Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 41 (2015) 9344–9349
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Large electrocaloric strength in the (100)-oriented relaxor ferroelectric Pb $[(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}]O_3$ single crystal at near morphotropic phase boundary

Biaolin Peng[a,b,c], Qi Zhang[d,e], Shanming Ke[a], Tao Li[a,b], Hanben Niu[b], Xierong Zeng[a,*], Huiqing Fan[f,*], Haitao Huang[c,*]

[a]Shenzhen Key Laboratory of Special Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China
[b]Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, PR China
[c]Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong SAR
[d]Department of Manufacturing and Materials, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, United Kingdom
[e]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, PR China
[f]State Key Laboratory of Solidification Processing School of Materials Science and Engineering Northwestern Polytechnical University, Xi'an 710072, PR China

Received 20 March 2015; accepted 27 March 2015
Available online 7 April 2015

Abstract

Relaxor ferroelectric $Pb[(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}]O_3$ (PNNT) single crystal with composition close to the morphotropic phase boundary (MPB) was successfully prepared using the molten salt method. The analysis results of XRD and TEM indicated that the as-grown crystal is of almost pure perovskite phase with coexistence of tetragonal and rhombohedral. Typical relaxor behavior was observed when the crystal was aged. Large electrocaloric strength *($\Delta T/\Delta E$)* of 44.97 mK cm/kV was obtained near the phase transition temperature of paraelectric to ferroelectric, indicating that PNNT is a promising material for application in cooling system. Moreover, it is found that the aging of point defects may make an important contribution to the electrocaloric performance of the single crystal, in addition to the contribution of the transition of phases induced by the electric field.

Keywords: PNNT single crystal; Relaxor ferroelectric; Electrocaloric strength; MPB

1. Introduction

Recently, there has been an increasing interest in the discovery of electrocaloric (*EC*) materials with potential applications for solid state cooling, due to the requirement of more efficient and environment friendly materials in modern refrigeration industry [1–13]. Among some new solid state refrigeration techniques, although the magnetocaloric cooling technology is more advanced at current, the *EC* cooling technology obviously sheds out to be a more viable candidate because the large electric fields for *EC* materials are easier to produce than the large magnetic fields (>1 T) for magnetocaloric materials [13]. The *EC* effect is that a reversible change in temperature (ΔT) of a polarable material by virtue of the change in entropy (ΔS) upon the application or withdrawing of an electric field under adiabatic conditions. To obtain a large ΔT, most research efforts have been made for it. For example, by means of thin film configurations, a large ΔT of 12 K was observed near the ferroelectric Curie temperature of the antiferroelectric $PbZr_{0.95}Ti_{0.05}O_3$ [1], and also a ΔT of 12.6 K in the relaxor ferroelectric polymer P(VDF-TrFE) [2], since that a higher breakdown strength can be achieved in thin film.

With a large ΔT or ΔS, some perovskite materials, both lead-containing and lead-free, have been considered for solid state *EC* cooling such as $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) [14], $Pb(Sc_{0.5}Ta_{0.}5)O_3$ (PST) [15], $(1-x)$ $Pb(Zn_{1/3}Nb_{2/3})O_3$–$x$$PbTiO_3$ (PZN–PT) [16], or $(1-x)$ $Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–PT) [17], $BaTiO_3$ (BT) and

*Corresponding authors. Tel.: +852 51628239/+86 13691768598.
E-mail addresses: zengxier@szu.edu.cn (X. Zeng), hqfan3@163.com (H. Fan), haitao.huang@polyu.edu.hk (H. Huang).

http://dx.doi.org/10.1016/j.ceramint.2015.03.285
0272-8842/

$(1-x)(Na_{0.5}Bi_{0.5})TiO_3$–$x$$KNbO_3$ [12,18], etc. However, for practical applications, apart from a large ΔT, an *EC* material with large EC strength ($\Delta T/\Delta E$) will be more appreciated since that a large ΔT can be obtained under a relatively smaller electric field and thus an improved reliability and reduced wear failure can be expected. Therefore, one critical question is how to design and develop dielectric materials which are capable of generating giant *EC* effect with relatively low applied electric field. It is well known that piezoelectric material with a composition close to the morphotropic phase boundary (MPB) can exhibit much higher piezoelectric activity due to the existence of a larger number of polar-states with similar energy levels in the mixed phase region with the coexistence of ferroelectric phases rather than at a critical line[19]. Therefore, it is believed that a large ΔT or ΔS can be obtained in dielectric material with composition near a MPB because the *EC* effect is directly related to the change of entropy caused by the transition of polar-states under the application or withdrawing of an electric field; thus a large $\Delta T/\Delta E$ can be achieved.

