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Shape memory effect in PZST system at exact morphotropic phase boundary

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ABSTRACT

Unmodified lead zirconate titanate stannate (PZST) system with compositional formula Pb $[(Zr_{0.7}Sn_{0.3})_xTi_{(1-x)}]O_3$, where $0.92 \leq x \leq 0.94$ has been studied at Morphotropic phase boundary (MPB) for dielectric, ferroelectric and shape memory effect. Field-induced strain measurements are presented to show that ~0.08% remnant strain pertaining to shape memory can be observed in PZST ceramics at near-exact MPB.

1. Introduction

Stress, temperature or electric field-induced antiferroelectric (AFE) to ferroelectric (FE) phase transition is responsible for shape memory effect (SME) in many lead based systems [1–8]. Pragya Pandit et al. [4] reported that the composition in the vicinity of MPB is favorable for such type of phase transition. The free energy difference between the AFE and FE states at MPB is very small, so that parent AFE phase can be driven to FE phase by application of electric field. If this induced metastable FE phase remains after the removal of electric field than it produces remnant strain in the sample. If this remnant strain can be removed by applying electric field in reverse direction, it is called shape memory effect [9–14].

Jaffe [15] has studied and given a phase-diagram of niobium modified (2% Nb) lead zirconate stannate titanate system (PNZST) at room temperature (RT) (see Fig. 1). In this phase diagram of PNZST system, there are two MPBs between AFE and FE phases. MPB between orthorhombic AFE (A_o) and rhombohedral FE (F_R) is not suitable for shape memory application due to large electric field requirement for phase switching. Generally dielectric breakdown takes place before the phase switching [16]. Berlincort [17] found that substitution of Sn^{4+} for Zr–Ti ratio extends the tetragonal AFE phase. We studied this system by varying Ti^{4+} content and keeping Zr–Sn ratio constant.

Till date, research papers have shown field induced strain properties in various modified PZST systems viz., PNbZST [18], PLaZST [19], PYZST [12] and PNdZST [20]. We present here the results of our studies on field-induced strain and polarization measurements on unmodified PZST system with variation in Ti^{4+} content. Taking clue from this Fig. 1, we are working close to MPB of tetragonal AFE (A_T) and rhombohedral FE (F_R) phases, shown by a circle in this figure.

The aim of this work is to approach the MPB as close as possible, so as to obtain a combination of FE and AFE phase in the same composition. The series of ceramic samples with chemical formula Pb $[(Zr_{0.7}Sn_{0.3})_xTi_{(1-x)}]O_3$, where x was initially varied as $x = 0.92,\ 0.93,\ 0.94$, were prepared. Ti^{4+} substitution favors ferroelectricity due to the smaller radii. Compositions $x = 0.92$

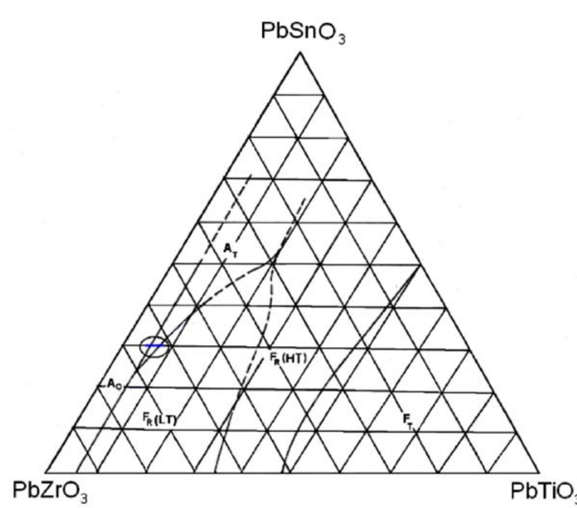

Fig. 1. Phase diagram of PNZST system at room temperature.

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and 0.93 were found to be ferroelectric at room temperature whereas the composition with $x = 0.94$ was observed to be antiferroelectric. Value of x was then varied upto third decimal point between $x = 0.93$ and 0.94 (0.933, 0.935 and 0.938), to approach the exact MPB.

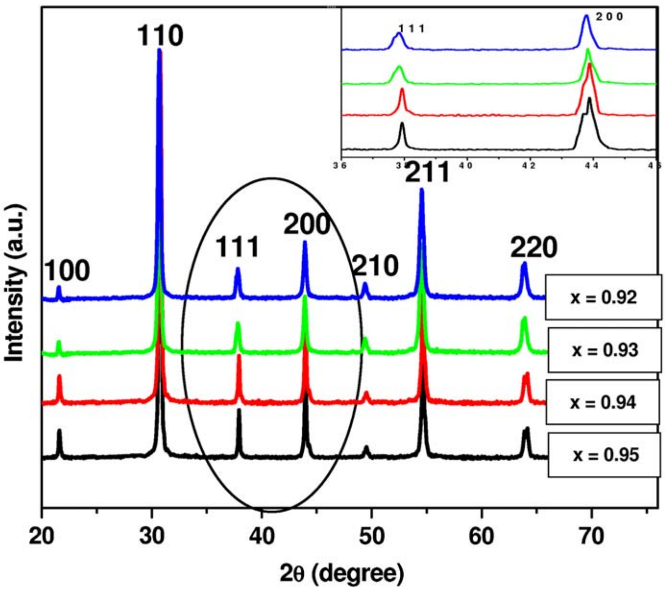

Fig. 2. XRD patterns at room temperature.

