Electron Paramagnetic Resonance of Fe^{3+} centres in $PbTiO_3$

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A number of applications of the dominant ferroelectric material $Pb(Zr_x,Ti_{1-x})O_3$ require 'hard' material; material with a high apparent coercive field. This is achieved by acceptor doping, commonly with Fe^{3+}, and the mechanism is assumed to be the pinning of domain wall motion by the resulting Fe^{3+}_{Ti}–V_O defect dipoles. Direct evidence for the presence of Fe^{3+}_{Ti}–V_O defects comes from Electron Paramagnetic Resonance (EPR). However, review of previous EPR of $PbTiO_3$ show the presence of different centres in different studies and with inconsistent local structure interpretations. We report EPR studies of Fe^{3+} centres in a number of $PbTiO_3$ crystals. Three S=5/2 tetragonal symmetry centres with large zero field splittings (ZFS), which include crystal field interactions, are identified. The centres are most readily identified by the room temperature values of the ZFS (b^0_2/h) of 17, 29, and 32 GHz, respectively. Superposition model calculations of the ZFS values using isolated Fe^{3+}_{Ti} and Fe^{3+}_{Ti}–V_O local structures were performed. These provide evidence that both the 29 and 32 GHz centres involve a nearest-neighbour apical oxygen vacancy and the 17 GHz centre is the isolated Fe^{3+}_{Ti} defect. The fourth-order ZFS terms for the three centres were also studied. The 17 and 32 GHz centres have similar magnitudes for b^4_4 and were larger than that for the 29 GHz centre. The term is dominated by contributions from in-plane nearest neighbours. Annealing experiments have been performed to provide further insight on the nature of the three centres. The 32 GHz centre was found to disappear, and the intensity of the 29 GHz centre increase, after an anneal at 290°C for 1hr. Vacuum annealing at higher temperatures and longer times had no further effect on the 29 GHz centres but the 17 GHz centre intensity slow decreases.

It is suggested that the 32 GHz centre is a metastable Fe^{3+}_{Ti}–V_O configuration that readily converts to the stable 29 GHz Fe^{3+}_{Ti}–V_O centre. The difference in b^4_4 values is consistent with the in-plane oxygen ligands relaxing away from the Fe^{3+}_{Ti} in the 29 GHz centre.

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