HIGH-FREQUENCY EPR ON FUNCTIONAL CENTERS IN FERROELECTRIC CERAMICS

R.-A. Eichel, K.-P. Dinse (TU Darmstadt, Physical Chemistry); A. Ozarowski, J. van Tol, L.C. Brunel (NHMFL, EMR Facility)

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, because of their superior properties and notably due to the ability of tailoring these properties 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, compounds with \(Zr/Ti\) ratios near the morphotropic phase boundary (MPB) exhibit extremely high electromechanical coupling due to the coexistence of rhombohedral Zr-rich and tetragonal Ti-rich phases. Recently, it has been proposed that a monoclinic phase at the MPB, as a subgroup of both structures, can build a bridge between these phases, favoring a polarization rotation. In this work, high-field EPR up to 240 GHz was employed on copper(II)-doped Pb\([Zr_{0.54}Ti_{0.46}]O_{3}\) first to critically review a proposed existence of two different copper centers, and second to discriminate between different proposed structural models for the MPB [1]. For both purposes the inherent enhanced ability to resolve small \(g\)-value differences at high fields is exploited. The X-band EPR experiments used predominantly up to now were not able to answer these questions unambiguously because of the presence of a large anisotropic copper hyperfine interaction, preventing definite assignment of the corresponding \(g\) values.

An important end-member of the PZT solid solution system is lead titanate. In particular, if doping with iron is considered, the local symmetry can be explored by monitoring the resulting fine-structure (FS) interaction, which will be modified by the presence of oxygen vacancies \(V_{O}\). If charge compensation 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 190 GHz, thus creating the basis for an accurate modeling of the structure by using a semi-empirical Newman superposition approach [2]. In the magnetic field range of 2–8 T, with the electron Zeeman energy being the dominant term in the spin Hamiltonian, it is possible to accurately determine the FS parameters of Fe\(^{3+}\) in polycrystalline PbTiO\(_{3}\) from the observed van Hove singularities, which are related to canonical orientations of the compound. High-frequency EPR thus is an indispensable tool for the investigation of technologically relevant PZT, which is commonly available only as a disordered compound.

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

Results for the copper(II)-doped Pb\([Zr_{0.54}Ti_{0.46}]O_{3}\) compound suggest that Cu\(^{2+}\) substitutes as an acceptor centre for \([Zr,Ti]^{4+}\) in oxygen octahedra with tetragonal, monoclinic and rhombohedral distortion, confirming the model of mesoscopic mixing at the morphotropic phase boundary [1].

For the intrinsic iron(III) impurity center in polycrystalline lead titanate, high-frequency EPR spectroscopy enabled the determination of the local-environment sensitive FS parameter \(D\). The observed mean value \(D = +35.28 \text{ GHz}\) can be rationalized if Fe\(^{3+}\) ions substitute for Ti\(^{4+}\) at the B-site of the perovskite ABO\(_{3}\) lattice forming a directly coordinated Fe\(^{3+}\)–\(V_{O}\) defect associate. A consistent fit of the multi-frequency data necessitated the use of a distribution of the \(D\) values with a variance of about 1 GHz. This statistical distribution of values is probably related to more distant defects and vacancies [2].

Acknowledgements

This work was supported by NHMFL through project 7300-015.

References