Effect of dopants on the electrocaloric effect of 0.92 Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.08 PbTiO$_3$ ceramics

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Abstract

This paper presents an extract of modifications of lead magnesium niobate–lead titanate in order to optimize its electrocaloric properties. Electrocaloric entropy (ΔS_{EC}) and temperature changes (ΔT_{EC}) are measured in a temperature range from $-5\,°C$ up to $100\,°C$ using differential scanning calorimetry. The influence of dopants (Li$^+$, Mn^{2+}, Sr^{2+}, Ta^{5+}) on the electrocaloric effect as well as on microstructure, dielectric and ferroelectric behavior is investigated. The maximum of relative permittivity can be shifted to lower or higher temperatures depending on the added dopant and decreased ferroelectric hysteresis losses were observed for all altered compositions. For the undoped PMN–8PT ceramics maximum ΔT_{EC} of 0.58 K and ΔS_{EC} of 0.51 J kg^{-1} K^{-1} were measured, when applying an electric field of 2 kV mm^{-1} at $30\,°C$. The electrocaloric temperature change showed lower values for all doped PMN–8PT. Remarkably, this is accompanied with an increase of the entropy change for the Li-doped sample.
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Keywords: Electrocaloric effect; Direct electrocaloric measurement; PMN–PT; Dielectric properties; Relaxor ferroelectrics

1. Introduction

The electrocaloric effect (ECE) is defined as an isothermal entropy or adiabatic temperature change of a dielectric material under application or removal of an electric field.[1] Discovered in 1930 in Rochelle Salt,[2] the ECE had not gained much attention for a long time, since the measured temperature changes (ΔT_{EC}) were not large enough for practical applications until the discovery of the giant electrocaloric effect, published in 2006, predicting temperature changes up to 12 K for PbZr$_{0.95}$Ti$_{0.05}$O$_3$—thin films at $226\,°C$.[3,4] Large electrocaloric temperature changes are expected by applying high electric fields[5] in the vicinity of the ferroelectric–paraelectric phase transition.[6] Therefore, electrocaloric materials which show high dielectric strength and a phase transition temperature near to the destined application profile are beneficial. The phase diagram of relaxor ferroelectric material lead magnesium niobate-lead titanate (PMN–PT) shows, that temperature of phase transition can be adjusted by varying the Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$:PbTiO$_3$ ratio.[7] High electrocaloric effects for PMN–PT thin films are predicted for compositions near the morphotropic phase boundary (around 30–35% PbTiO$_3$ content).[8,9] The phase transition temperatures of these compounds and thus the maximum of the electrocaloric temperature change are above $100\,°C$. Directly measured EC temperature changes for PMN–30PT bulk materials showed values of 1.55 K (at $170\,°C$, $\Delta E = 5$ kV mm^{-1})[10] and 2.7 K (at $157\,°C$, $\Delta E = 9$ kV mm^{-1}).[11] A decrease of the PT content leads to EC temperature changes of 1.59 K (at $18\,°C$, $\Delta E = 1.6$ kV mm^{-1}) for PMN–15PT[12] and 1.2 K (at $90\,°C$, $\Delta E = 5$ kV mm^{-1}) for PMN–10PT.[10] Aim of the here considered investigations was to shift the temperature of the maximum electrocaloric effect to a temperature range from 20 to $40\,°C$. Application of cooling systems in that temperature range are seen in electronic devices and battery systems. Therefore, the stoichiometric composition 0.92 Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.08 PbTiO$_3$ (PMN–8PT) was chosen, showing a maximum of the

permittivity around 30 °C. Within the present work, we consider the temperature of maximum permittivity, T_m, as a reference temperature characterizing the specific material composition and the effect of the added dopants. It does not denote the phase transition temperature, which is typically below T_m for undoped PMN–PT ceramics with a PT content below 30%.[10] The composition of PMN–8PT manifests the relaxor typical behavior, associated with a broad, frequency-dependent peak in the temperature dependence of permittivity and a slim hysteresis loop as well as retaining finite values of field-induced polarization above the transition temperature.[13] The undoped material shows relatively high ferroelectric losses and dielectric strengths of 6 kV mm^{-1} at a sample thickness of about 1 mm. By doping PMN–8PT we aim to decrease the ferroelectric losses, to enhance the dielectric strength as well as to improve the material's electrocaloric characteristics. The effect of different dopants like tantalum (Ta),[14–16] manganese (Mn),[17–19] lithium (Li)[20] and strontium (Sr)[21] on the dielectric and in some cases the ferroelectric properties of PMN–PT are already published, but we are not aware of studies on the impact of dopants on the electrocaloric effect of PMN–PT. In this work we contribute the investigation of the effect of these dopants on electrocaloric properties of PMN–8PT. We use a direct measurement set-up to consider temperature and entropy changes on application and withdrawal of an external electric field to quantify the electrocaloric effect. The dielectric and ferroelectric properties were also measured.

