Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Hardening behavior and highly enhanced mechanical quality factor in $(K_{0.5}Na_{0.5})NbO_3$–based ceramics

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ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form 7 January 2017
Accepted 9 January 2017
Available online xxx

Keywords:
Lead-free
Piezoelectric ceramics
KNN
Hardening effect
Mechanical quality factor

ABSTRACT

This paper relates the microstructure, crystallographic structure, ferroelectric, and piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics modified with 0.38 mol% $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (KCT) and different amounts of CuO. Results revealed that the addition of KCT and CuO were effective in enhancing the sinterability of KNN. The internal bias field (E_{ib}) increased from 0.3 kV/mm to 0.58 kV/mm at 0.5 mol% CuO–added KNN+KCT ceramics. The increase of E_{ib} corresponds very well with the observed increase of the mechanical quality factor (Q_m) from 112 to 2665 for 0.5 mol% CuO. Besides, addition of 0.5 mol% CuO to KNN+KCT resulted in a large increase of the EPR signal, which is related to the increased amount Cu^{2+} and a corresponding increase of the concentration of defect dipoles. This result is in good agreement with the increased E_{ib} and the resulting hardening behavior.

1. Introduction

$K_{0.5}Na_{0.5}NbO_3$ (KNN)–based lead–free piezoelectric ceramics have attracted much attention as promising candidates to replace widely–used lead–based materials. Excellent piezoelectric properties, such as a large piezoelectric constant (d_{33} = 416 pC/N) and a large planar coupling factor (k_p = 0.61) were reported in textured KNN–based ceramics by Saito et al. in 2004 [1]. Since then, a large number of KNN–based lead–free piezoelectric materials have been reported [2–5]. However, most studies were focused on enhancing d_{33} and k^2 by using the polymorphic phase boundary (PPB) concept and piezoelectrically–soft materials [6,7]. On the other hand, comparably less studies reported hard–type KNN–based materials, despite their potential for the use in high-power or resonance applications (*i.e.*, sensors, ultrasonic motors, transformers) [8–13].

In the case of high–power or high–frequency applications, hard–type piezoelectric materials with low dielectric loss, high mechanical quality factor (Q_m), high elastic hardness as verified by high frequency constant (N_p), and high electromechanical coupling factor (k^2) are required [14,15]. Piezoelectric hardening refers to the process of stabilization of the ferroelectric domain structure and clamping of the domain walls. This is typically achieved by one of the following mechanisms: reorientation of defect dipoles within the bulk of a domain (volume effect), agglomeration of charged defects at the domain walls (domain effect), or formation of space charge layers at grain boundaries (grain boundary effect) [16]. Among the most widely–used approaches to achieve the hardening effect is B–site acceptor doping with aliovalent dopants. For example, substitution of the B–site Zr^{4+}/Ti^{4+} with Fe^{3+} or $Mn^{3+,2+}$ in $Pb(Zr,Ti)O_3$ (PZT) results in the formation of charge–compensating oxygen vacancies, which subsequently pair with the acceptor–type dopants to form defect dipoles. These defect dipoles align parallel to the polarization direction, leading to the formation of an internal bias field (E_{ib}), which influences the domain wall mobility [14,16–23].

In the case of the lead–free KNN system, promising modifications were achieved by the addition of Cu, for example in the form of $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (KCT) [15,24–26], $K_4CuNb_8O_{23}$ (KCN) [27–29], or CuO [30,31], which improved the densification and additionally enhanced both Q_m and k_p from 90 and 34% in pure KNN to 1300 and 40% in 0.38 mol% KCT–added KNN, respectively [24]. This system could be further modified by adding CuO, which resulted in very high Q_m values (>3000) [32]. The hardening mechanism in CuO–doped KNN materials was investigated in detail by Eichel

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.01.013
0955-2219/

et al. using the electron paramagnetic resonance (EPR) analysis [33,34]. The divalent acceptor ion Cu^{2+} was found to incorporate into the Nb^{5+}–site and additionally form 3/2 oxygen vacancies $V_o^{\bullet\bullet}$. This situation results in the formation of two types of defect dipoles, namely the trimeric defect complex $(V_o^{\bullet\bullet}–Cu_{Nb}''' – V_o^{\bullet\bullet})^{\bullet}$ with a primarily elastic dipole moment impacting the electromechanical properties, and the dimeric defect complex $(Cu_{Nb}''' – V_o^{\bullet\bullet})'$ with an electric dipole moment in addition to an elastic distortion, which can impede domain–wall motion and may contribute to ferroelectric hardening [34]. However, it should be noted that the Cu–containing additives also considerably enhance the densification of KNN–based materials. For example, addition of CuO or KCT was found to increase the relative density of pure KNN from 92.4% to over 95% [26,35]. Due to the twofold effect of Cu addition it is therefore often not clear if the enhanced properties are merely due to acceptor doping or also partially due to increased relative density.

This work provides a systematic investigation of the microstructure, crystallographic structure, ferroelectric, and piezoelectric properties of KNN ceramics modified with 0.38 mol% KCT and 0–2 mol% CuO. Variation of the internal offset electrical bias field was investigated and evaluated with respect to the observed enhancement in Q_m. To better understand the influence of CuO on the changes in E_{ib} and Q_m, we investigated the incorporation of Cu^{2+} into the octahedral environment at the perovskite B-site by using the electron paramagnetic resonance (EPR) analysis. Details of the resonance measurement technique for determining Q_m were evaluated to allow for more precise comparison to values observed in previous studies.

