Comprehensive evaluation of electrocaloric effect and fatigue behavior in the $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.1\text{PbTiO}_3$ bulk relaxor ferroelectric ceramic

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Manuel Gesù Del Duca,¹ Jaka Tušek,^{2,a)} Angelo Maiorino,¹ Lovro Fulanović,³ Andraž Bradeško,^{3,4} Uroš Plaznik,² Barbara Malič,^{3,4} Ciro Aprea,¹ and Andrej Kitanovski²

AFFILIATIONS

¹Department of Industrial Engineering, Università di Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano, Salerno, Italy

²University of Ljubljana, Faculty of Mechanical Engineering, Aškerčeva 6, 1000 Ljubljana, Slovenia

³Jožef Stefan Institute, Jamova cesta 39, SI-100 Ljubljana, Slovenia

⁴Jožef Stefan International Postgraduate School, Jamova cesta 39, SI-100 Ljubljana, Slovenia

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^{a)}Author to whom correspondence should be addressed: jaka.tusek@fs.uni-lj.si

ABSTRACT

Electrocaloric refrigeration shows potential as a viable alternative to vapor-compression and/or thermo-electric refrigeration. One of the main challenges that need to be addressed in electrocaloric technology is the fatigue behavior of electrocaloric materials, in terms of both structural and functional aspects. Here, a comprehensive evaluation of the fatigue behavior of the $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.1PbTiO_3 (PMN-10PT) bulk relaxor ferroelectric (or shortly relaxor) ceramic at room temperature is performed. First, the temperature-change dependence on the slew rate was studied. It is shown that the adiabatic conditions are well approached at the slew rate above 1 kV s^{-1} , at which the adiabatic temperature change of 1.3 K was measured at the electric field change of 90 kV cm^{-1} . Then, the durability limits (i.e., the fatigue life) of ten PMN-10PT samples were investigated during unipolar electric field cycling. The results showed that the material could withstand up to 10^6 cycles at the electric field change of 90 kV cm^{-1} with only minor degradation of the functional properties (less than 5% of the maximum adiabatic temperature change). Hence, PMN-10PT can be considered as a promising material for use in an electrocaloric cooling device, but some critical issues that caused premature failure of several samples would need to be further addressed and improved.

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I. INTRODUCTION

A. Electrocaloric refrigeration

Refrigeration and cooling demands are growing exponentially, in particular, for space-cooling applications like air conditioning.¹ Most refrigeration and air-conditioning systems are based on vapor-compression technology, which uses a refrigerant fluid as the working substance. Unfortunately, these refrigerants are harmful to the environment. Although the detrimental effect on the ozone layer was addressed, many refrigerants remain to be phased out, as they still cause a significant greenhouse effect.^{2,3} Some of the scientific community have been focused on researching alternative refrigerant fluids with a lower global-warming potential (GWP) to be used in vapor-compression systems,^{4–7} while others have been

looking at alternative technologies, as reported in Brown and Domanski.⁸ Among these, magnetic (magnetocaloric) refrigeration has shown promising results in terms of energy efficiency and the use of environmentally harmless, solid-state refrigerants.^{9–13} However, there are many unresolved problems regarding the use of rare-earth materials and the competitive costs of such a technology.^{14–16}

Another refrigeration technology that shows great potential is electrocaloric refrigeration. When an electrocaloric material (ECM) is not subjected to an electric field, the electric dipole moments in the material are randomly oriented. If an electric field is applied, the electric dipole moments become oriented in the direction of the applied electric field, and this leads to a decrease in the disorder of the system. The result is a decrease in the entropy of the

material (isothermal entropy change) and an increase in its temperature if adiabatic conditions are applied (i.e., an adiabatic temperature change). This phenomenon is called the electrocaloric effect (ECE). The process is reversible, so the opposite occurs if the electric field is removed. In this case, the entropy increases and the temperature decreases. If the electric field is cyclically applied and removed, a cooling (or heating) cycle can be delivered.¹⁷ Different concepts for utilizing the ECE in practical cooling devices have been proposed over the years. One of the most promising solutions is to use a device with an active electrocaloric regenerator (AER). Such a concept was first proposed and tested by Sinyavsky and Brodyansky.¹⁸ In recent years, several studies were made to evaluate the performance of an AER based on numerical and experimental studies.^{19–24} Another investigated concept for the ECE is the use of thermal switches and electrocaloric materials in the form of thermal bridges or cascade systems.^{25–28} For small-scale applications (known as micro-cooling), a compact cooling device based on the ECE was reported by Ma *et al.*²⁹ using a flexible electrocaloric polymer film and an electrostatic actuation mechanism. Their prototype device produced a specific cooling power of 2.8 W g^{-1} and a coefficient of performance (COP) of 13 at 1.4 K of temperature span between the heat sink and the heat source (assuming complete recovery of the electrical energy). Very recently, Defay *et al.*³⁰ proposed an artificial electrical energy recovery system applied to an electrocaloric refrigerator prototype using a commercial multi-layer capacitor (MLC), composed of electrocaloric layers based on BaTiO_3 doped with detectable levels of Zr and Ca. The authors proved that it is possible to increase the COP of an electrocaloric refrigerator by a factor of 2.9, recovering 65% of the work done to drive the electrocaloric cycle.

