Materials Research Bulletin 47 (2012) 4503–4509

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Short communication

High pyroelectric response of lead zirconate stannate titanate based antiferroelectric ceramics with low Curie temperature

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ARTICLE INFO

Article history:
Received 9 May 2012
Received in revised form 16 June 2012
Accepted 23 August 2012
Available online 31 August 2012

Keywords:
A. Ceramics
D. Ferroelectricity
D. Dielectric properties

ABSTRACT

With a view to solve the problem that the Curie temperature of antiferroelectric ceramics was higher than the use temperature of uncooled infrared detectors, four groups of samples with different Ba content were prepared by conventional solid state reaction process, and the effects of Ba^{2+} content on the ferroelectric, dielectric and electric field-induced pyroelectric properties of four groups of samples were studied. The results indicated four groups of samples showed different dielectric properties which were attributed that the first and the fourth group of samples were in FE phase and the second and the third group of samples were in AFE phase. Large pyroelectric coefficient can be obtained in all four groups of specimens near room temperature by appropriate Ba doping. The maximum pyroelectric coefficient of 13,800 $\mu C/m^2$ K and figure of merit of 16.5×10^{-5} $Pa^{-0.5}$ at room temperature were obtained in $(Pb_{0.97-x}Ba_xLa_{0.02})(Zr_{0.7}Ti_{0.05}Sn_{0.25})O_3$ antiferroelectric ceramics with 0.138 mol Ba content.

1. Introduction

Infrared detectors made by ferroelectric materials are widely used in fire alarms, thermal imaging and intruder detectors due to their high temperature stability, high sensitivity and low cost [1–3]. Two modes for IR detection by ferroelectric materials are currently available [4–7]. One is conventional pyroelectric mode utilizing the decay of spontaneous polarization with increasing temperature without an applied dc field. The other mode is associated with the change of dielectric permittivity with temperature in the region of ferroelectric–paraelectric transition. In dielectric mode, the ferroelectric–paraelectric transition temperature should be in the region of Curie temperature, which is different from conventional pyroelectric mode which needs sufficiently high transition temperature so that the pyroelectric response is reversible and stable. Besides, in this mode, because the samples are not poled, the spontaneous polarization is absent or very small and the variation in dielectric permittivity by incident heating gives rise to a detectable signal voltage, so the pyroelectric coefficient can be written as [8].

$$p = \left(\frac{dD}{dT}\right)_E = \left(\frac{dP_s}{dT}\right)_E + \varepsilon_0\left(\frac{d\varepsilon_r}{dT}\right)_E E \approx \varepsilon_0\left(\frac{d\varepsilon_r}{dT}\right)_E E \qquad (1)$$

where D is the dielectric displacement, T is temperature, P_s is spontaneous polarization, E is applied electric field, ε_0 is the permittivity of free space and ε_r is the permittivity of pyroelectric materials.

So far, barium strontium titanate (BST) has been identified as one of the most promising candidate sensitive materials for uncooled infrared focal plane arrays due to its noticeable change in the dielectric constant near phase transition temperature [9,10]. However, this kind of material has a very serious problem that the dielectric peak broadens obviously when a dc bias field is applied and thus large pyroelectric coefficient can be not obtained according to Eq. (1). Recently, in order to improve the pyroelectric response of BST materials, various technologies have been done such as dopant [11–13], porous BST [14] and BST film [8,15–22]. However, there are still many problems. Doping decreases the dielectric constant and depresses the loss, but meanwhile the dielectric peak is also depressed for the introduction of impurities, so the $d\varepsilon_r/dT$ term in Eq. (1) decreases. This leads to the deterioration of pyroelectric coefficient. Although the pyroelectric response and figure of merit of porous BST are larger than that of dense ceramics, the machinability of porous ceramics is very poor, which limits its use in uncooled infrared focal plane arrays. Meanwhile, the pyroelectric response of BST film improves a lot, but it is still far smaller than that of BST ceramics. So in order to prepare uncooled infrared devices with high pyroelectric response, developing a new material system with high pyroelectric response is very necessary. In the past few years, PZST based

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http://dx.doi.org/10.1016/j.materresbull.2012.08.059

antiferroelectric ceramics have been widely used in high-density capacitor, high strain actuators and energy transducer owing to their outstanding field induced phase transitions and adjustable dielectric and piezoelectric properties [23–26] and they are also seen as important alternative materials used in infrared detectors because of their dc field-induced dielectric enhancement effect [27]. However, the high pyroelectric response in antiferroelectric ceramics comes across a problem that the Curie temperature is too high for practical use. In ferroelectric ceramics, the Curie temperature can be written as