2. Experimental procedure

The $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (KCT) powders were prepared separately by the conventional solid–state reaction from K_2CO_3 (Alfa Aesar, 99%), Na_2CO_3 (Alfa Aesar, 99.5%), Nb_2O_5 (Alfa Aesar, 99.9%), Ta_2O_5 (Alfa Aesar, 99.85%), and CuO (Alfa Aesar, 99.7%). In both cases the carbonate starting powders were dried to remove the moisture at 100 °C for 24 h. Subsequently all powders were weighed in a stoichiometric ratio, planetary ball–milled for 5 h in ethanol, and dried for 24 h. The KNN and KCT were calcined at 880 °C for 6 h and 900 °C for 4 h, respectively. The synthesized powders were carefully processed and immediately stored in a desiccator after they were dried to prevent the well-known problem of hygroscopicity [36]. Subsequently, 0.38 mol% of calcined KCT and x mol% of as–purchased CuO (x = 0, 0.5, 1.0, 1.5, and 2 mol%) were added to the calcined KNN powder, mixed with polyvinyl alcohol (10 wt%) as a binder, and then uniaxially pressed under 98 MPa into green disks with diameter of 10 mm. These green disks were sintered at temperatures between 1050 °C and 1130 °C for 4 h in air with a heating rate of 5 °C/min. The samples will be further abbreviated as KNN+KCT+xCuO.

The density of the sintered samples was measured by the Archimedes method. The crystal structure was characterized by X–ray diffractometer (XRD, AXS D8, Bruker Corporation, Germany) and the surface morphology of ground, polished, and thermally–etched samples were imaged using scanning electron microscopy (SEM, XL 30 FEG, Philips Corporation, Eindhoven, The Netherlands). For electrical measurements, the circular surfaces of the sintered samples were ground, polished, and covered by a silver paste, which was subsequently burned–in at 400 °C for 1 h. The samples were poled at 125 °C in silicone oil bath by applying a DC electric field of 4 kV/mm for 30 min and subsequently field–cooled to room temperature. All electrical measurements were performed 24 h after poling. The temperature–dependent dielectric permittivity (ε_r) and dielectric loss ($\tan\delta$) of poled samples were recorded using an impedance analyzer (HP4192A, Agilent Technologies, Santa Clara, CA, USA) attached to a furnace. The measurement frequencies ranged from 1 kHz to 1 MHz and the investigated temperature range was 25–550 °C. Field–dependent polarization (P–E) hysteresis loops were obtained using the commercial aixPES setup (aixACCT Systems GmbH, Aachen, Germany), which is equipped with a laser interferometer to simultaneously measure the strain hysteresis (S–E). The electromechanical coupling factor (k^2) and mechanical quality factor (Q_m) were evaluated by the resonance–antiresonance method using an impedance analyzer (Alpha–A High Performance Frequency Analyzer, Novocontrol Technologies, Germany) and a spring–loaded test fixture (Agilent 16034E, Agilent Technologies, Santa Clara, CA, USA), following the European Standard (EN 50324–2) [37]. The k^2, Q_m, and N_p were calculated using the equations below [37]:

$$\frac{1}{k^2} = 0.395\frac{f_r}{f_a - f_r} + 0.574 \quad (1)$$

and

$$Q_m = \frac{1}{2\pi f_r |Z| C_f \left\{1 - \left(f_r/f_a\right)\right\}^2} \quad (2)$$

and

$$N_p = f_r \cdot l \quad (3)$$

where f_r is the resonance frequency, f_a the antiresonance frequency, $|Z|$ the impedance at the resonance frequency, and C_f the capacitance at 1 kHz, and l is diameter of the sample. Note that the above equations are only valid for piezoelectric resonators with low losses, which satisfy the condition $M > 20$ [37]. The figure of merit M is calculated as:

$$M = Q_m \frac{k_{eff}^2}{1 - k_{eff}^2} > 20 \quad (4)$$

here $k_{eff}^2 = (f_a^2 – f_r^2)/f_a^2$ is the effective electromechanical coupling factor. The frequency–dependent impedance and phase angle values were measured using an applied electric field of 0.01 V/mm.

X–band (9.86 GHz) continuous-wave EPR measurements were performed with a Bruker EMX spectrometer and a super high–Q cavity (Bruker Corporation, Germany). The offset in the magnetic field and the exact g–factors in X–band measurements were determined with a polycrystalline DPPH (2–diphenyl–1–picrylhydrazyl) reference sample with well–known g–factor (g = 2.0036).

3. Result and discussion

The KNN+KCT samples with different amount of CuO were all sintered over a wide range of temperatures in order to determine the optimal sintering condition. Fig. 1 (a) summarizes examples of the variety of attempted sintering conditions for three different compositions investigated in order to achieve the sample density above 98%, as symbolized by the dashed line. In Fig. 1 (b), the final sintering temperature as a function of CuO content is shown with a second axis representing the final achieved densities at these temperatures. Increasing the amount of the added CuO reduced the required sintering temperature for achieving a relative density ≥98% from 1125 °C for pure KNN+KCT to 1075 °C for 2 mol% CuO. The highest relative density (over 99%) was obtained for the sample with 1.5 mol% CuO sintered at 1100 °C.

Fig. 2 provides SEM micrographs of ground, polished, and thermally–etched microstructures of CuO–added KNN+KCT ceramics, sintered at the previously–defined optimal temperatures for 4 h. All samples exhibit dense microstructures, confirming the density measurements (Fig. 1). The smallest average grain size of 1.8 μm was determined for the 0.5 mol% CuO–added KNN+KCT

Please cite this article in press as: H.-S. Han, et al., Hardening behavior and highly enhanced mechanical quality factor in $(K_{0.5}Na_{0.5})NbO_3$–based ceramics, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.01.013