High-Frequency EPR Studies on Co-Doped Ferroelectric Ceramics

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Introduction

Perovskite-type zirconate titanate oxides Pb\([Zr_{x}Ti_{1-x}]O_{3}\) (PZT \(x/1-x\)) are the most important piezoelectric materials used commercially for sensor and actuator applications. Furthermore, they are potential candidates for non-volatile memory devices. A great advantage of these materials is that device properties may be tailored by doping with aliovalent ions. Hence, considerable interest exists in the role of dopant ions, where even small concentrations have strong impact on PZT ferro- and piezoelectric properties. In particular, so-called co-doped compounds with simultaneously acceptor- and donor-dopants are of interest owing to their superior piezoelectric and electro-mechanical properties.

EPR is used to sensitively characterize structural and electronic properties of the (paramagnetic) dopant ions [1]. In case of the acceptor-type Fe\(^{3+}\) high-spin center, the local symmetry can be explored by monitoring the resulting fine-structure (FS) interaction, which will be modified by the presence of oxygen vacancies \(V_0\). If charge compensation through the creation of oxygen vacancies occurs in the nearest-neighbor \(O^2-\)ion shell, a large distortion of the octahedral symmetry results and because of the short distance, a large change of the intrinsic Fe\(^{3+}\) FS tensor will be induced. This work aims for an unambiguous determination of the FS parameter by application of high-frequency EPR up to 360 GHz, thus creating the basis for an accurate modeling of the structure by using a semi-empirical Newman superposition approach. Structural results obtained may then be compared with simultaneously performed density functional theoretic calculations [2]. Donor-type Gd\(^{3+}\) high-spin centers also possess a FS interaction [3]. For such systems, high-frequency EPR is an indispensable tool in order to accurately determine the FS parameters, if technologically relevant PZT compounds shall be investigated that are commonly available only as disordered compounds.

Experimental

The high-frequency EPR measurements over the temperature range 3 K – 300 K were performed on the 15/17 Tesla transmission instrument at the NHMFL.

Results and Discussion

High-frequency EPR spectroscopy enabled the determination of the local-environment sensitive FS parameter \(D\) for the extrinsic Fe\(^{3+}\) and Gd\(^{3+}\) dopants in polycrystalline PZT over a broad composition range [4,5]. The observed FS parameters give evidence for a formation of \(Fe^{3+}\)\(V_0\) defect dipoles in the ‘soft’ co-doped materials. On the basis of this information, the overall models for defect chemistry in ‘soft’ PZT compounds could be refined.

Additional experiments on ‘hard’ PZT in the technological relevant morphotropic phase boundary, give evidence for the existence of so-termed ‘nanodomains’ that in turn may be used to explain the extraordinary high piezoelectric response for these PZT compositions [6].

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References