Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 3405–3411

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Manganese effect on the relaxation behaviors of the space charge polarization in $Pb(Fe_{2/3}W_{1/3})_{0.9}Ti_{0.1}O_3$ ceramics

Cheng-Shong Hong [a,*], Sheng-Yuan Chu [b,c,d,e,f,**], Cheng-Che Tsai [g], Wen-Chang Su [b]

[a] Department of Electronic Engineering, National Kaohsiung Normal University, Kaohsiung County 824, Taiwan, ROC
[b] Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC
[c] Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, Taiwan, ROC
[d] Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan, ROC
[e] Institute of Nanotechnology and Microsystems Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC
[f] Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 700, Taiwan, ROC
[g] Department of Electronics Engineering and Computer Science Tung-Fang Design University, Kaohsiung County 829, Taiwan, ROC

Received 29 May 2010; received in revised form 17 February 2011; accepted 24 March 2011
Available online 12 June 2011

Abstract

The effects of manganese on the space charge polarization in $0.9Pb(Fe_{2/3}W_{1/3})O_3$–$0.1PbTiO_3$ (0.9PFW–0.1PT) ceramics are discussed using the Debye theory and the Arrhenius law. The static dipole moment of the space charge polarization is decreased by the MnO additives. The values of the Debye relaxation time τ_0 and the activation energy E_τ of the space charge polarization are similar at any temperature range before adding MnO. These values are changed after adding MnO and are obviously changed only at the lower temperature range. According to these results, it is suggested that the space charge polarizations are induced due to the charge imbalance in the micropolarization region and the conductive carriers. The charge imbalance and the conductive carriers are reduced by adding MnO additives since the compositional fluctuation is restrained and the electronic compensation is induced.

Keywords: Relaxor; Space charge polarization; Debye; Arrhenius; Relaxation time

1. Introduction

The complex perovskite type relaxor ferroelectric materials (RFE) show the ABO_3 structure where the A site and B site can be occupied by different metal cations which cause the compositional fluctuation effect [1–5]. In RFE materials, the polarization microregions have slightly different compositions which cause polarization of different natures. Hence, the peculiar dielectric physical properties are induced by such dipoles and their interactions [6]. To describe this phenomenon, researchers have provided several kinds of models, such as the inhomogeneous micro region model [7–14], the superparaelectric model [1,15,16], the glass model [17–19], the order-disorder model [20–23], the random fields model [24,25], the breath model [6], the micro-macro domain transition model [26,27] and the relaxation time distribution model [3,28]. In addition, the Debye theory considers that the dipoles have specific relaxation time and the dielectric response depends on the frequency of the external field [29]. The Arrhenius law considers that the relaxation time of dipoles depends on the environmental temperature [29]. These models can be used to discuss the characteristic of a dipole in a dielectric medium [3,6,28,30].

$Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) is one of the classical relaxors with lower sintering temperature (about 900 °C) and can be applied for multi-layer ceramic capacitors [31,32]. However, the lower Curie temperature T_c at −90 °C and the higher dielectric loss are disadvantages for practical applications [4,30–36]. The lattice structure and the dielectric properties of the pure PFW can be easily changed by adding $PbTiO_3$ (PT) composition, adding the dopants or changing the synthesizing process [4,30,33–36]. Zhou et al. synthesized the $Pb[(Fe_{2/3}W_{1/3})_{1-x}Mn_x]O_3$ solid solution for

---

* Corresponding author. Tel.: +886 7 7172930x7915; fax: +886 7 6051330.
** Corresponding author at: Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC.
Tel.: +886 6 2757575x62381; fax: +886 6 2345482.
E-mail addresses: cshong@nknu.edu.tw (C.-S. Hong), chusy@mail.ncku.edu.tw (S.-Y. Chu).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.03.082

pure PFW ceramics doped with $Mn(NO_3)_2$ [34]. When doping manganese cations, the dielectric loss is decreased, the second dielectric peak induced from the space charge polarization is vanished and the diffused phase transition is sharper. Similarly, Szwagierczak and Kulawik report that the resistivity is increased and the second dielectric peak is diminished after adding MnO_2 in pure PFW ceramics [30]. The MnO-additive effects in $(1 - x)$PFW–xPT ceramics are investigated by authors on the diffused phase property, the dielectric loss and the charge compensation [37].

