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Effects of dwell time during sintering on electrical properties of $0.98(K_{0.5}Na_{0.5})NbO_3$−$0.02LaFeO_3$ ceramics

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Abstract: The effects of dwell time on the phase structure, microstructure, and electrical properties were investigated for the $0.98(K_{0.5}Na_{0.5})NbO_3$−$0.02LaFeO_3$ ceramics (abbreviated as 0.98KNN−0.02LF). All the ceramics sintered for different dwell time are of pure phase and the peak intensity of the 0.98KNN−0.02LF ceramics becomes stronger with a longer dwell time. Denser microstructures with larger grain size are developed for the sample with a longer dwell time. The maximum dielectric permittivity decreases with increasing the dwell time, and the deteriorative dielectric properties are due to the increasing grain size and the domain wall motion. Ferroelectric properties results indicate that $2P_r$ value slightly decreases with increasing the dwell time, while the $2E_c$ value increases. Consequently, the 0.98KNN−0.02LF ceramic sintered at 1150 °C for 2 h shows optimum dielectric properties (ε_r=2253 and tan δ<5%) and ferroelectric properties ($2P_r$=34.51 μC/cm^2 and $2E_c$=5.07 kV/mm).

Key words: $(K_{0.5}Na_{0.5})NbO_3$; dwell time; dielectric properties; ferroelectric property; lead-free ceramics

1 Introduction

Recently, high temperature relaxor ferroelectrics have received considerable attention because they are potential candidates for high temperature ceramics capacitor [1−4]. $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based ceramics could be regarded as promising candidate materials for high temperature lead-free relaxor ferroelectrics. Relaxor behavior has been observed in systems, such as $(1-x)$KNN−xBaTiO$_3$ (x>0.10) [5], $(1-x)$KNN−xSrTiO$_3$ (x>0.15) [6−8], $(1-x)$KNN−xSrZrO$_3$ (x>0.15) [9], $(1-x)$KNN−xBiScO$_3$ (x>0.04) [10]. Among them, $(1-x)(K_{0.5}Na_{0.5})NbO_3$−$x(Ba_{0.5}Sr_{0.5})TiO_3$ ceramics are high temperature lead-free relaxor ferroelectrics and the 0.90KNN−0.10BST ceramics show a broad dielectric peak with the permittivity maximum near 1500 and low dielectric loss (<4%) in the temperature range of 25−350 °C [11]. Unfortunately, the dielectric permittivity and usage temperature range still cannot satisfy the requirement for preparing the high temperature ceramics capacitor. In order to further improve the dielectric relaxor properties of KNN ceramics, $LaFeO_3$ was added into KNN ceramics, 0.98KNN−$0.02LaFeO_3$ (LF) ceramic shows optimum dielectric properties that the dielectric permittivity maximum is near 2000 and dielectric loss is less than 4% in the temperature range of 21−400 °C [12].

It is well-known that the properties of KNN-based ceramics are extremely sensitive to the processing conditions, especially the sintering temperature [13−15]. So far, KNN-based ceramics are mostly prepared within a narrow processing window in terms of sintering temperature [16,17]. Effects of heating rate on the phase structure, microstructure evolution, and electrical properties of KNN-based lead-free ceramics have also been reported [18]. Until now, however, the investigations of the effects of dwell time on 0.98KNN−0.02LF ceramics are rare. For the ceramic sintering, the effect of dwell time is not as important as the sintering temperature. However, we cannot neglect the effects of the dwell time on optimizing and improving the capabilities of the ceramic. It is known that suitable dwell time can ensure temperature uniform in ceramics in every sintering temperature region and offer sufficient time for grain growth and homogeneity of microstructure [19]. When the dwell time is too long or too short, there are many problems. Too long dwell time

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can increase the abnormal grain growth, which may cause the inhomogeneous grain and deteriorate dielectric properties; while, a shorter dwell time can inhibit the grain to well grow and increase the defects of crystal lattice.

Based on the above-mentioned considerations, high quality 0.98KNN−0.02LF ceramics were produced by a conventional solid-state sintering method in the present work. The aim of this work is to investigate the effects of dwell time on the phase structure, microstructure, and electrical properties of 0.98KNN−0.02LF ceramics.

