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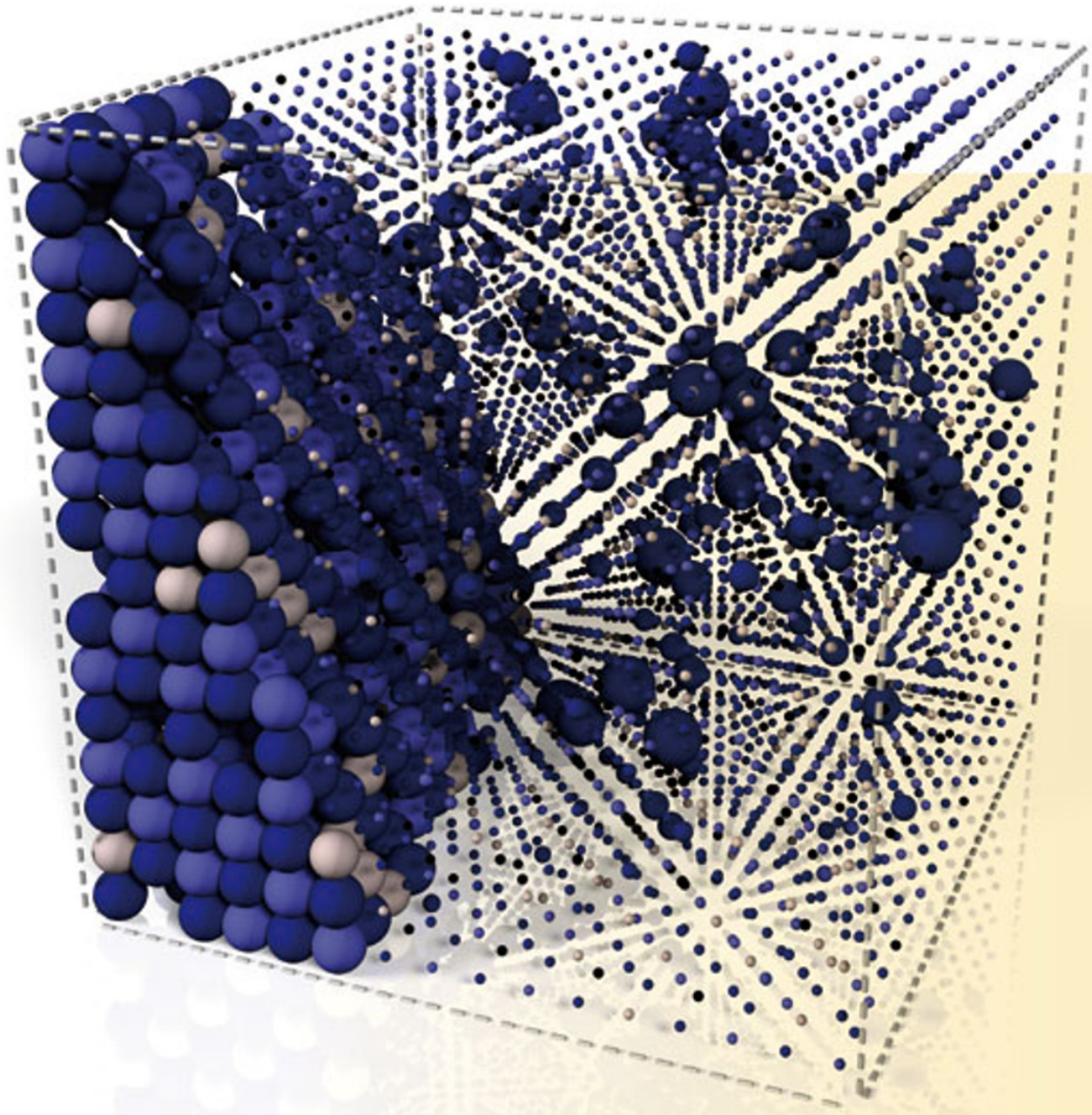
# Frontiers in Electronic Materials

Correlation Effects, Spintronics, and Memristive Phenomena –
Fundamentals and Applications



# Frontiers in Electronic Materials

A Collection of Extended Abstracts
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*Edited by*
*Joerg Heber, Darrell Schlom, Yoshinori Tokura,*
*Rainer Waser, and Matthias Wuttig*

