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Point defect engineering of high temperature piezoelectric BiScO₃–PbTiO₃ for high power operation

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A R T I C L E   I N F O

A B S T R A C T

BiScO₃–PbTiO₃ is used as a model system of BiMO₃–PbTiO₃ perovskite solid solutions with enhanced electromechanical response at ferroelectric morphotropic phase boundaries, and high Curie temperature to demonstrate specific point defect engineering for high power operation. The objective is to obtain a range of piezoelectric ceramics comparable to hard Pb(Zr,Ti)O₃ materials, optimized for the different applications. In this work, a comprehensive study of Mn substitution for Sc is provided. Care is taken to isolate the effects of the point defects from those of concomitant structural and microstructural changes that have been previously described after MnO₂ addition. Results strongly suggest that Mn substitution results in the formation of (Mn_{Sc}'-$V_O^{\bullet\bullet}$) dipolar complexes that effectively clamp domain walls. This is the same mechanism responsible of hardening in Pb(Zr,Ti)O₃. Indeed, $Bi_{0.36}Pb_{0.64}Sc_{0.36-x}$ $Mn_xTi_{0.64}O_3$ with x = 0.02 is shown to be a high sensitivity piezoelectric with strongly reduced losses, suitable for high power operation between 200 and 400 °C.

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1. Introduction

BiScO₃–PbTiO₃ is the most promising system among perovskite solid solutions with general formula BiMO₃–PbTiO₃ (where M is a trivalent cation in octahedral coordination) and enhanced electromechanical response at ferroelectric morphotropic phase boundaries (MPBs), which show high Curie temperatures [1–6]. These compounds are being investigated extensively as alternative to state-of-the-art Pb(Zr,Ti)O₃ (PZT) for expanding the operation temperature of high sensitivity piezoelectric ceramics beyond 200 °C, up to 400 °C [7–9].

The binary system (1-x)BiScO₃-xPbTiO₃ presents a MPB between ferroelectric polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetry at x~0.64, composition for which the Curie temperature T_C is ≈450 °C, while piezoelectric coefficients d_{33} of ~450 pC N⁻¹ are typically achieved after poling [1,2]. This T_C is 100 °C above that of Pb(Zr,Ti)O₃. Likewise d_{33} significantly exceeds the figure of ≈245 pC N⁻¹ obtained for ceramics of the latter material at its MPB [10]. Moreover, the charge piezoelectric coefficient is comparable to those of available commercial high sensitivity piezoelectric ceramics of chemically engineered PZT [11].

The very high piezoelectric response of the Pb(Zr,Ti)O₃ per-ovskite solid solution at the MPB is known to result from the presence of an intermediate monoclinic phase with Cm space group, which provides a structural bridge between the rhombohedral and tetragonal polymorphs [12], and the occurrence of lattice transverse softening at the monoclinic-tetragonal boundary [13]. This results in very high transverse polarizability and thus, in large shear piezoelectricity that is ultimately responsible of the high effective piezoelectric coefficients obtained. The same mechanism must be operative in BiScO₃–PbTiO₃, for an analogous monoclinic phase has been described [14,15]. However, this single crystal contribution only account for 1/3 of the total piezoelectric coefficient of PZT ceramics [10].

The additional, actually major contribution to the piezoelectric response is originated from ferroelectric/ferroelastic domain wall movements [10,16]. Indeed, the tailoring of this contribution by point defect (or chemical) engineering of Pb(Zr,Ti)O₃ has been key to the success of this material technology, and has enabled the available wide family of high sensitivity piezoelectric ceramics optimized for a range of applications. It is currently acknowledged that the viability of novel materials alternative to PZT, either environmentally friendly ones or piezoelectrics for harsh environments, requires the development of analogous point defect engineering for the different oxide compounds. This has not systematically been addressed for any of the BiMO₃–PbTiO₃ systems up to now, and it is done here for model BiScO₃–PbTiO₃.
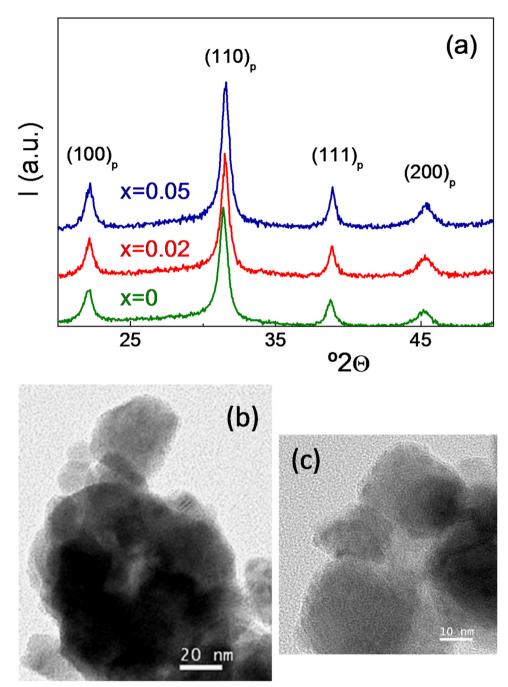
Fig. 1. (a) XRD patterns of the nanocrystalline $Bi_{0.36}Pb_{0.64}Sc_{0.36-x}Mn_xTi_{0.64}O_3$ powders with x = 0, 0.02 and 0.05, obtained by mechanosynthesis, and (b,c) TEM images of that with x = 0.02.

Roughly speaking, there are two main families of $Pb(Zr,Ti)O_3$ based materials, referred as hard and soft PZTs. The former is characterized by reduced domain wall activity and thus, small dielectric and mechanical losses. Low losses are required for high power applications like ultrasound generation or ultrasonic motors, where heating under operation is an issue [11,16]. Hardening is currently achieved by substitution of trivalent species, such a Fe^{3+} for Ti/Zr^{4+} at the B-site. Oxygen vacancies are created for charge compensation, which associate with the acceptor species forming dipolar defects that electrostatically interact with the spontaneous polarization, effectively clamping the domain walls [17,18]. A similar hardening has been reported for $BiScO_3$–$PbTiO_3$ after MnO_2 addition [19,20].

As a matter of fact, the MnO_2 additive was initially used as an effective means of increasing the resistivity of $BiScO_3$–$PbTiO_3$ ceramics at the targeted operation temperatures, from $\sim10^8$ and 10^5 up to 10^{10} and 10^7 Ω cm at 300 and 450 °C, respectively [19]. Piezoelectric high sensitivity materials with stable functionality up to temperatures above 400 °C were obtained by this procedure [7]. The actual mechanism for the enhanced resistivity was later studied [21]. In this report, Mn was shown to incorporate into the perovskite structure as Mn^{3+} substituting for Sc^{3+} (Mn_{Sc}^{x} in the Kröger-Vink notation). A twofold effect was described: firstly, Mn^{2+} was formed after trapping of the conduction electrons excited from existing oxygen vacancies; and secondly, this Mn^{2+} associated with oxygen vacancies forming (Mn_{Sc}'-$V_O^{\bullet\bullet}$) dipolar defects, whose