DF 7: Point defect spectroscopy and engeneering

Time: Tuesday 10:00–13:00 Location: EB 107

Invited Talk DF 7.1 Tue 10:00 EB 107

Modelling of Point Defects in Ferroelectric Materials — •Karsten Albe[1] and Paul Erhart[2] — [1]Institut f. Materialwissenschaft, Petersenstr. 23, TU Darmstadt — [2]Lawrence Livermore National Laboratory, Materials Science Division, USA

The properties of ferroelectric materials and their behavior in the presence of electric fields are intimately related to the presence of defects. Oxygen vacancies, for instance, play a key role in aging and fatigue impeding domain wall motion or by acting as local disturbances of the polarization Experimental investigations of point defect properties either provide averaged bulk data or very localized information and can therefore be ambiguous. Quantum mechanical calculations based on density functional theory (DFT), on the other hand, are capable of providing fundamental insights into the energetics of defects as well as their kinetic and electronic properties. In this contribution, two examples will be discussed. For the prototype material barium titanate (BT), DFT calculations are used for verifying established defect models which have been employed to explain the experimental observations (in particular, conductivity and diffusivity measurements). Moreover, the formation of di-vacancies is explored which is an important ingredient for understanding the deterioration of ferroelectric switchability. In the second part, the energy surface of unbound oxygen vacancies and oxygen vacancies complexed with Fe or Cu in lead titanate (PT) is studied. The results are utilized to interpret recent electron spin resonance experiments and discussed in the context of existing defect models.

Invited Talk DF 7.2 Tue 10:40 EB 107

Polarons in lithium niobate — •Ortwin Schirmer — FB Physik, Universität Osnabrück

$LiNbO_3$ is an extraordinary testing ground for various manifestations of polarons. The Li-substoichiometry of its congruently melting composition facilitates the formation of bound hole (O^-), bound single electron (Nb_{Li}^{4+}) and bound electron bi-polarons (Nb_{Li}^{4+} - Nb_{Nb}^{4+}). Also free electron polarons (Nb_{Nb}^{4+}) can be prepared. In all cases these polarons are small, i.e. the ranges of the carrier amplitude and related lattice distortions extend over about one bond length. On the basis of detailed experimental information on bound hole polarons in numerous oxide materials, methods established for color centers have recently been modified to interpret the details of the corresponding strong optical absorption bands. This approach is extended to electron polarons in $LiNbO_3$. It allows to understand the related phenomena, most of them known since a long time, from a common viewpoint. Among the treated features will be the interpretation of the peak energies and shapes of the optical absorption bands, the binding energies of bipolarons as well as their dissociation and recombination.

DF 7.3 Tue 11:20 EB 107

Local structure and symmetry of paramagnetic ions in microscopic and nanoscopic ferroelectric materials — •Emre Erdem[1], Kamil Kiraz[2], Mehmet Somer[2], and Rüdiger -A. Eichel[1] — [1]Eduard-Zintl-Institut, Technische Universität Darmstadt, D-64287 Darmstadt, Deutschland — [2]Koc University, Department of Chemistry, Rumelifeneri Yolu, Sariyer, 80910 Istanbul Turkey

In this work, multi-frequency (9.5 GHz up to 319 GHz) electron paramagnetic resonance (EPR) spectroscopy is used in order to study the role of aliovalent and isovalent functional centres and their impact on lattice vacancies in $PbTiO_3$ and $PbZr_xTi_{1-x}O_3$. The examination of nanocrystalline ferroelectrics with perovskite structure and the determination of their physical and chemical properties are one of the challenges of the solid state physics and material science due to their potential application in device technology. To determine the structural changes which occur in correlation with size effects and size driven phase transition in $PbTiO_3$, dielectric, Raman and multi-frequency EPR measurements were carried out on Cr, Fe, Gd and Cu doped micro- and nanopowders. Through the size-dependent multi-frequency EPR spectra the spin-Hamiltonian parameters were determined and correlated with structural investigations and dielectric measurements.