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# INFLUENCE OF ADDITIVES WITH LOW MELTING TEMPERATURES ON STRUCTURE, MICROSTRUCTURE, PHASE TRANSITIONS, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF $BiScO_3 - PbTiO_3$ CERAMICS

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Piezoelectric materials referred as "smart" ones are widely used in industry [1]. Though most used PZT ceramics have excellent properties, they have rather low $T_C$ values and are considered as ecologically hazardous substances. This stimulates the development of new efficient materials with higher $T_C$ values and with reduced lead content [2]. Enhancement of piezoelectric properties is expected and was discovered in nanostructured materials with reduced domain size [3]. However, dielectric and piezoelectric characteristics usually have non monotonous dependence on average grain size of ceramics. In this work, an approach based on the introduction of the over stoichiometric additives has been used to improve functional properties of perovskite $BiScO_3$-$PbTiO_3$ ceramics. Crystal structure parameters of ceramic solid solutions close to morphotropic boundary $0.36BiScO_3$ - $0.64PbTiO_3$ doped by additives with low melting temperatures in amounts up to 5 w. % were studied (Fig.1).

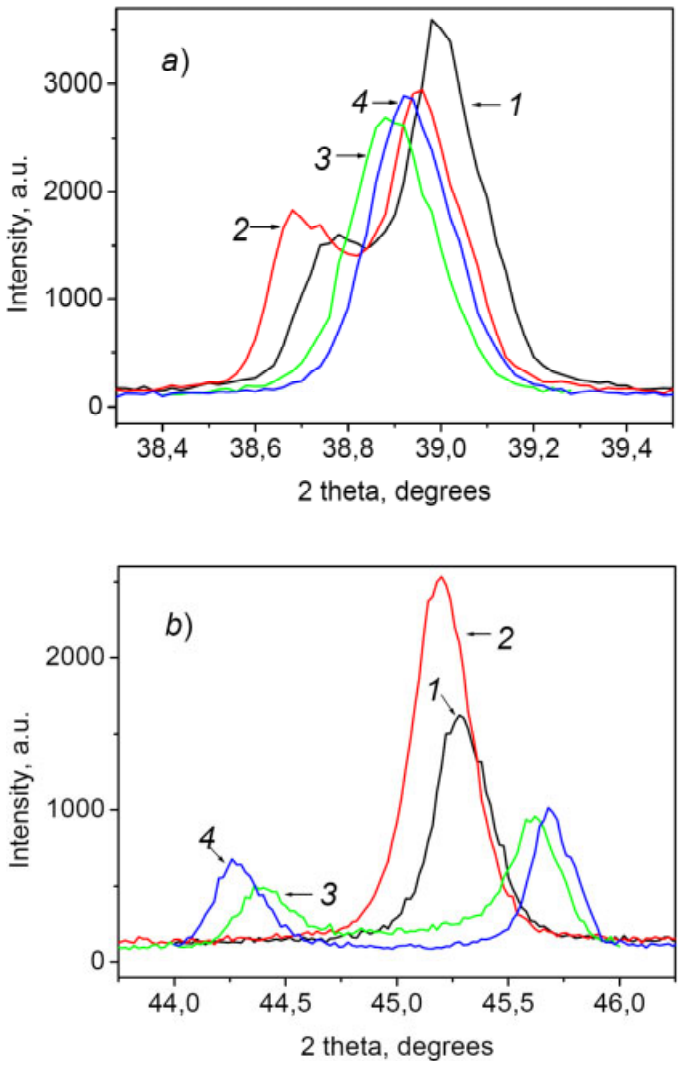


Fig. 1. X-Ray diffraction peaks with $h^2+k^2+l^2=3$ (*a*) and $h^2+k^2+l^2=4$ (*b*) of the samples $0.36BiScO_3$ - $0.64PbTiO_3$ sintered at 1050 K modified by complex additives: 3 w. % $Bi_2O_3$ + 0.5 w. % $Ni_2O_3$ (*1*), 3 w. % $Bi_2O_3$ + 0.5 w. % $MnO_2$ (*2*), 1 w. % LiF (*3*) and 5 w. % LiF (*4*). The effects of additives on sintering temperature, stoichiometry, structure parameters, microstructure, and functional properties of ceramics were checked. Introduction of these additives influenced the structure of solid solutions, and compositions *1* and *2* had rhombohedral structure, while compositions *3* and *4* had tetragonal structure. Shift of the diffraction peaks positions pointed to small changes in the unit cell parameters of the samples.

