Materials Letters 175 (2016) 300–304

Contents lists available at ScienceDirect

Materials Letters

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

Temperature dependence of mechanical degradation in lead-free alkali niobate ceramics under unipolar loading

Alexander Martin [a,*], Ken-ichi Kakimoto [a], Keiichi Hatano [b], Yutaka Doshida [b]

[a] Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[b] Materials R&D Department, R&D Laboratory, Taiyo Yuden Co., Ltd., Takasaki, Gunma 370-3347, Japan

ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form
4 March 2016
Accepted 19 March 2016
Available online 6 April 2016

Keywords:
Actuators
Fatigue
Flexural strength
Lead-free
Phase transformation

ABSTRACT

Piezoelectric actuators are used under high electric fields, which can cause crack formation as a consequence, and therefore require sufficient mechanical properties to guarantee long lifetime and reliability. We measured the flexural strength before and after unipolar fatigue under different temperatures of undoped $Li_{0.06}Na_{0.52}K_{0.42}NbO_3$ (LNKN6) and the same compound with additives (LNKN6-A). Before performing fatigue tests, the flexural strength σ_0 was 111 MPa and 177 MPa for LNKN6 and LNKN6-A, respectively. After electric cycling over a certain amount of time, only slight changes in the piezoelectric properties were observed. However, mechanical degradation appeared in LNKN6 whereas LNKN6-A remained the as-poled flexural strength throughout each test. The results suggest that a smaller grain size is an advantage in case of crack formation during unipolar fatigue. In addition, LNKN6 showed after cycling a bimodal Weibull distribution. Under room temperature, the highest mechanical degradation of about 35% was observed. Noteworthy is the fact that after 50°C, less mechanical degradation was observed. It is suggested, that phase transition from tetragonal to orthorhombic lead to improved mechanical properties.

1. Introduction

Piezoelectric ceramics in actuator applications, such as fuel injectors, nanopositioners and pulse drive, demonstrate high efficiency, unlimited resolution and ultrahigh accelerations [1–3]. The coupling of mechanical strains with high electric AC fields, lead to decreases in piezoelectric and dielectric properties of lead zirconate titanate (PZT) after a certain amount of electric cycles. Two main processes can be deduced as the main reason for fatigue during unipolar cycling. The first is space charge accumulation, which describes the shift of space charges due to a depolarization field and their accumulation at the grain boundary. The second and more critical process is micro crack formation. Besides causing a decrease in the electric and piezoelectric properties, additional degradation in the mechanical strength occurs [4,5]. On PZT, many studies have shown that cracks form and propagate in piezoelectric ceramics under cyclic electric fields in dependence of grain size [6] and temperature [7].

Doped $Na_{0.5}K_{0.5}NbO_3$ (NKN), such as $[Li_x(Na_{0.5}K_{0.5})_{1-x}NbO_3]$ (LNKN), are promising lead-free alternatives. LNKN ceramics have a lower permittivity ε than PZT and consequently do not generate much heat during application [8]. Furthermore, LNKN ceramics can be cofired with Cu [9] and have high piezoelectric properties and Curie temperature (T_C=460°C) [10,11]. Therefore, these materials are promising for industrial applications, such as multilayer actuators under high temperature conditions. However, only a few publications dealt with the fatigue behavior of alkali niobate ceramics and none of them observed the mechanical degradation under high electric fields [12].

For this reason we measured the changes in flexural strength of LNKN ceramics after unipolar fatigue tests at different temperatures.

2. Experimental procedure

For fatigue tests under AC loading two different materials were used: $Li_{0.06}Na_{0.52}K_{0.42}NbO_3$ (LNKN6) and $Li_{0.06}Na_{0.52}K_{0.42}NbO_3$ with additives: 0.65 mol% Li_2CO_3, 1.3 mol% SiO_2, 0.2 mol% $MnCO_3$, 0.5 mol% $SrCO_3$, and 0.5 mol% ZrO_2 (LNKN6-A). More information about the materials can be found in [13]. The ceramic samples were rectangular bars with a thickness of about 0.6 mm, width of 2.1 mm, and length of 10 mm. The bulk densities were determined via the Archimedes method, before coating the largest surfaces with silver and annealing the samples at 700°C for 5 min. Subsequently, the samples were poled in silicone oil under an applied

* Corresponding author.
E-mail address: martin.alexander@nitech.ac.jp (A. Martin).

http://dx.doi.org/10.1016/j.matlet.2016.03.103
0167-577X/

electrical field of $E=3$ kV/mm for 30 min and a temperature of 100°C for LNKN6 and 150°C for LNKN6-A. The samples were cooled down to 40°C with the electric field still switched on. The piezoelectric constants d_{33} and d_{31} were estimated using a Berlincourt-type quasistatic meter (Academia Sinica ZJ-6B) and by resonance and antiresonance methods based on IEEE standards using an impedance analyzer (Agilent 4294A), respectively. To apply the cyclic electric fields, the samples were placed between a metallic needle and electrode. To avoid arcing, this set-up was immersed in a bath of silicone oil. A function generator (Multifunction Synthesizer WF 1943A, NF Corporation, Yokohama, Japan) connected to an amplifier (Model 610D, TRek Inc, New York, USA) was used to apply a sinusoidal unipolar signal with a frequency of 50 Hz onto the samples for up to 10^6 cycles. The amplitude during these fatigue tests was 4 kV/mm; this is approximately four times the coercive field E_c for LNKN6 and approximately 3 times that for LNKN6-A. The fatigue tests were performed at selected temperatures between room temperature and 100°C. The temperature of the sample during the electric fatigue test was measured by using a temperature sensor (Keyence thermosensor, Osaka, Japan). Care was taken that the applied electric field was aligned in the same direction as the polarization field of each sample. 3-point bending tests were carried out using an Instron 5582 with a load cell capacity of 5 kN and a crosshead speed of 0.1 mm/min. To quantify the average bending strength and reliability of each composition, the flexural strength data for each material is fit to a Weibull distribution, which is a common practice for determining the material strength of ceramics. The Weibull distribution is described using the following equation:

