemical characteristics of the 0.9(PZN-PMN)-0.1PT pseudoternary system were investigated.

The addition of 40 mol % PMN to the PZN-0.1PT system stabilized perovskite phase by ~94 %. To fully stabilize perovskite phase and to enhance dielectric properties, excess addition of constitutive metal oxides (PbO, MgO, and ZnO) was made, and the resultant characteristics in the phase stabilization were examined. Sintered 0.9(PZN-PMN)-0.1PT specimen with approximately 100 %

perovskite phase was successfully obtained by the addition of 5 wt % excess PbO or 5 mol% excess MgO.

The formation of perovskite phase in the PZN-PMN system (prepared by the columbite route) is characterized by an initial rapid formation of Mg-rich perovskite phase, followed by a sluggish formation of Zn-rich perovskite phase. This conclusion was made by examining XRD patterns, EPMA spectra, and a temperature-dependence of dielectric permittivity of the PZMN (PZN-PMN) specimens prepared by the MN+ZN ($\text{MgNb}_2\text{O}_6 + \text{ZnNb}_2\text{O}_6$) precursors. The increase in the weight loss and the decrease in the sintered density of the PbO+MN+ZN specimen (above 1100 °C) was attributed to the decomposition of perovskite phase to form the Zn-rich pyrochlore phase and liquid PbO. On the other hand, due to the formation of pyrochlore phase of mixed divalent cations ($\text{Pb}_2(\text{Zn,Mg})_{0.32}\text{Nb}_{1.87}\text{O}_7$), the pyrochlore/perovskite transformation in the PbO+MZN ($(\text{Mg,Zn})\text{Nb}_2\text{O}_6$) precursor system proceeded uniformly with a spatial homogeneity in the microchemistry. Further analysis of the kinetic data suggested that the formation of perovskite phase from the pyrochlore matrix is a diffusion-controlled process.