Pulsed High Frequency EPR Investigation of Gadolinium-doped $PbZrO_3$ and $PbTiO_3$

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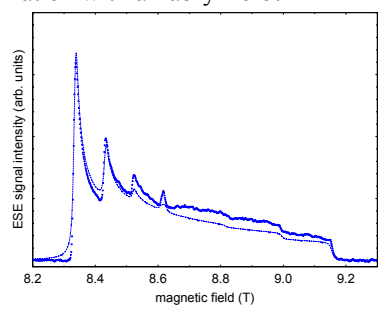
Introduction

Lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$, PZT) ceramics are used for a wide range of applications, like piezoelectric actuators and non-volatile memory devices. Doping by off-valent ions plays a crucial role for facilitating the switching of domains at moderate electric fields. EPR can be used to determine the local topology at the dopant site if "high spin" ions like Gd^{3+} (S = 7/2) are used [1]. We could demonstrate that pulsed HF-EPR can be performed even for compounds exhibiting large microwave losses, if a set up without invoking a mw cavity is used. In applying pulsed HF-EPR for the study of Gd doped ferroelectrics, we were probing for additional paramagnetic centers, not originating from "ideally" substituting Gd^{3+} ions.

Experimental

The existing spectrometer was recently modified to allow for pulsed operation in combination with a Fabry-Pérot resonator [2]. To enable the study of highly absorbing material, the resonator was replaced by a mirror, although a significant reduction of the mw amplitude B_1 results. Powder samples were placed in a 1 mm deep and 3 mm diameter hole in a teflon disk, covered by a mylar sheet and backed by a brass mirror.



Results and Discussion

With pulsed EPR, broad absorption features are detected without distortion. Echo detected EPR show spectra of sufficient S/N could be observed starting at about 6 K, because T_2 times larger than 500 ns are realized below this temperature. In the case of Gd:$PbTiO_3$ apart from the well structured EPR pattern shown in the figure, an unstructured broad absorption pattern was observed at lower temperatures. Spectral analysis indicated that Gd^{3+} ions are also positioned at highly distorted sites in the crystal. This might indicate that charge compensation leads to the formation of closely correlated Gd^{3+}-V_{Pb}-Gd^{3+} defects in addition to Gd^{3+} inserted substitutionally at Pb^{2+} sites. For the orthorhombic anti-ferroelectric low temperature phase of $PbZrO_3$ two inequivalent crystallographic Pb^{2+} sites of equal abundance are available. The contribution of Gd^{3+}inserted substitutionally at these sites could be confirmed although additional sites are also present. For details see [3].

Conclusions

The possibility to perform pulsed EPR at high frequencies was demonstrated for samples with high mw dissipation. The simple resonator-free set provided sufficient mw field amplitude, if the sample of 3 mm diameter and 1 mm thickness was placed close to the reflecting mirror. With currently available source power of 40 mW (240 GHz) an estimated $B_1 \cong 0.01$ mT was obtained. Echo dephasing times of up to 10 µs were observed when cooling the sample below 2 K.

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References

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