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Piezoelectric materials: roads to enhanced properties

Dragan Damjanovic[1] (Ceramics Laboratory, Swiss Federal Institute of Technology in Lausanne – EPFL, 1015 Lausanne, Switzerland)

1. Introduction

The last decade has witnessed a considerable advancement in ferroelectric and piezoelectric materials: from discovery of the giant piezoelectric response in relaxor-ferroelectrics, via *ab-initio* description of piezoelectric instabilities, discovery of monoclinic phase in the phase diagram of $Pb(Zr,Ti)O_3$, (PZT) development of new lead-free piezoelectrics and first devices based on them, advances in micro-machined transducers and high frequency devices to envisioning of nano-piezoelectrics for applications such as energy harvesting. Competition to the piezoelectric effect has also become significant, with examples including capacitive transducers and flexoelectric effect. These paper reviews recent developments in these topics. In particular, mechanisms contributing to the piezoelectric effect are discussed in terms of the domain walls structure and domain walls dynamics, atomic defects, nature of the morphotropic phase boundary, and phase instabilities. A new concept of MPB and new materials, such as lead-free alternatives to PZT, high temperature and high frequency piezoelectric materials are discussed.

2. A new view of the morphotropic phase boundary

In most extensively used piezoelectric material, ferroelectric $Pb(Zr,Ti)O_3$, the properties are highest at the morphotropic phase boundary (MPB). In PZT, the MPB is the region of the phase diagram where rhombohedral and tetragonal phases meet via an intermediary monoclinic phase. The origin of the high properties has been related to enhanced polarization rotation in this region. The role of the monoclinic phase in the enhancement process is discussed. It is shown that a monoclinic phase by itself is not a sufficient condition for a system to exhibit exceptional properties. It is also shown that polarization rotation is not the only process that can enhance electro-mechanical properties in the MPB region. Another process called polarization extension may have a comparable effect.[1)] This mechanism, well known in temperature-driven phase transitions, has been indirectly predicted by *ab-initio* calculations and then directly observed experimentally in nonferroelectric AlN-ScN and related solid solutions.[2, 3)] A modified composition-driven phase diagram for ferroelectric solid solution that benefits from both polarization rotation and polarization extension has been recently proposed by the author. It contains an MPB between a ferroelectric and a nonpolar materials and is discussed in detail.[4)]

3. Domain wall structure, domain wall motion and piezoelectric properties -

Domain walls contribute to the macroscopic electro-mechanical properties of ferroelectric materials in a number of ways. In some cases it appears that the very presence of engineered domain walls leads to local modification of the lattice response and greatly enhances the properties. The mechanism is possibly related to elastically incompatible and/or charged engineered domain walls. This is one possible explanation for the large piezoelectric properties in domain engineered crystals and textured ceramics [$Pb(Zn_{1/3}Nb_{2/3})O_3$ -$PbTiO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$ -$PbTiO_3$, $BaTiO_3$[5)]] and will be discussed in some detail for $BaTiO_3$.[6)]

Domain wall motion (both reversible and irreversible) is another process that can lead to large enhancement of the properties. In a recent study, this mechanism has been studied *in-situ* using high energy and time resolved X-ray diffraction.[7)] The study reveals that in some PZT ceramics the lattice response contributes relatively little to the total piezoelectric response and that intergrain interactions account for surprisingly large part of the macroscopic properties. This result explains in part why properties of ferroelectric ceramics depend so much on their microstructure. A study of domain wall contributions based on broad-band dielectric spectroscopy (mHz – GHz) is also presented. It reveals several distinct domain-wall related contributions to the electro-mechanical response in ferroelectric ceramics. [8, 9)]

4. New compositions

There is a strong world-wide drive to develop lead-free piezoelectric materials. Because PZT is so

[1]E-mail: dragan.damjanovic@epfl.ch

successful material the potential replacements are searched among systems that exhibit the same type of the morphotropic phase boundary and domain wall contributions as PZT. Presently most promising candidates [$(K,Na)NbO_3$-, $(Bi_{1/2}Na_{1/2})O_3$- and $BaTiO_3$- based solid solutions are reviewed (phase diagrams, properties, temperature stability) and reasons why they do not exhibit PZT-like large piezoelectric properties are discussed. Other potential systems, e.g., $BiFeO_3$-based solid solutions are also discussed.

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