B. Electrocaloric materials

The ECE was experimentally measured and reported on Rochelle salt by Kobeko and Kurtchatov³¹ in 1930. Then, a variety of studies were made during the 20th century,^{32–34} but only after the discovery of the so-called giant ECE, with an adiabatic temperature change of 12 K at the electric field change of 480 kV cm^{-1} at 226°C in Zr-rich $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) thin films in 2006,³⁵ interest in electrocaloric technology was renewed. In the same year, Mischenko *et al.* also demonstrated a giant ECE (the adiabatic temperature change of 5 K at the electric field change of 895 kV cm^{-1}) in the relaxor ferroelectric (or shortly relaxor³⁶) $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.1\text{PbTiO}_3$ near its dielectric peak temperature of 60°C ,³⁷ widening the potential for practical applications. Similarly, a large ECE in the ferroelectric poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer was reported by Neese *et al.*,³⁸ with an isothermal entropy change of more than $55 \text{ J kg}^{-1} \text{ K}^{-1}$ and an adiabatic temperature change of more than 12 K at the electric field change of 2090 kV cm^{-1} . Furthermore, the authors also investigated the ECE in the relaxor ferroelectric polymer P(VDF-TrFE-chlorofluoroethylene) [P(VDF-TrFE-CFE)] near room temperature, obtaining almost the same results as for the ferroelectric ceramic material. After the discovery of the giant ECE, several materials were considered for electrocaloric cooling applications. An extensive review of these materials was made by Valant.³⁹ In addition, Shi *et al.* carried out a comprehensive review of ECMs

and electrocaloric cooling devices.⁴⁰ Recently, many scientific efforts have been focused on searching for lead-free ECMs, since there are some limitations for industrial applications related to the quantity of lead in these materials as part of RoHS (Restriction of Hazardous Substances, Directive 2015/863).⁴¹ For example, an ECE with an adiabatic temperature change of 0.28 K near the transition temperature of 84°C at the electric field change of 25 kV cm^{-1} was measured in lead-free $0.9(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--}0.1\text{Sr}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (KNN-0.1SSN) polycrystalline ferroelectric ceramics by the indirect method based on the Maxwell relation by Kumar and Singh.⁴² Using this method, the ECE of lead-free $\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_y\text{Ti}_{1-y}\text{O}_3$ ceramics⁴³ and $[\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3]$ thick-film ceramics⁴⁴ was also evaluated. Furthermore, Koruza *et al.*⁴⁵ measured an adiabatic temperature change of 1.9 K at an electric field of 159 kV cm^{-1} in lead-free relaxor ferroelectric $0.85\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--}0.15\text{SrTiO}_3$ (KNN-STO) ceramics by the direct method. A giant electrocaloric effect (with an adiabatic temperature change of 4.5 K) was also measured by the direct method in lead-free $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ bulk ceramics.⁴⁶ A comparison between the ECE calculated using the direct and indirect methods for the lead-free $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{--}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic was reported by Lu *et al.*⁴⁷ A significant difference between the indirect (with Maxwell relation) and direct measurements was obtained (0.26 K and 0.46 K, respectively). A difference between the direct and indirect methods was also noticed for the relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer P(VDF-TrFE-CFE) by Lu *et al.*^{48,49} The authors showed that the directly measured adiabatic temperature change is much more significant than the one deduced using the Maxwell relation. This is due to the non-ergodic behavior of relaxors, which are characterized by polar nanoregions (PNRs) with randomly distributed directions of the dipole moment.⁵⁰ Relaxors are not in thermal or mechanical equilibrium, and therefore the indirect method based on the Maxwell relation might not be suitable for evaluating the ECE in these kinds of materials. An extensive description of the different methods to evaluate the ECE can be found in Kutnjak and Rozic⁵¹ and Liu *et al.*⁵² In detail, Liu *et al.*⁵² emphasized the use of an IR camera to measure the adiabatic temperature change in ECMs directly. An IR camera can directly image the spatial distribution of the calorific response, which is its main advantage over other techniques, such as differential scanning calorimetry, thermocouples, or other specially designed calorimeters. The direct measurement of the adiabatic temperature change with an IR camera was also successfully applied to study the calorific response in elastocaloric^{53,54} and magnetocaloric materials.⁵⁵ Considering ECMs, Guo *et al.*⁵⁶ measured an adiabatic temperature change of 5.2 K at the electric field change of 900 kV cm^{-1} at room temperature in poly(vinylidene fluoride-trifluoroethylene chlorofluoroethylene) terpolymer (62.6/29.4/8 mol. %, 11–12 μm thick) using an IR camera. Furthermore, Liu *et al.*⁵⁷ demonstrated the usefulness of an IR camera in detecting a deviation of the ECE up to 0.3 K between the central region and the regions near the terminals in Ni-electrode commercial MLCs made from a proprietary BaTiO_3 -based dielectric.

