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Multi-Frequency and Multi-Pulse EPR Spectroscopy for the Study of Structural and Dynamic Properties of Defect Centers in Perovskite Oxides

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Multi-frequency and multi-pulse Electron Paramagnetic Resonance (EPR) spectroscopy provides a sensitive technique to study the defect structure in piezoelectric lead zirconate titanate $\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ (PZT) as well as sodium potassium niobate $[\text{K}_y\text{Na}_{1-y}]\text{NbO}_3$ (KNN) ceramic compounds [1,2], which is an important issue as it impacts the materials properties of ferroelectric devices. In particular acceptor-doped ‘hard’ ceramics with high concentration of oxygen vacancies show increased change of their electrical properties with time, the phenomenon being termed as *ferroelectric aging*. On an atomic scale, it is shown that acceptor ions, such as Fe^{3+} or Cu^{2+} , are incorporated at the perovskite B-site, forming defect dipoles with a directly coordinated oxygen vacancy for reason of charge compensation [3-6]. Although the overall concentration of oxygen vacancies is increased for acceptor-doped PZT compounds, the concentration of mobile oxygen vacancies remains constant or even is reduced owing to the formation of defect dipoles of the additionally created vacancies.

On the other hand, donor-doped ceramics with no significant oxygen vacancy concentration and charge compensation by lead vacancies in distant coordination spheres [7] 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. In particular, defect associates analogous to acceptor-modified compounds have been identified also in ‘soft’ donor-acceptor co-doped compounds [8-10].

Another important issue in the class of ferroelectric materials is the control and understanding of so-termed *internal bias fields* in order to enhance device reliability. Internal bias fields manifest in voltage shifts of the ferroelectric hysteresis loop and may occur when the device remains in a particular polarization state for a given period of time. Such effects have been proposed arising due to the existence of inherent defect dipoles and their dynamics are being discussed in terms of the *ferroelectric aging* phenomenon. Whereas the fast rearranging processes that take part in domain growth and domain wall motion during poling are quite well understood, there is currently only a few such detailed information available about the switching dynamics of defect dipoles. In particular, defect dipoles do not switch during fast field cycling because such a process has to involve short-range-order oxygen vacancy diffusion around the acceptor centre and consequently has to be considerably slower

than the domain switching process and certainly has to involve considerably higher thermal and electric-field energies [11].

A further issue of relevance are high-temperature piezoelectric actuator and transducer applications. The $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$ (BSPT) solid solution system is a promising candidate owing to the considerably higher Curie temperature T_C for the ferroelectric-paraelectric transition as compared to conventional piezoelectrics, such as PZT. However, a major drawback for high-temperature piezoelectric devices is the fact that polycrystalline ferroelectric materials often are extrinsic semiconductors owing to impurities and charged defects. As a consequence they possess an inherently high level of conductivity at elevated temperatures. A strategy to circumvent this problem is the doping with manganese. The effect of multi-valency manganese doping on the defect structure and enhanced resistivity consists in the trapping of conduction electrons at the manganese functional center sites. Furthermore, through the formation of defect associates between the manganese ions and oxygen vacancies the ionic conductivity is reduced. Concerning the overall mechanism of charge compensation both kind of defects tend to mutual compensate.

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