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Short communication

Fatigue-less electrocaloric effect in relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ multilayer elements

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ABSTRACT

A study was made of the electrocaloric (EC) effect's stability in relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ multilayer elements. The sample was subjected to 10^6 unipolar cycles at an electric field amplitude of 110 kV cm^{-1}. The dielectric and ferroelectric properties of the material change only slightly, while the microstructure does not reveal any detrimental evidence of the cycling. The initially measured EC temperature change of 1.45 K decreases by only 0.01 K upon cycling, exhibiting a fatigue-less behavior. The results justify the choice of relaxor multilayers as the working bodies in EC cooling devices, where the material should withstand numerous electric field cycles with high amplitudes, sometimes exceeding 100 kV cm^{-1}.

1. Introduction

The semiconductor industry is seeing the progress in microprocessors starting to stagnate as they are generating too much heat in a confined space. As a result, small and efficient cooling devices are increasingly in demand [1]. One solution could be to base these devices on the electrocaloric (EC) effect, i.e., an adiabatic temperature change induced by the application or removal of an external electric field in a polar material [2–4]. The advantages of such EC cooling devices are the high energy efficiency, the absence of harmful refrigerants, the low noise, and the ease of miniaturization. Since the discovery of the giant EC effect [5], lots of efforts have been devoted to designing an EC cooling device [6–9]. However, only a few demo-devices have been realized and the largest temperature span of 3.3 K was reported by Plaznik et al. [7]. During the EC cycle the ceramic material is subjected to high electric field amplitudes, e.g., for bulk ceramics the largest temperature changes (ΔT_{EC}) of approximately 4 K were determined at electric fields of 150 kV cm^{-1} [10,11]. Considering that such high electric fields will be applied and removed ~10^9–10^{10} number of times in a real EC cooling device [12], understanding the EC stability with electric field cycling is crucial. While investigations of the deterioration of remanent polarization or dielectric permittivity with electric field cycling are well documented for ferroelectrics [13–18] and relaxors [19–22], a study of EC fatigue with extensive number of cycles has, to the best of our knowledge, not yet been realized – in the only EC reliability study, reported in 2013 by Bai et al. [23], the EC effect in a $BaTiO_3$ single crystal has been studied up to only 10 electric field cycles.

The relaxor ferroelectric (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ solid solution, PMN-PT, is characterized by a high EC response. The reported ΔT_{EC} values at room temperature are the largest for relaxor, PMN-rich, PMN-PT compositions [11,24,25]. Studies by Luo et al. [20] and by Jiang et al. [21] showed that relaxor ceramic materials are more resistant to electric-field-cycling degradation than ferroelectrics. Furthermore, the achievable energy efficiency of an EC cooling device is higher for materials with low hysteresis losses, i.e., with slim polarization–electric field loops [26]. Therefore, the prototype relaxor PMN is a reasonable choice for an EC cooling device.

It has been shown recently [27–29] that the EC properties of PMN-PT bulk ceramics can be reproduced in PMN-PT multilayer (ML) elements. Nonetheless, the voltages used in ML elements are significantly reduced compared to bulk ceramics. This fact, combined with the ability of MLs produced by tape casting to scale-up,

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gives a compelling advantage to ML over bulk ceramic elements for further implementation in EC cooling devices.

We report on the stability of the (i) EC effect, (ii) dielectric, and (iii) ferroelectric properties with electric field cycling performed on a relaxor ML element. We show that the PMN elements withstand cycling at an amplitude of 110 kV cm^{-1} without any noticeable changes in the dielectric properties and without any evidence for consequences in the microstructure. Most importantly, the initially measured EC temperature change of 1.45 K decreases by only 0.01 K after 10^6 cycles.

2. Materials and methods

The PMN powder was prepared by mechanochemical synthesis from constituent oxides (PbO 99.9%, MgO 99.95%, TiO_2 99.8%, and Nb_2O_5 99.9%) by milling in a planetary mill at 300 rpm for 90 h. The powder was mixed with organic additives into a slurry, which was used for tape casting. The platinum electrodes (Ferro, USA) were screen printed on the green tape, which was then stacked and laminated. The MLs were sintered in a two-step heating process, which included burnout of the organic phase at 450 °C for 5 h and sintering at 1000 °C for 2 h. The details of the powder and ML preparation process are described elsewhere [28]. The ML consisted of five PMN layers with four inner platinum electrodes.

For the field-emission scanning electron microscopy (FE-SEM, JSM-7600, JEOL, Japan) analysis, the cross-section samples were ground, polished, and thermally etched at 850 °C. The grain size is expressed as the Feret's diameter and the grain size distribution was determined by a stereological analysis of the micrographs, for which more than 200 grains were measured using the Image Tool Software [30,31]. The thicknesses of the ceramic and platinum layers obtained from the low-magnification FE-SEM micrographs are approximately 32 μm and 4 μm, respectively. The thermally etched cross-section (shown later in the results section) revealed a uniform microstructure with an average grain size of 5.75 ± 2.80 μm. The relative density of the ceramic was estimated to exceed 95% of the theoretical density (8.17 g cm^{-3} according to the JCPDS database [32]) based on the analyzed micrographs. No secondary phases could be detected, in agreement with the results of the X-ray diffraction analysis.