Among all the ECMs, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN)^{58–62} and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN-PT)^{34,37,59,63–70} are two of the most investigated groups of materials. However, researchers were mainly focused on the characterization of the ECMs, i.e., on an evaluation of the dielectric and thermodynamic properties. Only recently the

first experimental study on its application in a cooling device was performed using the $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.1\text{PbTiO}_3$ (PMN-10PT) bulk ceramic to assemble an AER.²⁴ This prototype represented an upgraded version of a previously reported device.²² Despite all these studies, only minor attention was given to the fatigue behavior of ECMs, which limits their use for practical applications, where 10^6 or more working cycles will be required. Fatigue is a phenomenon that depends on the loading conditions, and it can be observed especially at high electric fields, which are often required to achieve high adiabatic temperature changes. Hence, it is essential to understand the fatigue behavior of ECMs before any practical applications of ECMs can be seriously considered.

C. Fatigue behavior of ECMs

Although extensive investigations were performed into the deterioration of the dielectric/ferroelectric/piezoelectric properties, as well as the fatigue-crack propagation mechanisms of ferroelectrics,⁷¹ only a few analyses of EC fatigue can be found, i.e., the effect of electric field cycling on the adiabatic temperature change and the lifetime of the material (durability limits). Fatigue can be defined as the failure of a material during cycling due to external forces. For an ECM, these forces are the external electric fields. Fatigue results in the initiation and growth of cracks^{72,73} that can lead to the failure of the material after a certain number of cycles.^{74,75} During its lifetime, an ECM is subjected to repeated applied electric fields to generate the desired cooling effect. Hence, it can be subjected to degradation of the functional properties or, in the worst case, to mechanical failure. The latter can happen since the unipolar fatigue can lead to a weakening of the microstructure and to the development of microcracks.⁷⁶ In addition to fatigue, the main mechanism of failure in ferroelectric materials (devices) is electrical breakdown.⁷⁷ Some inhomogeneities, such as voids, pores, or the presence of secondary phases, can reduce the breakdown electric field significantly.⁷⁸ Another possible reason leading to the failure of a ferroelectric material is the stress induced in the material stem from the combination of its electrode configuration and specific electromechanical coupling. Indeed, there are some materials that show relatively large electromechanical effects, such as PMN-10PT,⁷⁹ which can lead to a mechanical failure due to the stress induced in the material.

Nevertheless, the fatigue behavior of ferroelectrics from electrocaloric point of view was not yet studied comprehensively. Bai *et al.*⁸⁰ reported the first EC-effect reliability study on a BaTiO_3 single crystal, but they considered a small number of cycles and low electric fields. Then, Fulanović *et al.*⁶² investigated the EC stability of a $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ multilayer element subjected to 10^6 unipolar cycles at the electric field change of 110 kV cm^{-1} , which corresponds to the adiabatic temperature change of about 1.5 K. A very slight reduction of the adiabatic temperature change (less than 1% of the maximum adiabatic temperature change) was measured upon cycling and no degradation damages related to fatigue in the cross section microstructure were found. Recently, a stability study of the ECE under electric field cycling of $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics was reported by Weyland *et al.*⁸¹ They showed a small degradation of the adiabatic temperature change after 10^6 cycles at the electric field change of 20 kV cm^{-1} , which corresponds to the adiabatic