2 Experimental

The 0.98KNN−0.02LF ceramics were prepared by using the conventional solid-state sintering method. Reagent-grade oxide and carbonate powders of K_2CO_3, Na_2CO_3, Nb_2O_5, La_2O_3, and Fe_2O_3 were used as the starting materials. Before being weighed, these powders were first separately dried in an oven at 110 °C for 5 h. They were milled for 24 h using planetary milling with zirconia ball media and alcohol. After drying, the mixed powder was calcined in an alumina crucible at 950 °C for 5 h. These calcined powders were ball-milled again for 12 h, then dried and pressed into disks of 12 mm in diameter and 1 mm in thickness under 300 MPa using polyvinyl alcohol (PVA) as a binder. After burning off PVA, the pellets were finally sintered at 1150 °C for variable dwell time in the sealed Al_2O_3 crucibles. The obtained samples were polished. Silver paste was fired on both sides of the samples at 810 °C for 20 min as the electrodes for the sake of measurements.

The phase structures of the sintered ceramics were examined using X-ray powder diffraction analysis with a Cu K_α radiation (Philips X-Pert ProDiffractometer, Almelo, The Netherlands) at room temperature. The microstructure evolution was observed using a scanning electron microscope (SEM) (model JSM−6360, JEOL, Japan). The dielectric spectrum measurements were performed using the LCR meter (Agilent E4980, USA) at a heating rate of 3 °C/min in a temperature range of 21−520 °C and a frequency range of 1−1000 kHz.

3 Results and discussion

Figure 1 shows the room temperature XRD patterns of 0.98KNN−0.02LF ceramics with different dwell time during sintering. The patterns reveal that all samples are pure pseudo-cubic perovskite phase and no secondary impurity could be detected in the 2θ range detected. The XRD peaks are found to be sharp and distinct, indicating good homogeneity and crystallinity of the samples. It also can be seen that the diffraction peak positions of the 0.98KNN−0.02LF ceramics do not change with the variation of dwell time. The inset is the enlarged XRD patterns of 0.98KNN−0.02LF ceramics sintered for different dwell time. It can be seen that the peak intensity of the 0.98KNN−0.02LF ceramic sintered for a dwell time of 5 h is stronger than that of ceramic with other dwell time; the peak position of 0.98KNN−0.02LF ceramics is shifted to a lower angle with increasing the dwell time, and the spacing distance increases gradually, which can be deduced by Bragg's equation, $2d\sin\theta=k\lambda$.

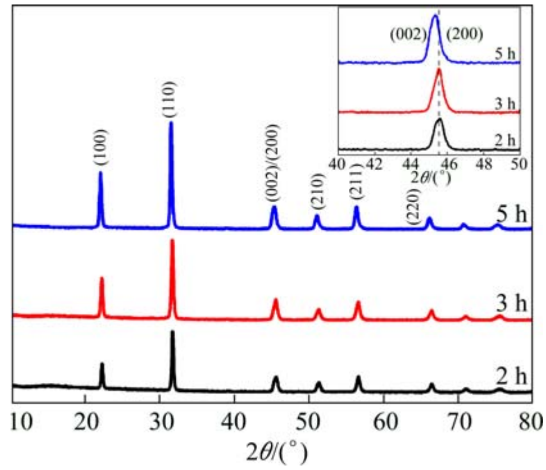

Fig. 1 XRD patterns of 0.98KNN−0.02LF ceramics sintered with different dwell time (the inset is the enlarged XRD patterns)

Figure 2 shows SEM images of surface microstructure for 0.98KNN−0.02LF ceramics sintered for different dwell time. As shown in Fig. 2(a), the grain sizes are distinctly smaller and more uniform compared with Figs. 2(b) and (c). The average grain size is about 1 μm for the sample sintered for the dwell time of 2 h and some distinct pores are found at grain boundaries. In Figs. 2(b) and (c), the samples show in general a bimodal grain size distribution. The small grain sizes are 1.0−2.0 μm and the coarse grain sizes are 3.0−5.0 μm for the sample sintered for the dwell time of 3 h, and the small grain sizes are 1.0−2.5 μm and the coarse grain sizes are 4.0−5.0 μm for the sample sintered for the dwell time of 5 h. Size increase is noted for the samples sintered for 3 h and 5 h. According to the phenomenological kinetic grain growth equation, with the increase in dwell time, grain size increases [19]. Moreover, it is clearly found that the pores are gradually decreased with increasing the dwell time. This result demonstrates that the dwell time has a great influence on the microstructure evolution of 0.98KNN−0.02LF ceramics.

