# High-Frequency EPR on Functional Centers in Ferroelectric Ceramics

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## Introduction

The characterization of defect structure in piezoelectric lead zirconate titanate $Pb[Zr_xTi_{1-x}]O_3$ (PZT $x/1-x$) ceramic compounds is an important issue as it has major impact on device properties [1]. In particular, acceptor-doped ceramics with high concentration of oxygen vacancies ($V_O^{\bullet\bullet}$) show increased change of their electrical properties with time, the phenomenon being termed as *ferroelectric aging*. On the other hand, donor-doped ceramics with no significant $V_O^{\bullet\bullet}$ concentration are more stable in time concerning their electrical properties. By simultaneously co-doping with acceptor- and donor dopants, PZT compounds of excellent piezoelectric characteristics can be obtained.

## 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

Concerning acceptor-doped '*hard*' materials, the manganese functional-centre site in manganese-modified polycrystalline lead titanate ($PbTiO_3$) was studied. Exploiting the accurately determined fine-structure parameters by means of high-frequency EPR, isovalent $Mn^{4+}$ ions were identified as substituting for $Ti^{4+}$ at the B-site of the perovskite $ABO_3$ lattice. Based on Newman superposition-model calculations, it could be shown that the value of the experimentally obtained fine-structure parameters are only consistent with a microstructure in which the manganese functional center follows the titanium ion cooperative displacement in the ferroelectric phase [2]. Moreover, the effect of external electric fields on the orientation of $(Mn''_{Ti} - V_O^{\bullet\bullet})^{\times}$ defect dipoles in ferroelectric $BaTiO_3$ single crystals and its interplay with the domain structure were investigated. The results show that in specimens aged in the ferroelectric state for a defined time, the defect dipoles orient along the direction of spontaneous polarization and follow the domain switching upon poling with correspondingly high electric fields [3]. Additionally, the defect structure of another acceptor dopant could be characterized. In '*hard*' copper-modified polycrystalline $PbTiO_3$ ferroelectrics it was shown by means of hyperfine sublevel correlation spectroscopy (HYSCORE) and DFT calculations that copper is incorporated at the octahedrally coordinated Ti site, acting as an acceptor. Because of charge compensation the formation of Cu impurity–oxygen vacancy pairs is energetically very favorable. The corresponding $(Cu''_{Ti} - V_O^{\bullet\bullet})^{\times}$ defect dipole is found to be orientated along the [001] axis [4]. Concerning '*soft*' compounds, in 1 mol.% $La^{3+}$ and 0.5 mol.% $Fe^{3+}$ co-doped $Pb[Zr_{0.54}Ti_{0.46}]O_3$ ceramics it was shown that iron still forms a charged $(Fe''_{Ti} - V_O^{\bullet\bullet})^{\times}$ defect dipole [5]. This feature of the defect associates has hitherto been identified only in hard, exclusively $Fe^{3+}$-doped PZT compounds. The present results show, however, that a similar defect association also exists in soft, donor-acceptor co-doped PZT. This phenomenon was also observed in 1 mol% $Gd^{3+}$ and 0.5 mol% $Fe^{3+}$ codoped soft $Pb[Zr_{0.525}Ti_{0.475}]O_3$ ceramics [6]. Here, it was additionally shown that the gadolinium functional center rather forms no defect associate with lattice vacancies and thus exists as an 'isolated' functional center. Consequently, also the lead vacancies that are created for charge compensation have to exist as isolated centers in the compound.

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## References

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