temperature change of about 0.2 K. This was attributed to the migration of oxygen vacancies often determined in oxide ceramics that increase the conductivity of the sample. Therefore, the increased current resulted in an increased Joule effect that reduced the temperature change of the material. It was further shown that reversing the polarity of the electric field after every 10^5 cycles changes the migration direction of oxygen vacancies and prevents charge accumulation at grain boundaries and electrodes, which results in full stability of the ECE. Bradeško *et al.*⁸² studied the EC fatigue of the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramic at the electric field change of 70 kV cm^{-1} at room temperature (between 22 °C and 25 °C) and at 50 °C, which corresponded to the adiabatic temperature changes of about 1.3 K. They found that, when subjected to electric field cycling at room temperature, the material shows a significant degradation (up to 90% relative) of its useful cooling capability already after 2×10^4 cycles. The authors attribute this EC fatigue mechanism to the establishment of a rhombohedral ferroelectric phase that progressively emerges during the field cycling. This phase leads to an increase in grain-boundary conductivity, and thus macroscopic Joule heating of the sample, which reduces the useful cooling effect. Interestingly, the above mentioned phase transformation did not occur when cycling the sample at the elevated temperature (at 50 °C), which resulted in a stable EC response even after 5.5×10^5 cycles.

In this study, a comprehensive evaluation of the EC response of the PMN-10PT bulk relaxor ceramic via direct measurements (using an IR camera) and its fatigue behavior was performed, as well as an investigation of the durability limits (fatigue life) of this material under unipolar electric field cycling. To the best of our knowledge, this is the first such study where the fatigue life of the ECM was evaluated comprehensively with ten samples from the same batch (previous studies were focused on a single sample only). The aim is to understand whether this material could be suitable for an application in a cooling device, considering its durability limits as well as the degradation of the functional properties when subjected to 10^6 cycles.

II. EXPERIMENTAL METHODOLOGY

A. Samples preparation

For the synthesis of the PMN-10PT ceramic powder, PbO (99.9%, Aldrich), MgO (98%, Aldrich), TiO_2 (99.8%, Alfa Aesar), and Nb_2O_5 (99.9%, Aldrich) were used. A mixture of these oxides in the molar ratio corresponding to the stoichiometry of PMN-10PT was homogenized and then high-energy milled in a planetary mill (Retsch, Model PM 400) at 300 rpm for 96 h. Afterward, the powder was milled in an attritor mill at 800 rpm for 4 h in isopropanol and dried. The powder compacts were pressed uniaxially at 50 MPa and then iso-statically at 300 MPa and sintered in double alumina crucibles in the presence of PMN-10PT packing powder at 1200 °C for 2 h. For the experiments, PMN-10PT ceramic plates with a thickness of $200\text{ }\mu\text{m}$ were cut to a surface of $10 \times 20\text{ mm}^2$. For details about the synthesis of the material, refer to Plazník *et al.*²² A microstructure analysis performed on the field-emission scanning electron microscope (FE-SEM) revealed a dense and homogeneous microstructure of PMN-10PT ceramics (see Fig. S1 in the [supplementary material](#)). The grain size and its

distribution are comparable with the previously reported microstructures of PMN-PT-based materials.⁸³ After cutting, Cr/Au electrodes were deposited on both faces by radiofrequency (RF) magnetron sputtering (5 Pa) to obtain an electrode area equal to 144 mm². The material properties, such as density, specific heat, and thermal conductivity, can be found in Uršič *et al.*⁶¹ A two-component, electrically conductive epoxy-adhesive and copper wires were used to connect the samples to the voltage source. Finally, the samples were coated with a thin layer of flexible paint (Spray Dye+) with an emissivity of 0.95.

B. Measurements of polarization and the adiabatic temperature change

A new experimental setup was built to perform the polarization measurements (see Fig. S2 in the [supplementary material](#)). A data-acquisition card with a high-voltage amplifier (TREK 2220, a voltage gain of 200 V_{out} V_{in}⁻¹) was used to apply the electric field to the sample by the application of the voltage signal controlled by a personal computer using LabView software. Such a system allows changing the voltage in the range between 0 and 2000 V. A current-to-voltage converter was employed for measuring the current flowing through the sample by the shunt-resistor method. Two parallel resistors of 100 Ω were used to provide an equivalent resistance value of 50 Ω. A personal computer acquired all the data related to the current and voltage with a sample rate of 2 kHz. The uncertainty of the current measurement was estimated at ±0.3 μA. For performing the tests at room temperature (23.5 ± 0.5 °C), the sample was placed in a measurement chamber (in air) with an internal size of 148 × 77.5 × 64 mm³.