The electric field cycling was performed at room temperature by the application and removal of the voltage controlled by a data-acquisition card (National instruments, USA) and a high-voltage amplifier 20/20C (Trek, USA). The unipolar step signal with a frequency of 2 Hz and a voltage of 350 V was applied. The EC effect was measured using the direct method with a small thermistor glued to the sample, and a digital multimeter, as described in ref. [33] The dielectric permittivity versus temperature and polarization–electric field (P-E) hysteresis loops were determined prior to and following the EC cycling. The permittivity was measured on a LCR meter 4284 (Hewlett Packard, USA) with an ac probing signal of 1 V in the frequency range of 100 Hz to 100 kHz and at temperatures from −100 °C to 120 °C. For the P-E loops measured at room temperature the Sawyer-Tower Bridge was used with a triangle signal at 10 mHz and the peak-to-peak voltage of 700 V.

3. Results and discussion

The measured ΔT_{EC} values for 65, 88, and 110 kV cm^{-1} at 26 °C were 0.97, 1.23, and 1.45 K, respectively, which agrees well with the results of Peräntie et al. [24]. The normalized ΔT_{EC} value versus the number of applied electric field cycles is presented in Fig. 1. In total, the ML sample was subjected to 10^6 electric field cycles at 110 kV cm^{-1}. The ΔT_{EC} value deviated during the cycling by about

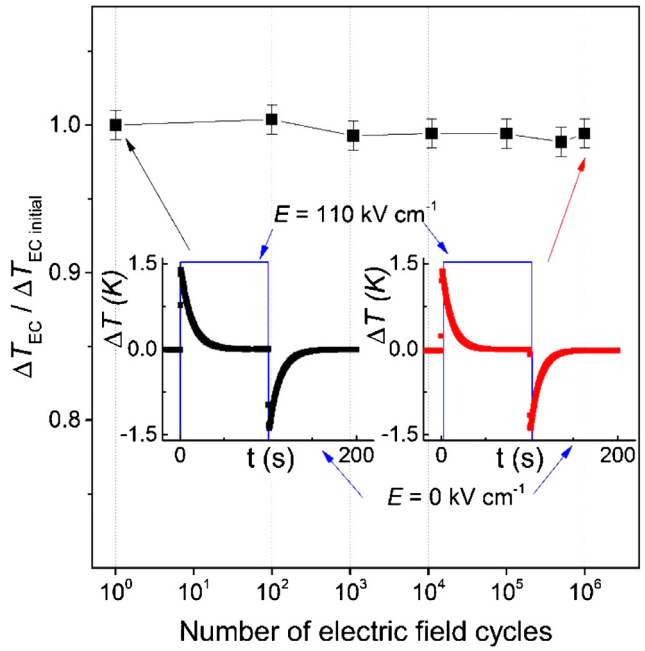

Fig. 1. The EC temperature change normalized by the initial ΔT_{EC} value as a function of the electric field cycles for the PMN ML element. The time dependence of ΔT, upon the applied step-like electric field (blue line), versus time before and after cycling are exhibited in the left and right insets, respectively.

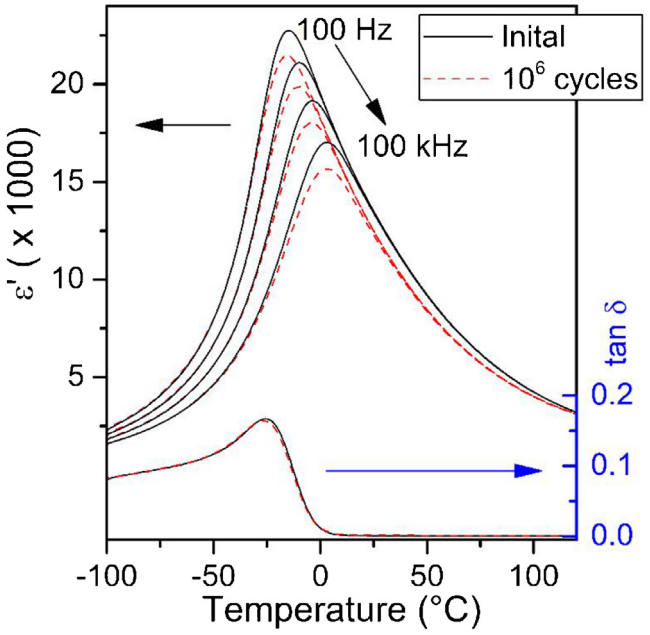

Fig. 2. Temperature dependence of the dielectric permittivity measured at frequencies between 100 Hz and 100 kHz and dielectric losses (tan δ) at 1 kHz for the PMN ML element before and after cycling.

1%, which is in the range of the measurement uncertainty [33]. The Joule heating was not observed in any of the EC measurements. As examples, the plots of the temperature changes (ΔT) versus time determined before and after the cycling are included as insets to Fig. 1, and as can be seen the temperature changes upon application and removal of the electric field are symmetrical.

The dielectric permittivity versus temperature plots of the PMN samples obtained before and after cycling are collected in Fig. 2. The peak dielectric permittivity of the virgin sample is approximately 21,000 at 1 kHz and the peak temperature (T_m) is at −10 °C, which

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