Due to the compositional fluctuation in RFE materials, the charge imbalance in the micropolarization region and the conductive carriers are often induced and cause the space charge polarization [38–44]. In PFW–PT ceramic system, the space charge polarization is usually existent and is effectively decreased by doping manganese cations [30,33–37]. However, few papers carefully report the effect of the manganese cations on the dielectric relaxation behaviors of the space charge polarization for PFW–PT ceramic. In the present work, the relaxation behaviors of the space charge polarization are investigated using the Debye theory and Arrhenius law for pure and MnO added 0.9PFW–0.1PT ceramics. According to the experimental data and fitting results, the static dipole moment, the Debye relaxation time and the activation energy of the space charge polarization are determined and discussed. Furthermore, the effects of MnO additives on the dielectric relaxation behaviors of the space charge polarization are also investigated.

2. Experiment and ceramic preparation

Raw materials were mixed using pure reagent PbO, Fe_2O_3, WO_3, TiO_2 and MnO powders (99.5% purity). The materials $0.9Pb(Fe_{2/3}W_{1/3})O_3$–$0.1PbTiO_3$ with or without adding 0.15 wt.% MnO were synthesized by calcining at 750 °C for 2 h, then followed by pulverization. After that, the samples were pressed into a disk of 12-mm diameter and 2-mm thickness at a pressure of 25 kg/cm^2. Specimens were sintered isothermally at a heating rate of 5 °C/min at about 900 °C for 2 h. In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, and then subsequently fired at 750 °C for 25 min. The dielectric properties of the samples were measured using an impedance analyzer (HP4294A) in the temperature-controlled container. The phase relations for the sintered samples were identified using an X-ray diffractometer (XRD). Fig. 1 shows the X-ray patterns of 0.9PFW–0.1PT and 0.9PFW–0.1PT–0.15 wt.% MnO compounds. Pure perovskite structures are obtained [37].

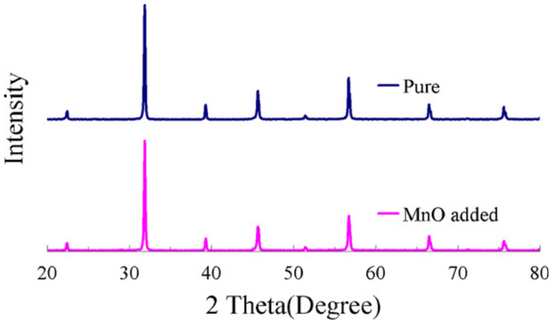

Fig. 1. The Bragg peaks of 2θ in the range between 20° and 80° of pure and MnO added 0.9PFW–0.1PT ceramics.

3. Theory

3.1. Debye theory

The dielectric response is caused by the polarization of dipoles. These dipoles can be switched by the external field. When the frequency of the external field is lower, the relaxation processes of these dipoles are rapid compared with the external field and cause the polarization. When the frequency of the external field is higher, some motions of these dipoles exhibit a time lag with respect to the external field and induce the relaxation phenomenon. This relaxation phenomenon is suggested by the Debye theory. The Debye equations are shown as [29]:

$$\varepsilon^* = \varepsilon_s \frac{1}{1+\omega^2\tau^2} + j\varepsilon_s \frac{\omega\tau}{1+\omega^2\tau^2} \tag{1}$$

$$\varepsilon' = \varepsilon_s \frac{1}{1+\omega^2\tau^2} \tag{2}$$

$$\varepsilon'' = \varepsilon_s \frac{\omega\tau}{1+\omega^2\tau^2} \tag{3}$$

where ε^* is the complex dielectric constant, ε_s is the static dielectric constant as the frequency of external field is zero, ω is the measurement angular frequency and τ is the relaxation time of dipoles. ε' is the real dielectric constant. ε'' is the dielectric loss and is induced by the relaxation effect of dipoles in an applied alternating field. Eq. (3) is usually used to find the relaxation time of dipole and the static dielectric constant ε_s by $\varepsilon_s = 2\varepsilon'$ when $\omega\tau = 1$.

3.2. Arrhenius law

As mentioned before, the frequency response of dipole mainly depends on its relaxation time. The relaxation time of the dipoles not only depends on the mechanisms of polarization, the atomic polarization, the ionic polarization, the orientation polarization and the space charge polarization, also depends on the environmental temperature. The Arrhenius law is usually used to explain the relationship of the relaxation time of dipole and the environmental temperature. The equation is shown as [29]:

$$\tau = \tau_0 \exp\left(\frac{E_\tau}{k_B T}\right) \tag{4}$$

where τ is the relaxation time of dipole, τ_0 is the Debye relaxation time, E_τ is the activation energy, k_B is the Boltzmann constant and T is the environmental temperature. The values of τ_0 and E_τ are usually used to determine the characteristic of dipoles [3,6,28,30].