Decrease of the phase formation temperature and increase in density of doped ceramics was revealed. Diffraction peaks of samples *1* and *4* sintered at 1223 K were characterized by larger half width values that indicated on small (less than 100 nm) size of coherent length in these ceramics.

The samples were prepared by the solid state reaction method and additionally characterized by SEM, DTA/DSC, SHG, and dielectric spectroscopy methods. Piezoelectric parameters $d_{33}$ and $k_t$ of the preliminary poled samples were measured by the standard methods.

Variation of regimes of temperature treatment allowed us to prepare single phase samples characterized by wide variations in microstructure, with grain size varying from submicron to tens μm (Fig. 2).

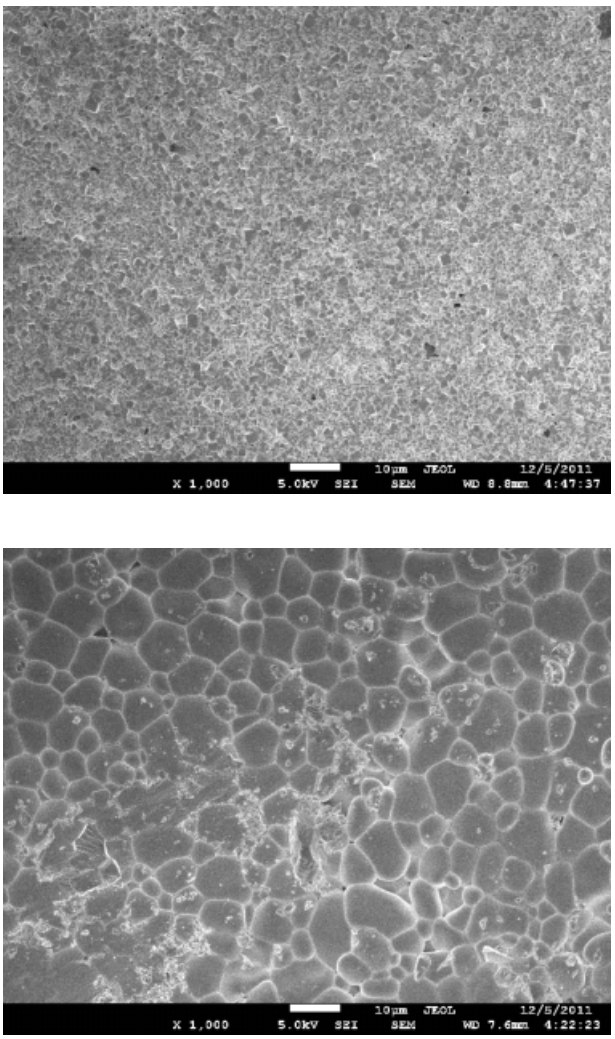


Fig. 2. Microstructure of ceramics $0.36BiScO_3 – 0.64PbTiO_3$ *1* and *2* sintered at $T_S$ = 1223 K, 2 h (*а*) and at $T_S$ =1298 K, 2 h (*б*), respectively.

White bars = 10 μм.

Ceramics *1* have grains with average size ~ 1 μм ($T$s = 1223 K) and with average size ~ 10 - 20 μм ($T$s = 1323 K). Ceramics *1* prepared at $T$s = 1223 K have sharp grain boundaries while those prepared at $T$s = 1323 K are characterized by melted boundaries determined by the manifestation of the liquid phase sintering mechanism. Ceramics *2* sintered at $T$s = 1298 K have uniform grains with size 5 - 10 μм. Ceramics *3* sintered at $T$s = 1298 K have large non uniform grains up to 20 μм. Ceramics 4 prepared at $T$s = 1273 K have highly packed grains with size 4 -8 μм. In these ceramics, small crystalline grains with size ~ 100 nm related to the presence of admixture phase were also revealed.

The 1st order sharp ferroelectric phase transitions marked by peaks in dielectric permittivity and dielectric loss versus temperature curves were observed at temperatures near 700 K. In some compositions, effects of dielectric relaxation related to the presence of oxygen vacancies in anion sublattice were observed.

High $d_{33}$ ~ 400 pC/N and $k_t$ ~0.7 values were measured in modified ceramics. The enhancement of piezoelectric properties observed, suppression of the relaxation effect in ceramics *1*, *2*, *4*, increase in resistance in ceramics *2* - *4* are grounded and discussed in relation to the type and content of additives.

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