In this work, a (100)-oriented relaxor ferroelectric $Pb(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}O_3$ (PNNT) single crystal with composition close to the morphotropic phase boundary (MPB) was prepared by using the molten salt method. It is found that large *EC* strength ($\Delta T/\Delta E$) of 44.97 mK cm/kV can be achieved near the phase transition temperature of paraelectric to ferroelectric. Moreover, it is also found that the aging of point defects may play a very important role both on the relaxor behavior and *EC* performance of the single crystal.

2. Material and methods

$Pb[(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}]O_3$ (PNNT) single crystals were prepared using the molten salt method. PbO, TiO_2, ZnO, and Nb_2O_5 with purities of $>99.9\%$ were used as raw materials. The mixture of Pb_3O_4 and B_2O_3 was used as flux to improve the homogeneity and flowability of the melt during the process of crystal growth and the weight ration of $Pb[(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}]O_3$:$Pb_3O_4$:$B_2O_3$ was 50:49:1. Firstly, the mixed raw materials in a platinum crucible was rapidly heated to 1200 °C with a heating rate of 300 °C/h and hold on 5 h in a homemade crystal growth furnace for solution homogenization. After that, the melt was slowly cooled to 850 °C with a cooling rate of 1.5 °C/h for crystal growth and then cooled to room temperature with a cooling rate of 100 °C/h. Finally, dark green granular single crystals (Fig. 1(a and b)) were obtained when rinsed using boiling nitric acid for 10 h.

The density of PNNT single crystal was measured using the Archimedes method. The crystallinity was analyzed by X-ray diffraction (XRD, X'Pert PRO MPD, Philips, Eindhoven, Netherlands). The microstructure was studied by transmission electron microscopy (TEM, Tecnai F30G^2, FEI, America). For the measurements of electrical properties, the as-grown PNNT single crystal was polished to final thickness of 0.5 mm along the free surface and Au/Cr electrode were evaporated on both surfaces. Dielectric permittivity measurement were carried out using an impedance analyzer (4294 A, Agilent, CA, USA) with a perturbation voltage $V_{ac}=500$ mV. The polarization and electric field hysteresis loops (*P–E*) were measured at 1 Hz using a ferroelectric analyzer (TF-2000; Aix ACCT, Aachen, Germany) under the waveform excitation signal of triangle. The *EC* performance was calculated according to the *P–E* results.

3. Results and discussion

3.1. Structure analysis

Fig. 2 shows the XRD pattern of the PNNT single crystal polished along the free surface. It can be seen that the sample exhibited a good crystallization quality and an almost pure perovskite phase (pyrochlore phase content is less than 0.1%) with highly (100) preferential orientation. The peak of (100) was broadened and split into two obvious T(001) and T(100) peaks, indicating the existence of the tetragonal phase. Also, a small amount of rhombohedral phase can be detected by using a multi-peak fitting method [20], indicating that the composition of the PNNT single crystal is near the MPB region. The EDS results show that the composition of the sample is almost consistent with its molecular formula, as shown in the inset of Fig. 2.

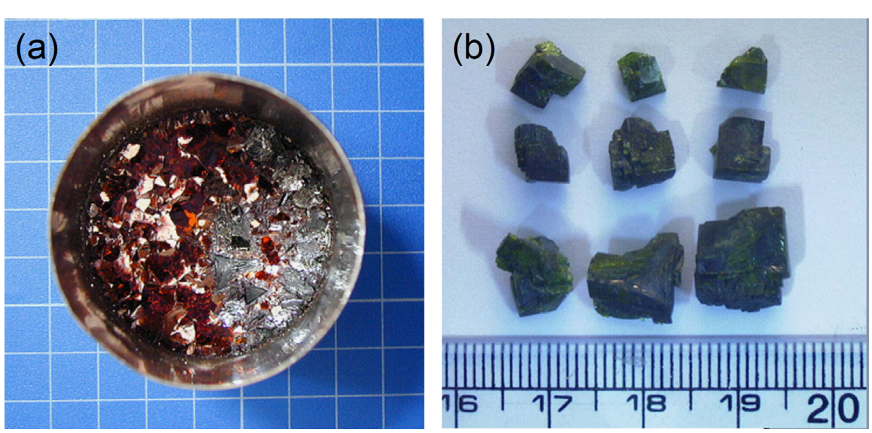

Fig. 1. (a) As-grown $Pb[(Ni_{1/3}Nb_{2/3})_{0.6}Ti_{0.4}]O_3$ single crystals in a platinum crucible after prepared by a flux method and (b) rinsed crystals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)