2. Experimental procedure

The undoped PMN–8PT ceramic powder was synthesized using the columbite route.[22] Raw materials, PbO (Alfa Aesar), MgNb$_2$O$_6$ (H.C. Starck) and TiO$_2$ (Tronox TR-HP2) were mixed in the stoichiometric ratio and milled in water using a planetary ball mill (Fritsch, Pulverisette 5) at 200 rpm for 2 h. Then the powder was dried, sieved and calcined in an alumina crucible at 800 °C for 2 h to obtain the perovskite structure of the powder. The calcined powder was subsequently mixed with a small amount of polyvinyl alcohol (Merck), pressed into discs with 10 mm in diameter and about 1.3 mm in thickness and sintered under lead enriched atmosphere at 1000 °C for 2 h with a heating rate of 5 K min^{-1}. For preparation of altered compositions, dopants were added to the stoichiometric PMN–8PT composition in a concentration of 3 mol% either in form of their carbonates (SrCO$_3$ (Alfa Aesar), MnCO$_3$ (Bulgareactivason), Li$_2$CO$_3$ (Merck)) or as metal oxides (Ta$_2$O$_5$ (H. C. Starck)). After mixing, calcining and pressing as stated above, the doped PMN–PT samples were sintered under lead enriched atmosphere at 1200 °C for 2 h, to achieve dense samples. All sintered discs showed diameter around 8.5 mm and a thickness of about 1 mm. For electrical measurements, electrodes of silver conductive pastes were painted and fired at 800 °C for 20 min. Capacitance and dielectric loss tangent were measured between 0.1 and 100 kHz in a temperature range from −40 to 140 °C using an LCR meter (HP 4263A). The polarization–electric field (*P–E*) hysteresis loop measurements were carried out using a Sawyer Tower circuit with an analog input and digital *I/O*
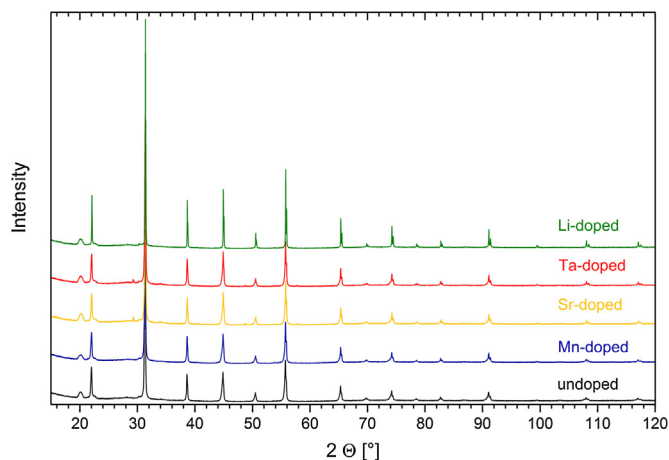

Fig. 1. X-ray diffraction pattern of undoped and doped PMN–8PT.

module (Measurement Computing, USB-1616HS-4). Electrocaloric temperature and entropy changes were measured directly with a modified differential scanning calorimeter (DSC, Netzsch DSC 204) under application and withdrawal of an electric field of 1.0, 1.5 and 2 kV mm^{-1}. The measurement setup was similar to the measurement system used by Le Goupil et al. to determine the ECE on $\langle 0\,0\,1 \rangle$-PMN–30PT single crystals.[23] The microstructure of ceramic disc samples was determined by field emission scanning electron microscopy (FESEM) (Zeiss Gemini DSM 982). The porosity of the samples was determined using the FESEM images and the software Axiovision (Rel. 4.7.2.0, Zeiss). The X-ray diffraction (XRD) measurements were performed using the diffractometer D8 Advance (Bruker AXS) with a step $\Delta(2\theta) = 0.02°$ and a counting time of 3 s in the range of 10–120° at room temperature.

3. Results

The prepared disk samples were characterized by XRD measurements (Fig. 1). The reflection at 20° corresponds to beeswax, which was used to mount the samples. For the Ta- and Sr-doped samples the reflections at 29° and 49° indicate the presence of a secondary pyrochlore phase.[14] The XRD pattern of the undoped as well as of the Mn- and Li-doped samples showed the pure perovskite phase.

Assuming that metallic ions prefer to enter sites with equal valence and similar radii[24] we expect strontium ions to occupy A-site and manganese, tantalum and lithium ions[20] to occupy B-site. The XRD measurement and Rietveld analysis did not provide sufficient data which allows for an experimental validation of this assumption.

Fig. 2 shows FESEM images of the cross-section of doped and undoped PMN–8PT.

For the undoped (Fig. 2a) and the Sr-doped (Fig. 2c) samples a broad grain size distribution was observed, while for the Mn-, Ta- and Li-doped samples (Fig. 2b, d and e) microstructure was more homogeneous. The average grain size decreased when Mn- and Ta-dopants were added, while Sr- and Li-doping led to increased pore sizes. For the undoped sample the observed porosity of 3.1% is in good agreement with the measured