305
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Microstructural Characteristics of $(Na_{0.5}K_{0.5})NbO_3$ Ceramics with Additives: Transmission Electron Microscopy Study

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$Na_{0.5}K_{0.5}NbO_3$ (NKN) has attracted much attention as an alternative to $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics and lead-free piezoelectric materials because of its high piezoelectric properties and a high Curie temperature (T_c) [1, 2]. However, the high sintering temperature for NKN is an obstacle for realizing multilayer devices because they require low driving force, miniaturization, and hybridization. Specifically, the NKN ceramics have to be sintered at around 900 °C because the melting point of silver (Ag), commonly used as an electrode in multilayer devices, is 961 °C and the Na_2O evaporates during the sintering process at temperatures above 1000 °C [3, 4].

One of the solutions proposed to these problems is to add a small amount of ceramic compounds whose melting points are lower than 900 °C as the sintering additives and to promote the low temperature sintering via liquid phase. A few research groups have reported that the NKN ceramics with additives, e.g. CuO and ZnO, had been successfully sintered at around 900 °C without any degradation of the piezoelectric properties [5-7]. They suggested that the interaction of ZnO and CuO would make the formation of the liquid phase, thus enhance the densifications of the matrix by the liquid phase sintering.

We have investigated the microstructures in NKN ceramics with additives (CuO, ZnO and the mixture) with transmission electron microscopy (TEM). As a new microstructural constituent, different types of pockets have been observed at the grain boundaries of NKN and also inside the NKN matrix. The characteristics of pockets were investigated from a microstructural point of view using various TEM techniques. The analysis of chemical elements in the pocket was carried out with energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) analysis. We found a CuO pocket as a new microstructural constituent when the CuO was introduced as an additive [8]. When the same methodologies were employed in order to understand the behaviors of the ZnO and CuO pockets when CuO and ZnO were added to the NKN ceramics (NKNCZ), two types of pockets, composed of CuO and ZnO as a dominant component, were observed in the microstructure as new microstructure constituents (Fig. 1). When the additive content of ZnO was increased to 3.0 mol%, there are interactions between CuO and ZnO and both elements are found in the compound pocket. The sintering kinetics was enhanced by the presence of both additives. In Figs. 2(b) and 2(c), the phase present in the pocket was identified as ZnO [hexagonal, P63mc (186), a = 3.250 Å, c = 5.207 Å; JCPDS number 36-1451], and the diffraction pattern was indexed along the zone axis of $[2\bar{1}\bar{1}0]$. The pockets were melted partially or completely by the interactions with element Na in the matrix which has formed a eutectic compound whose melting point is lower than the sintering temperature. The reaction starts at the interfaces between the pocket and matrix and the kinetics depends not only on the size of the pocket but also on the environments where the pockets are located [9].

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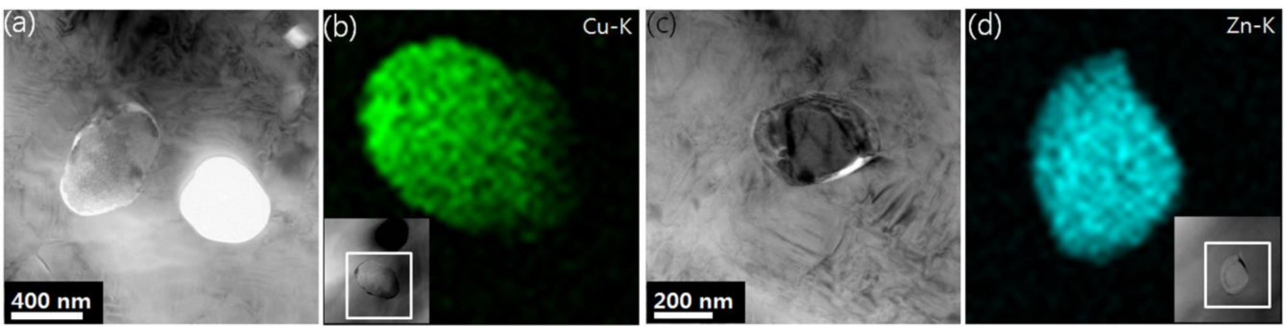

Figure 1. (a) and (c) BFTEM images NKNCZ ceramic sintered at 920 °C for one hour with 1.5 mol% CuO and 3.0 mol% ZnO showing the compound pocket. (b) and (d) Local elemental mappings by the EDS analysis, Cu-K and Zn-K, in the liquid pockets in (a) and (c).

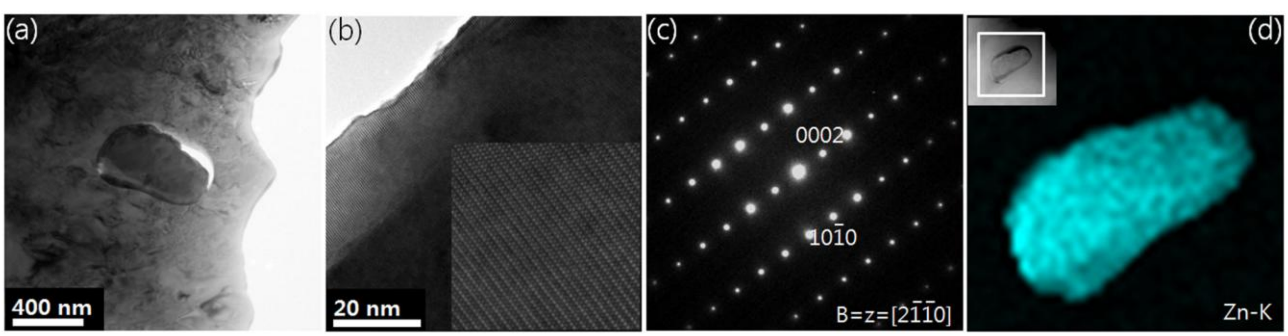

Figure 2. (a) BFTEM image taken under multi-beam diffraction condition. (b) HRTEM image of the pocket. (c) Selected area electron diffraction (SAED) pattern taken from the pocket. (d) Local elemental mappings by the EDS analysis, Zn-K.