Figure 3 shows the bulk density (BD) of 0.98KNN−0.02LF ceramics sintered for different dwell time with increasing the dwell time from 2 h to 5 h, the bulk density slightly increases from 4.26 g/cm^3 to 4.29 g/cm^3. This evolution agrees well with the $LiTaO_3$-

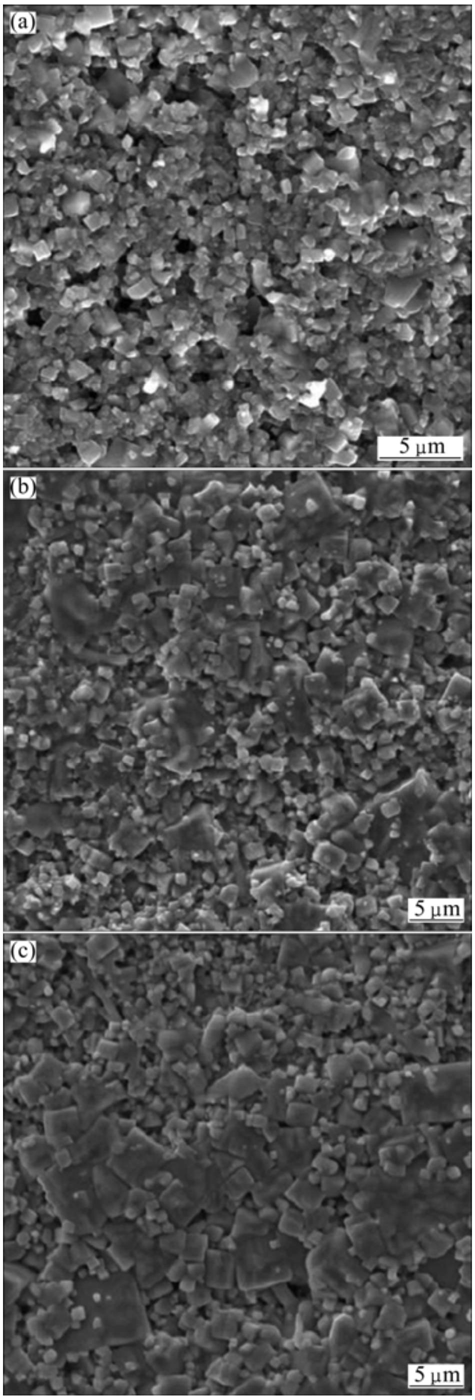

Fig. 2 SEM images of surface microstructure for 0.98KNN−0.02LF ceramics sintered for different dwell time: (a) 2 h; (b) 3 h; (c) 5 h

modified KNN ceramics that an increase of density is observed for dwell time of 10 h [20]. This is because these pores gradually decrease with increasing the dwell time. The average grain size and the density of this ceramic tend to increase with increasing the dwell time, probably because the grain growth is controlled by the boundary diffusion [21]. This indicates that the sintering process can enhance the diffusion and promote the densification of the sample.

Different microstructures may affect the electrical properties. Figure 4 provides the temperature dependent of dielectric permittivity (ε_r) and dielectric loss (tan δ) for 0.98KNN−0.02LF ceramics with different dwell time during sintering (measured at 10 kHz). It can be observed in Fig. 4(a) that the maximum dielectric permittivity decreases with increasing the dwell time, but the phase transition temperature is unmodified. These results agree well with the XRD patterns and indicate

