C - 13

Densification Behaviors and Piezoelectric Properties of SiO_2, MnO_2-doped PNN-PT-PZ Ceramics

(SiO_2, MnO_2 첨가 PNN-PT-PZ 세라믹스계의 치밀화 거동과 압전특성)

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It has been known that, without degrading the piezoelectric properties, the sintering temperature of the PZT-based ceramics could be significantly reduced by the formation of $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ (referred to as PNN-PT-PZ) pseudoternary solid solution. Recently, Zhilun and his co-workers(*) demonstrated that, with the aid of suitable dopants (CdO, SiO_2, and MnO_2), the PNN-PT-PZ polycrystalline system could be sintered to a high density ($\rho \geq 7.8$ g/cm^3) at a temperature as low as 900 °C and showed the enhanced piezoelectric properties after sintering ($k_p = \sim 0.60$, $d_{33} = \sim 400 \times 10^{-12}$ C/N and $Q_m = \sim 1000$). They attributed the low-temperature sintering of PNN-PT-PZ specimens to a transient (intermediate) liquid-phase containing SiO_2/PbO. However, the effects and roles of each dopant (SiO_2, MnO_2 and CdO) on the densification/grain-growth and piezoelectric properties were not investigated. Furthermore, the nature of low-temperature liquid-phase sintering of the PNN-PT-PZ system was not clarified. In view of these, the main purpose of the present study is to elucidate the roles of additives (MnO_2, SiO_2, and CdO) in controlling densification/grain-growth behaviors and piezoelectric properties of the PNN-PT-PZ polycrystalline system at the MPB composition.

It was shown that the sintering of both the undoped (composition I) and doped specimens (SiO_2, MnO_2, and CdO) involved intergranular liquid phases. The addition of

SiO_2 (< 1 wt%) to PNN-PT-PZ specimen enhances densification, but suppresses grain growth significantly. The presence of Mn-oxide during sintering in air atmosphere expedites the rate of grain growth and leads to the enhanced formation of oxygen vacancies ($V\ddot{o}$), decreasing the piezoelectric constant (d_{33}) and increasing the mechanical quality factor (Q_m) significantly. Morphological features of polished microstructures further suggest that the grain growth of both SiO_2 and MnO_2-doped specimens is progressed by a diffusion-controlled process through the liquid phases formed during sintering. Neither the sintered density nor the rate of grain growth was affected by the addition of CdO. However, the presence of a small amount of CdO (~ 2 mol%) remarkably increases the relative dielectric permittivity (at 1 kHz) and the piezoelectric constant, practically acting as a softener in the PNN-PT-PZ pseudoternary system.

(*) G. Zhilun, L. Longtu, G. Suhua, and Z. Xiaowen,
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