The adiabatic temperature changes were measured directly using an FLIR A655sc infrared (IR) camera with an absolute accuracy of ±2% of the reading, equipped with a 24.6-mm focal length lens and a 640 × 480 pixel IR sensor with a spatial resolution of 204 μm. To capture the rapid temperature changes, the thermal images were recorded with a frame rate of 50 Hz. The adiabatic temperature changes presented in this work were obtained by averaging the temperatures from the thermal images over the entire surface of the sample, excluding the terminals and the edges not covered by the electrode. Furthermore, the adiabatic temperature change was also measured using a small bead thermistor (resistance at 25 °C equal to ~500 kΩ) hermetically sealed (glass seal of 0.2 mm) and glued to the sample. The resistance of the thermistor was measured with a digital multimeter (Keithley 2100) with a sampling frequency of 20 Hz. Platinum/iridium lead wires were used to connect the thermistor to the digital multimeter. The uncertainty of the measurements with the thermistor was estimated to be ±0.2 K. Hence, a comparison between the adiabatic temperature changes obtained by the two different direct methods was performed as well. The adiabatic temperature change measurements were performed by applying unipolar voltages in the range between 200 V and 1800 V, with a step of 200 V, that correspond to electric field changes in the range between 10 kV cm⁻¹ and 90 kV cm⁻¹, with a step of 10 kV cm⁻¹. For each test, a trapezoidal pulse was sequentially applied three times to the sample to evaluate the repeatability of the temperature changes. Each electric field change was followed by a holding time of 60 s to allow for the heat transfer

between the sample and the environment. This means that the electric field was kept constant on the sample for 60 s after its application/removal. The ramp time was selected according to the slew rate that represents the change of voltage per unit of time. It defines the speed of the polarization/depolarization process. The adiabatic temperature change ΔT_{ad} was calculated according to the following equation:

$$\Delta T_{ad,i} = T_{2,i} - T_{1,i}, \quad (1)$$

$$\Delta T_{ad} = \sum_{i=1}^3 \frac{\Delta T_{ad,i}}{3}, \quad (2)$$

where $T_{2,i}$ is the temperature of the sample immediately after the application/removal of the electric field and $T_{1,i}$ is the initial temperature before the electric field is applied/removed. The subscript i refers to the i th measurement. The error in the adiabatic temperature change $\delta \Delta T_{ad}$ was calculated according to the error-propagation rules for indirect measurements,⁸⁴ as follows:

$$\delta \Delta T_{ad,i} = \sqrt{(\delta T_{2,i})^2 + (\delta T_{1,i})^2}, \quad (3)$$

$$\delta \Delta T_{ad} = \sqrt{\sum_{i=1}^3 \left(\frac{\delta \Delta T_{ad,i}}{3} \right)^2}, \quad (4)$$

where $\delta T_{2,i}$ is the error related to the temperature $T_{2,i}$ and $\delta T_{1,i}$ is the error related to the temperature $T_{1,i}$.

Before the adiabatic temperature change measurements at different electric fields were performed, the effect of the slew rate on the adiabatic temperature change and the polarization behavior was analyzed. This investigation is fundamental since the slew rate can strongly affect the polarization response of the material, as shown by Muliana.⁸⁵ Furthermore, it was crucial to identify the adiabatic conditions before the direct measurements of the adiabatic temperature changes were performed. In detail, the slew rate should be high enough to minimize the heat losses and the latent heat's release to the ambient, and therefore to approximate the adiabatic conditions. In this study, the slew rate was varied between 10⁻² kV s⁻¹ and 10² kV s⁻¹ at the electric field change of 70 kV cm⁻¹.

C. Fatigue-life investigation

The investigation of the fatigue behavior was performed at the electric field change of 90 kV cm⁻¹. This value is lower than the breakdown field of PMN-10PT ceramics. As shown in Vrabelj *et al.*,⁸³ PMN-10PT samples, prepared by the same processing method as ours, can withstand electric fields of up to 160 kV cm⁻¹. Electric field change of 90 kV cm⁻¹ is also in the range of other fatigue studies performed on the electrocaloric PMN-based samples.^{62,82} Ten PMN-10PT samples from the same batch were cycled under a unipolar trapezoidal pulse with a frequency of 10 Hz until they failed or reached runout, which was set to 10⁶ cycles. The ramp time of the pulse was set to 40 ms, whereas the holding time was set to 10 ms. These parameters are close to the operating conditions that are expected to apply to real electrocaloric cooling devices. The functional fatigue was evaluated by measuring the

adiabatic temperature change and the polarization every 10^5 cycles, which were performed using a trapezoidal pulse with a longer holding time (to ensure temperature equilibrium with an ambient before the electric field was applied/removed), as described in Sec. II B.