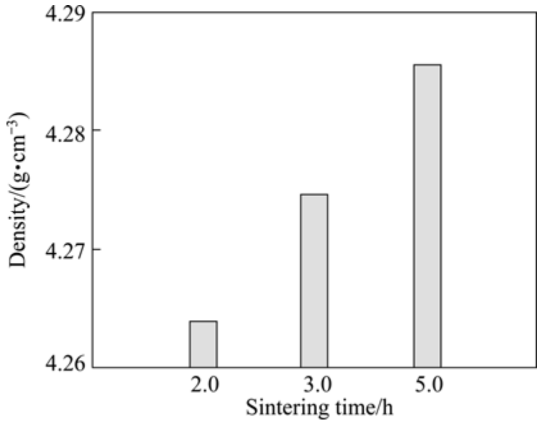

Fig. 3 Bulk density of 0.98KNN−0.02LF ceramics sintered for different dwell time

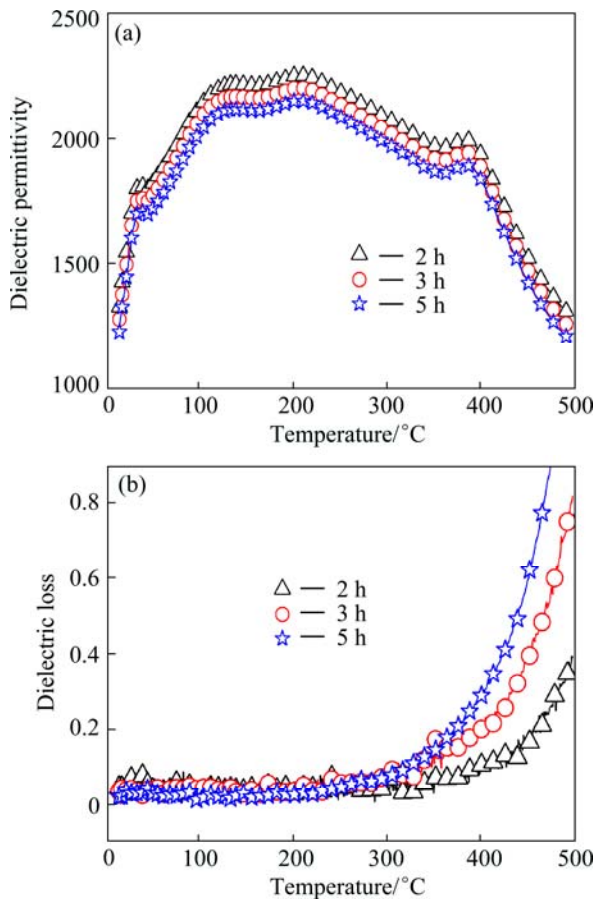

Fig. 4 Temperature dependence of dielectric permittivity (a) and dielectric loss (b) for 0.98KNN−0.02LF ceramics sintered for different dwell time (measured at 10 kHz)

that there are no secondary impurities occurring. The decreased ε_r value can be attributed to the larger grain size with increasing the dwell time. It is well known that the piezoelectric and dielectric properties drop rapidly below a critical grain size and reach saturation at a larger grain size [22]. With increasing the grain size, the contribution from extrinsic effects, i.e. domain wall motion, will increase. It can be observed in Fig. 4(b) that the dielectric loss slightly decreases with increasing the dwell time when the temperature is below 400 °C; the dielectric loss increases rapidly with increasing the dwell time when the temperature is beyond 400 °C owing to the conductive loss. A similar behavior has also been observed in PZT−PCN systems [23]. According to Fig. 4, the dielectric permittivity maximum (ε_{max}) of 0.98KNN-0.02LF ceramics under the optimum dwell time has a value of approximately 2253 and tan δ is lower than 5% at a broad usage temperature range (100−400 °C). These results indicate its potential application in high temperature multilayer ceramics capacitor field.

Figure 5(a) shows the plot of the *P*—*E* loops of 0.98KNN− 0.02LF ceramics sintered for different dwell time, measured at room temperature and the frequency of 1 Hz. Saturated *P*—*E* hysteresis loops are demonstrated for all 0.98KNN−0.02LF ceramics in the present work. Generally, the existence of *P*—*E* hysteresis loops is considered an evidence that the material is ferroelectrics. In this study, the saturated *P*—*E* hysteresis loops confirm the ferroelectric nature of 0.98KNN−0.02LF ceramics. Figure 5(b) shows the $2P_r$ and $2E_c$ values of 0.98KNN−0.02LF ceramics sintered at different dwell time. The observed $2P_r$ value slightly decreases with increasing the dwell time, giving a maximum value of 34.51 μC/cm^2 with a dwell time of 2 h. Different from $2P_r$, the observed $2E_c$ value increases from 5.07 kV/mm to 6.08 kV/mm with the increase of dwell time (from 2 h to 5 h).