DF 7.4 Tue 11:40 EB 107

The effect of (Gd^{3+},Cu^{2+}) and (Gd^{3+},Fe^{3+}) Co-Doping on the Defect Chemistry of $PbTiO_3$ — •Michael Drahus[1], Rüdiger Eichel[1], Emre Erdem[1], Hans Kungl[2], and Michael Hoffman[2] — [1]Eduard-Zintl-Institut, Technische Universität Darmstadt, Germany — [2]Institut für Keramik im Maschinenbau, Universtität Karlsruhe

The effect of Co-doping $PbTiO_3$ with (Gd^{3+}, Cu^{2+}) and (Gd^{3+}, Fe^{3+}) on dopant cation association of oxygen vacancies is examined with multiply-frequency EPR. Also, the possibility of the Gd cation substuting on both the A and B site as a self compensating acceptor donor is explored. Acceptordonor codoping has shown encouraging results as a way to reduce the Polarization Fatigue in both thin film and bulk Ferroelectrics. Therefore an understanding of the defect chemistry initiated by these scenarios is important for determining the underlying mechanism of polarization fatigue suppression

DF 7.5 Tue 12:00 EB 107

Influence of extrinsic defects on the recombination behavior of light-induced hole and electron polarons in $KNbO_3$ — •Bettina Schoke, Christoph Merschjann, Stefan Torbrügge, and Mirco Imlau — Department of Physics, University of Osnabrück, Germany

We study excitation and recombination processes of small hole and electron polarons in nominally pure and iron doped $KNbO_3$ samples by means of time–resolved excited–state–absorption (ESA) spectroscopy. The light–induced absorption $\alpha_{li}(t)$ in the visible and infrared spectral–range is measured after optical excitation with intense ns laser pulses ($\lambda = 532\,nm, \tau = 8\,ns$). In nominally pure $KNbO_3$ we observe the formation and relaxation of free (Nb_{Nb}^{4+}) electron polarons and bound O^- hole polarons within a single decay of α_{li} after a two–photon process of excitation. Their mutual recombination via incoherent hopping transport is crucially accelerated by Iron doping which additionally causes a slow decay component in $KNbO_3$:Fe. The reduction of the polaron hopping transport length in Fe-doped samples can be attributed to the increased number densities of optically-generated O^- hole polarons by additional one-quantum excitations due to extrinsic defects.

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DF 7.6 Tue 12:20 EB 107

Solid-state NMR on defects in lead titanates — •Marko Bertmer[1], Rüdiger Eichel[2], and Hans Kungl[3] — [1]Experimentelle Physik 2, Leipzig, Deutschland — [2]Physikalische Chemie III, Darmstadt, Deutschland — [3]Institut für Keramik im Maschinenbau, Karlsruhe, Deutschland

Failure of ferroelectrics is not well understood. In our approach, we employ various solid-state NMR techniques to characterize and quantify chemical structures that arise from crystallographic defects. Especially, the existence and distributions of ^1H as water or other species is a primary goal in our research.

^1H spectra are known to be often of low resolution due to the strong homonuclear dipolar coupling. With sophisticated NMR techniques, e. g. echo methods and multiple quantum transitions, we want to get more insight into the defect structures. This enables both improvement in spectral resolution as well as to obtain information about the dynamics of present chemical structures such as water.

Additionally, all nuclei present in lead titanates are accessible by NMR with different degree of sensitivity. Especially, with self-built equipment we are able to increase the abundance of the ^{17}O nuclei and therefore allow for detection.

DF 7.7 Tue 12:40 EB 107

Gitterplatzbestimmung und Ausheilverhalten von Hf implantiertem CaF_2 — •Thomas Geruschke und Reiner Vianden — Helmholtz - Institut für Strahlen und Kernphysik, Nußallee 14-16, 53115 Bonn, Deutschland

Untersucht wurden Hafnium implantierte Kalziumfluorid Einkristalle der Firma Schott AG. Die Gitterschäden, die durch die Implantation entstanden sind, wurden mittels RBS (Rutherford back scattering) abgeschätzt. Der Gitterplatz der implantierten Hf Ionen wurde entlang der <110> Kristallachse durch Gitterführungsexperimente bestimmt. Diese Experimente zeigten, das sich direkt nach der Implantation die Hf Ionen hauptsächlich (ca. 90%) auf regulären Ca Gitterplätzen be-

finden. Ein Vergleich des RBS Winkelscans mit Monte Carlo Simulationen bestätigt dies.
Das Ausheilen der Implantationsschäden durch ein isochrones Temperprogramm wurde mittels der Methode der gestörten γ - γ Winkelkorrelation (PAC) untersucht. Es zeigte sich eine starke Quadrupolwechselwirkung mit einer Frequenz von ν_u=1200MHz (η=0.43) ab einer Ausheiltemperatur von 550°C. Der Ursprung dieser Wechselwirkung sind Punktdefekte in unmittelbarer Sondenumgebung. Ob es sich dabei um Fluorfehlstellen oder substitutionellen Sauerstoff auf Fluorplätzen handelt ist noch Gegenstand der Untersuchung.