$$T_c = \gamma C\left(C = \frac{Np^2}{3\varepsilon_0\kappa}\right) \tag{2}$$

where γ is Lorentz coefficient, ε_0 is the permittivity of free space, p is the spontaneous of single dipole, P is the spontaneous, N is the number of dipoles within the unit volume, κ is Boltzmann constant. Microscopic dipole and macro Curie–Weiss temperature is contacted by Eq. (2) and it can be also seen that the Curie temperature is determined by the number of dipoles and the coupling strength between them. For conventional lead titanate ($PbTiO_3$) ceramics, the spontaneous polarization in addition to the contribution of Ti^{4+} ion displacement, should also include the contribution of the electronic displacement polarization, other ion displacement polarization and other electronic displacement polarization. Besides, Pb^{2+} has outer electron cloud structure of non-inert gas type in which the polarization between outer electron cloud and Ti^{4+}, O^{2-}, Ti^{4+}, O^{2-} and Pb^{2+} is large. Thus, in $PbTiO_3$ ceramics, the displacement of Pb^{2+} (0.047 nm) is very great, which causes high Curie temperature of $PbTiO_3$ ceramics. Relative to large displacement of lead ions, in barium titanate ($BaTiO_3$) ceramics, the displacement of Ba^{2+} (0.005 nm) is very small, which is attributed that Ba^{2+} has the outer electron cloud structure of inert gas-type, so the Curie temperature of $BaTiO_3$ (120 °C) is far lower than that of $PbTiO_3$ (490 °C). Based on the theory above, in this study, Ba^{2+} with outer electron cloud of inert gas-type placing Pb^{2+} with the outer electron cloud structure of non-inert gas type was used in preparing PZST ceramics with low Curie temperature and high pyroelectric response and the effects of Ba^{2+} content on the ferroelectric, dielectric and dc field-induced pyroelectric properties of PZST ceramics with different Zr/Ti were studied.

2. Experimental

Four groups of ceramics were prepared by conventional solid state synthesis.

The first group: $(Pb_{0.97-x}Ba_xLa_{0.02})(Zr_{0.6}Ti_{0.1}Sn_{0.3})O_3$ ($x = 0.09$, 0.1, 0.11).

The second group: $(Pb_{0.97-x}Ba_xLa_{0.02})(Zr_{0.65}Ti_{0.09}Sn_{0.26})O_3$ ($x = 0.117$, 0.13).

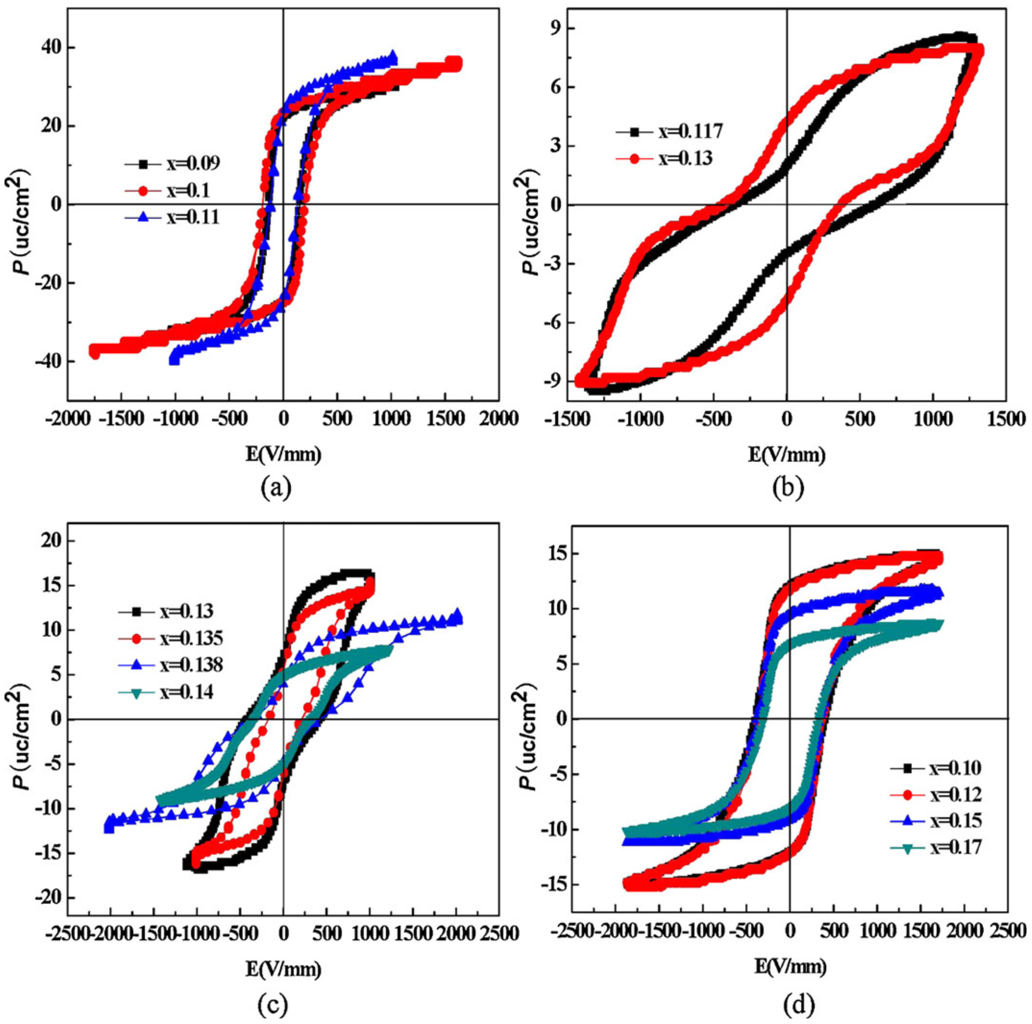

Fig. 1. P–E hysteresis loops of (a) the first group of specimens, (b) the second group of specimens, (c) the third group of specimens and (d) the fourth group of specimens.