$$F=1-\exp\{-(\sigma/\sigma_0)^m\} \quad (1)$$

where F is the probability of failure and σ is the applied tension. The average strength σ_0 provides an estimate of the strength observed over the entire sample set. The Weibull modulus m gives a measure of the variability in the strength data, whereby larger values of m correspond to a smaller amount of variation in the data. To determine the Weibull distributions, 15 samples were tested for each composition and fatigue condition, including the poled case as well.

3. Results and discussion

The microstructures of both materials were observed via laser microscopy and can be seen in Fig. 1.

Noteworthy is the decrease in grain size, which was obtained using different dopants. The average grain size, as well as further basic physical and electrical characteristics of the compositions are shown in Table 1.

The density ρ and Young's modulus Y of both materials did not differ much and was about 4.30 g/cm^3 and 80 GPa, respectively. The piezoelectric coefficients d_{33} and d_{31} were both increased for LNKN6. We showed in a previous paper that poled LNKN6 and LNKN6-A show a partial phase transformation at around 50°C, which was showcased by a maximum in the permittivity. LNKN6-A exhibited a more stable temperature dependence of the dielectric permittivity over the range of room temperature to 150°C [14].

Fig. 2(a) and (b) show the changes in d_{33} and d_{31} values of LNKN6 and LNKN6-a before and after fatigue temperatures between room temperature and 100°C. The highlighted line represents the values of the poled samples.

In case of d_{33}, both samples did not change significantly after the fatigue process. However, compared to LNKN6-A, LNKN6 showed a higher margin of error throughout the experiments. This fact was also observed for d_{31} values. Hereby, LNKN6-A showed a slight decrease at room temperature, whereas LNKN6 increased in value for fatigue temperatures from room temperature up to 100°C. Changes of about 10% were measured, which might have been caused by further domain switching during the external unipolar field.

Fig. 3(a) and (b) show the Weibull distributions of LNKN6 and LNKN6-A, respectively. To ensure an overview of the results, only the distributions of room temperature and as-poled samples were linear fitted in the figures.

It was shown that LNKN6 did not change significantly the flexural strength after poling. The values for unpoled as well as poled were about 115 MPa with a Weibull parameter m between 15 and 20. Due to smaller grain size, LNKN6-A showed improved mechanical properties, which increased after the polarization process [15]. Unpoled samples showed a flexural strength σ_0 of 131 MPa, whereas as-poled samples showed an improved value of 177 MPa. The Weibull parameter m was similar for the unpoled and as-poled samples and was estimated to 9.1 and 10, respectively. Many studies for different materials observed the toughening effect after polarization of the sample [16–18]. A major reason is the additional consumed energy due to stress-induced 90° domain switching processes in the vicinity of the crack tip. This toughening effect depends on the energy needed for 90° switching, and the number of switchable 90° domains, which is determined by the orientations of crack path and polarization. Indentation tests showed that the fracture toughness increased parallel to the poling direction whereas a degradation can be observed in perpendicular direction [19].

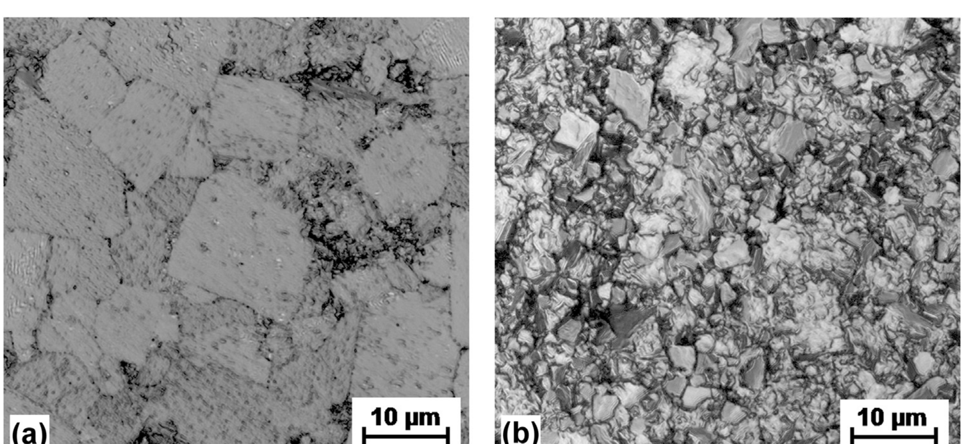

Fig. 1. Microstructure of LNKN6 (a) and LNKN-A (b).