III. RESULTS AND DISCUSSION

A. Impact of the slew rate on the material response

Figure 1 shows the temperature changes in the electrocaloric material measured at different slew rates during both the polarization (red line) and the depolarization (light-blue line) processes. We can see the variation of the temperature change of the material as a function of the slew rate for a fixed electric field change at room temperature. Three distinct areas can be identified. The first one is identified below 0.01 kV s^{-1} , where the temperature change is almost constant and approximately equal to 0.2 K (which is within the measurement uncertainty). Hence, it can be concluded that the conditions are considered isothermal if the slew rate is less than 0.01 kV s^{-1} . Then, the temperature change starts to increase, with the slew rate reaching its maximum at around 1 kV s^{-1} . Above this value, the temperature change is kept approximately constant, regardless of the slew rate. Hence, it is possible to conclude that the value of the temperature change reached a slew rate above 1 kV s^{-1} , i.e., the maximum temperature change, representing the adiabatic temperature change of the material. Furthermore, all the experiments performed by applying a rapid switching on/off of the electric field (slew rates above 1 kV s^{-1}) can be considered as adiabatic. However, it is important to notice that the limits for the isothermal and adiabatic conditions are, in general, strongly dependent on the sample geometry and other parameters that impact on its heat exchange with the surroundings (the medium in which the sample is placed and the fluid dynamics around the sample) and they cannot be generalized.

FIG. 1. Effect of the slew rate on the material's temperature change for a fixed electric field change (70 kV cm^{-1}) at room temperature, measured with the IR camera.

B. The electrocaloric effect

Once the adiabatic conditions were identified, the adiabatic temperature changes at different electric field changes and room temperature were measured during both the polarization and the depolarization processes with a slew rate of 10 kV s^{-1} (Fig. 2).

It is evident from Fig. 2 that the adiabatic temperature change increases with the electric field, approximately according to $\Delta T_{ad} \approx E^2$, during both the polarization and the depolarization processes. The results show good agreement with the previous experimental outcomes of Plaznik *et al.*,²² reported for the depolarization process. The differences between the adiabatic temperature change measured during the polarization and depolarization processes due to the hysteresis losses are very small, with a temperature irreversibility (T_{irr}) up to 50.0 mK , which means that the material exhibits only a minor hysteresis. The maximum adiabatic temperature change of $1.3 \pm 0.3 \text{ K}$ was measured at the electric field change of 90 kV cm^{-1} . The adiabatic temperature changes were also measured with a thermistor glued to the surface of the sample. A significant difference between the adiabatic temperature change measured with the IR camera and the thermistor is evident (Fig. 2). Molin *et al.*⁸⁶ showed that measuring the adiabatic temperature change of the same batch of samples with four different direct methods can lead to different results (up to 15%). In this case, there is a substantial decrease in the adiabatic temperature change measured with the thermistor in comparison to the IR camera. These deviations increase with the electric field, and they are in the range between -23.4% and -32.3% of the adiabatic temperature change measured with the IR camera. The main reason for these deviations is related to the thermal losses that occur due to the contact of the thermistor with the surface of the electrocaloric material, which means that the material (or at least the part of the material where the thermistor is placed) is no longer in the adiabatic condition. A zero-dimensional model developed by Rožič *et al.*⁸⁷ can be used to consider this phenomenon and correct the adiabatic temperature change measured with the thermistor.

FIG. 2. Adiabatic temperature change (left y axis) and temperature irreversibility (right y axis) during the polarization and depolarization processes for different electric field changes at room temperature.

FIG. 3. Temperature distribution (in °C) immediately after the polarization and depolarization processes for different electric field changes at room temperature.

Furthermore, it should be noted that the adiabatic temperature changes with the thermistor were measured at a single point on the surface of the sample. In contrast, the adiabatic temperature changes measured by the IR camera were evaluated by considering the entire electroded surface. Hence, we performed an analysis of the temperature distribution on the sample surface to evaluate possible spatial discrepancies of the adiabatic temperature change.