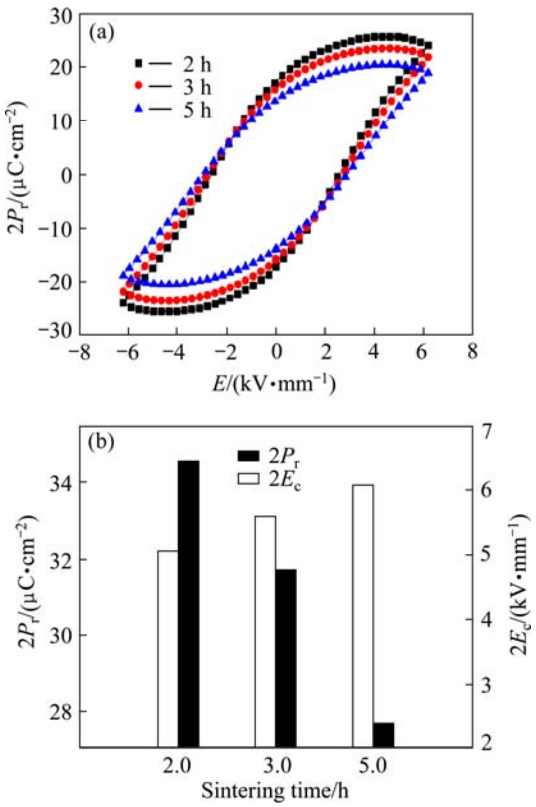

Fig. 5 *P*—*E* loops (a) and $2P_r$ and $2E_c$ values (b) of 0.98KNN−0.02LF ceramics sintered for different dwell time (measured at room temperature and frequency of 1 Hz)

4 Conclusions

1) The 0.98KNN−0.02LF lead-free ceramics sintered with different dwell time were prepared by the conventional solid-state sintering method. The phase structures in all samples are pure pseudo-cubic perovskite. The dwell time affects the microstructure and density of 0.98KNN−0.02LF ceramics. An increased bimodal grain size distribution and bulk density are observed for the samples prepared with increasing the dwell time.

2) The ε_{max} and $2P_r$ values of 0.98KNN−0.02LF ceramics decrease, and the $2E_c$ value increases with increasing the dwell time. The optimum dwell time for 0.98KNN−0.02LF ceramics should be 2 h. Dielectric properties of 0.98KNN−0.02LF ceramics under the optimum dwell time are ε_r=2253 and tan δ<5% and ferroelectric properties are $2P_r$=34.51 μC/cm^2 and $2E_c$=5.07 kV/mm.

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保温时间对 $0.98(K_{0.5}Na_{0.5})NbO_3$−$0.02LaFeO_3$ 陶瓷电性能的影响

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摘 要：研究保温时间对 $0.98(K_{0.5}Na_{0.5})NbO_3$−$0.02LaFeO_3$(缩写为 0.98KNN−0.02LF)无铅陶瓷相结构、显微组织、介电性能及铁电性能的影响。所有烧结样品均为纯的伪立方钙钛矿相，保温时间对相结构影响不大。随着保温时间的延长，样品的 XRD 衍射峰逐渐增强，并且向低角度移动。SEM 观察结果显示，随着保温时间的延长，陶瓷样品的致密性提高，晶粒异常长大并出现孪晶结构。介电温谱表明，随着保温时间的延长，介电性能有所降低。电滞回线结果表明，$2P_r$ 随着保温时间的延长而增大的程度有所减小，而 $2E_c$ 略有增加。在 1150 °C 烧结 2 h 得的到陶瓷的性能较优：ε_r=2253，tan δ<5%，$2P_r$=34.51 μC/cm^2，$2E_c$=5.07 kV/mm。

关键词：铌酸钾钠；保温时间；介电性能；铁电性能；无铅陶瓷

(Edited by Hua YANG)