2. Experimental procedure

All samples used in this study were prepared by solid-state route. Purity of the starting raw materials was 99.9% (Aldrich Chem. Ltd.). The mixed powders were calcined at 950 °C for 4 h and pellets were sintered at ~1250 °C for 2 h. Relative density of all the sintered pellets was more than 95%. XRD of the sintered pellets showed pervoskite structure.

For electrical characterizations, the sintered samples were polished to obtain parallel and smooth faces. Gold electrodes were made by thermal evaporation on the faces of the pellets. After electroding, the samples were heat-treated at 450 °C for 30 min to ensure the contact between the electrodes and the ceramic surfaces. The dielectric properties of the sintered samples were studied as functions of both temperature and frequency with the impedance analyzer (HP 9142A). The capacitance and the dielectric loss tangent were determined in the temperature range 30 °C ≤ T ≤ 220 °C with the frequency ranging from 1 kHz ≤ f ≤ 500 kHz. Measurements were carried out at the heating rate of 0.5 °C/min. The ferroelectric hysteresis (P–E) loops were measured using work station (Radiant Technologies, USA) at room temperature and 0.1 Hz frequency. Field induced strain measurements were carried out on a LVDT based strain meter (SS 50 strain measurement system, Sensor Tech. Ltd., Canada).

3. Results and discussion

Fig. 2 show room temperature X-ray diffraction patterns of all compositions. It is clear that all compositions have pervoskite

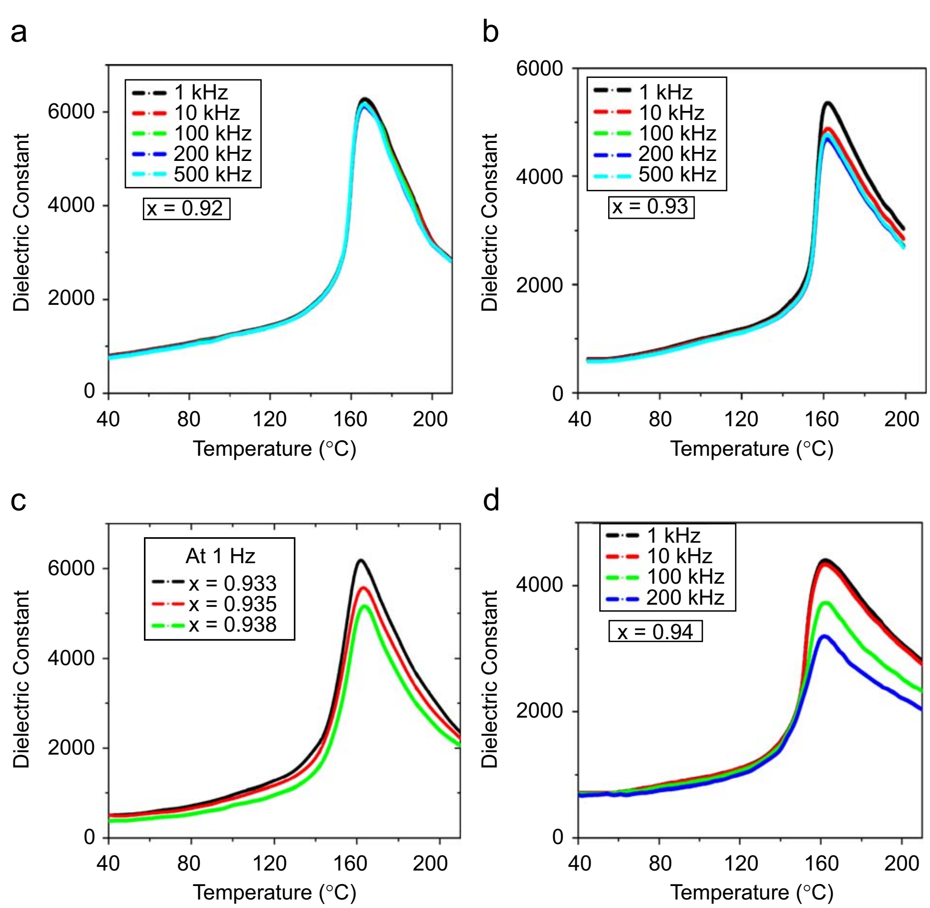

Fig. 3. Dielectric constant of PZST compositions at varying temperature.