Figure 3 shows the temperature distribution measured after the polarization and depolarization processes for different electric field changes. These temperatures represent the sample conditions immediately after the electrocaloric effect occurs. It is worth pointing out that the temperature variations measured on the surface of the sample caused by the electrocaloric effect are less pronounced near the boundaries between the electroded and non-electroded areas. Besides, it can also be seen how the terminals affect the temperature distribution on the surface of the sample. The temperature changes near the terminals (in the middle and in the lower-right corner of the sample) are less pronounced than those measured on other areas of the sample after the polarization (depolarization) process. Interestingly, as clearly seen from Fig. 3, even though the terminal in the middle of the sample is placed on the other side of the sample, practically no temperature changes occur at the spot where the terminal is placed. The reason for that is the conductive heat losses through the terminals. The same also occurs at the spot where the thermistor is placed (not shown in Fig. 3), which is the main reason that it shows significantly smaller temperature changes compared to the IR camera. Furthermore, it is evident that the temperature is not entirely homogeneous over the surface of the sample. On the contrary, after the depolarization process, this temperature heterogeneity is less remarkable. A detailed analysis of the distribution of the adiabatic temperature change on the surface of the sample is reported in S.3 in the [supplementary material](#).

C. Fatigue behavior

After evaluating the adiabatic temperature change for different electric field changes, an analysis of the fatigue behavior of the PMN-10PT was performed (at the maximum value of the electric field change allowed by the experimental setup, which is 90 kV

FIG. 4. Electrocaloric fatigue during cycling up to 10^6 cycles.

cm^{-1} , with a slew rate equal to 45 kV s^{-1}). First, the functional (electrocaloric) fatigue of the material was investigated, and then its durability limits were explored. Figure 4 shows the normalized adiabatic temperature changes measured during the fatigue cycling.

A very slight degradation of the adiabatic temperature changes during cycling for both the polarization and the depolarization was observed (Fig. 4). On the right y axis of Fig. 4, the cycling losses, represented by the decreasing of the adiabatic temperature change in comparison with the adiabatic temperature change of the unfatigued sample, are reported. It is clear that these reductions are relatively constant as the number of cycles increases. In detail, the cycling losses are kept below 5% of the adiabatic temperature change of the unfatigued sample and occur already after the initial 10^5 cycles. It should be noted that unlike the fatigue behavior of the PMN bulk ceramic at room temperature showed by Bradeško *et al.*,⁸² regarding the sample temperature during cycling, no excessive heating (Joule effect) occurred in the PMN-10PT during EC cycling up to 10^6 cycles. This is very promising for application of this material in the electrocaloric refrigeration system where a long operating time with stable ECE is required (over 10^6 cycles). However, a similar fatigue behavior as shown in this work was recently reported in BZT ceramics,⁸¹ as well as in PMN multi-layer ceramic elements,⁶² where only minor degradation of the adiabatic temperature changes was detected upon 10^6 cycles at the electric field change of 20 kV cm^{-1} and 110 kV cm^{-1} , respectively.

Figure 5 shows the effect of fatigue on the polarization behavior. Figure 5(a) shows polarization curves that were recorded every 10^5 cycles. It should be noted that the polarization retains the same trend for both the fatigued and the unfatigued samples. A degradation of this functional property during the fatigue cycling was observed only after the initial 10^5 cycles. Then, the polarization behavior up to 10^6 cycles, in general, remains the same. In Fig. 5(b), the behavior of the saturation polarization (black line, left y axis) during cycling is shown, as well as the maximum current (gray line, right y axis). Both the saturation polarization and the maximum current were significantly decreased during the initial 10^5 cycles, while during further cycling they remained relatively

FIG. 5. Polarization fatigue during cycling up to 10^6 cycles: (a) polarization (P) as a function of applied electric field (E) and (b) saturated polarization and maximum current values.

constant. The percentage deviations in comparison with the values for the unfatigued sample are approximately equal to -14% and -17% for saturation polarization and the maximum current, respectively. The slight degradation of the saturation polarization under a unipolar voltage is most probably due to the space-charge field, which is commonly observed upon unipolar cycling.^{71,88,89}

Finally, the durability limits of the PMN-10PT were evaluated by testing ten samples at the electric field change of 90 kV cm^{-1} (Table I). Most of the tests (i.e., eight) were performed on material

TABLE I. Overview of fatigue-life test results.

Sample	Number of cycles before failure	Terminal positions
#1	45 000	Middle/edge
#2	300 000	Middle/edge
#3	Runout	Middle/middle
#4	1	Middle/middle
#5	1	Middle/middle
#6	1	Middle/middle
#7	750 000	Middle/middle
#8	Runout	Middle/middle
#9	1	Middle/middle
#10	Runout	Middle/middle

with the terminals placed in the middle part of the surface on both sides of the sample. Two samples were used to test possible differences in the fatigue life of the material caused by a different location of the terminals, since it is shown in S.3 in the [supplementary material](#) (and Fig. 3) that the terminal located at the middle of the sample decreases the average adiabatic temperature change over the sample more significantly than located at the corner of the sample. In this case, one terminal was placed at the corner of the electroded area [see Fig. S3(a) in the [supplementary material](#)] and another one in the middle part of the surface of the sample. In electrocaloric devices, it is favorable to locate the terminal at the corner of the ECM in order to disturb the heat transfer process with the heat sink/source as little as possible.^{19,22,24} However, the samples with a terminal near the boundaries of the electroded failed after 45,000 and 300,000 cycles, which is relatively low and the reasons for that need to be further investigated. On the other hand, three samples with the two terminals placed in the middle of the surface of the electroded area reached the runout, demonstrating the good reliability of this material, while one failed after 750,000 cycles. However, four of these samples broke already after the first electric field change. This can be most probably attributed to a certain critical defect in the material's microstructure (especially due to the size of the sample) that reduce the electrical breakdown field,⁷⁷ such as cracks that occurred during the sample preparation (e.g., cutting), larger pores or some secondary phase that is more conductive.⁷⁸ These results indicate that more stringent control of ceramic processing is needed to produce specimens at the scale and quality required in electrocaloric devices.

IV. CONCLUSIONS

We have conducted a comprehensive analysis of the electrocaloric effect in the relaxor PMN-10PT bulk ceramic and its fatigue behavior, including an evaluation of its durability limits. In the first part, the temperature changes of PMN-10PT relaxor ceramics were investigated for different slew rates. The experiments demonstrated the strong influence of the slew rate on the temperature change of the EC material. The results allowed us to identify the proper conditions to perform direct measurements of the adiabatic temperature change. Adiabatic conditions can be achieved for a slew rate above 1 kV s^{-1} (for the conditions applied here). Hence, under these adiabatic conditions, the adiabatic temperature change was measured at different electric field changes at room temperature, showing good agreement with the previous experimental results. A maximum adiabatic temperature change of 1.3 K was measured at the external electric field change of 90 kV cm^{-1} (with an IR camera).

In the second part, a study of the EC fatigue and durability limits of the material was performed. The adiabatic temperature change was measured during cycling of the ECM up to 10^6 cycles. The results showed that the degradation of its functional properties could be considered as negligible (less than 5% of the maximum adiabatic temperature change). It has been further shown that the location of the terminals affects the fatigue life of the ECM and that locating the terminal near the corner of the sample causes its premature failure. However, it can be concluded that the PMN-10PT ceramic can withstand up to 10^6 cycles at the applied

electric field change of 90 kV cm^{-1} (with adiabatic temperature changes of about 1.3 K). Indeed, three samples out of ten tested in the fatigue experiments reached the runout. On the other hand, four samples broke after the application of the first electric field change, which is probably related to critical defects in the microstructure that drastically reduced the electrical breakdown field. The reasons for the premature failure (reduced electrical breakdown field) need to be diagnosed and eliminated (preparation of large-size, defect-free samples are particularly challenging), but PMN-10PT can be considered as a promising material for use in an electrocaloric cooling device since it allows durable operations without losing its functional properties. However, it emerges that the processing of large-scale ceramic samples and its repeatability has a fundamental role in the fatigue behavior of the ECMs tested in this study and their durability limits. Indeed, high-quality specimens with good repeatability are needed for the application in cooling devices, and therefore further efforts should put to improve the production process of the ceramic ECMs as much as possible.

Finally, the applied methodology and the experimental approach combining a detailed evaluation of both functional fatigue (by measuring adiabatic temperature changes before and after fatigue cycling) and structural fatigue (durability limits) were shown to be highly suitable for studying ECMs prior their application in a cooling device. This is especially important since the durability limit analysis of several large-scale samples of the same batch revealed large scatter of samples' repeatability in terms of fatigue life. We therefore believe that this methodology should inspire further studies of fatigue behavior of ECMs.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#), S.1 for the field-emission scanning electron microscope image of a PMN-10PT sample, S.2 for a photo of the experimental setup with the polarization measurement device, and S.3 for the spatial analysis of the adiabatic temperature change of the studied PMN-10PT samples.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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