



## Determination of the Site of Substitution of Manganese in $\text{CaTiO}_3$ by Multi-frequency EPR

Maier, R.A. (National Institute of Standards and Technology) and Ozarowski, A. (NHMFL)

### Introduction

$\text{CaTiO}_3$  ceramic compositions were prepared with a range of manganese dopant concentrations above and below the dilute doping limit to determine the site of occupancy and valence state of the substituted ion in its perovskite host. While transition metal dopants often substitute as aliovalent defects in perovskite materials,<sup>1</sup> electron paramagnetic resonance (EPR) spectroscopy performed on polycrystalline samples reveals that amphoteric dopant substitution (complementary substitution of  $\text{Mn}^{2+}$  on the A-site and  $\text{Mn}^{4+}$  on the B-site) is the only mechanism of substitution for  $\text{CaTiO}_3$ . The site of substitution and valence of manganese was found to be independent of the Ca/Ti stoichiometry, dopant concentration, or presence of co-dopants. While the  $\text{Mn}^{2+}$  ion is clearly observed using standard continuous wave X-band EPR spectroscopy technique, the  $\text{Mn}^{4+}$  signal is only observed using higher frequency EPR methods.

### Experimental

$\text{CaTiO}_3$  samples with A and B-site manganese substitution with chemical formula  $\text{CaTi}_{1-x}\text{Mn}_x\text{O}_3$  with  $x=0.0005, 0.001, 0.002, 0.005, 0.01, \text{ and } 0.02$  were prepared using a standard mixed oxide technique. Powders were sintered at  $1350^\circ\text{C}$  for 6 hrs to achieve greater than 95% theoretical density.

Continuous wave EPR measurements were conducted at X-band using a Bruker Biospin (Billerica, MA) ELEXSYS E580 spectrometer equipped with a super high Q ER4122-SHQE cavity. The modulation amplitude was set to 0.5 mT at 100 kHz, and the incident microwave power was 15 mW at approximately 9.85 GHz. Spectra were collected over a 400 mT range with a total of 2048 points with a conversion time of 170.9 ms and sweep time of 350 s. High-frequency continuous wave EPR measurements were conducted on a 15/17 T SC magnet and the transmission spectrometer at NHMFL.

### Results and Discussion

The spectra shown in **Fig.1** reveal that there is only one paramagnetic defect responsible for the EPR signal at X-band with  $g$ -factor  $> 2$  with the relevant spin-Hamiltonian parameters used to fit the data (*Easyspin*<sup>2</sup>) given as:  $g_{iso} = 2.001$ ,  $A_{iso} = 239$  MHz,  $D = -438$  MHz, and  $E = -42$  MHz. Higher concentrations of Mn result in line broadening. The fitted results in **Fig.1** were provided by keeping the spin Hamiltonian parameters fixed and only adjusting the Lorentzian line shape, confirming the defect responsible for the EPR signal is the same at all concentrations. At higher frequencies, in **Fig.2**, a second feature with  $g$ -factor  $< 2$  is observed. It is clear from **Fig.2** that the EPR parameters ( $g$ -factor and hyperfine splitting constant) are the same and independent of the dopant concentration. Only the line broadening is affected by dopant concentration which is indicative of dipole-dipole interactions in the concentrated systems.

### Conclusions

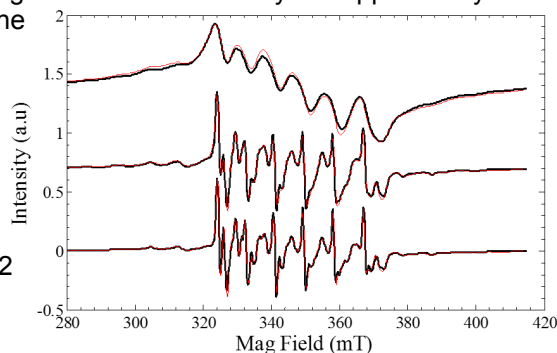
Experimental X-band EPR analysis was performed on Mn-doped  $\text{CaTiO}_3$  ceramics. The presence of  $\text{Mn}^{2+}$  is observed at X-band substituting for the Ca-site, while the  $\text{Mn}^{4+}$  signal is only observed at higher frequencies substituting for the Ti-site. Multi-frequency EPR analysis confirms the preference of Mn to substitute by means of an amphoteric mechanism, and density functional theory and x-ray absorption analysis of the samples confirms the Mn site assignments and will be published with the EPR data in an upcoming manuscript.

### Acknowledgements

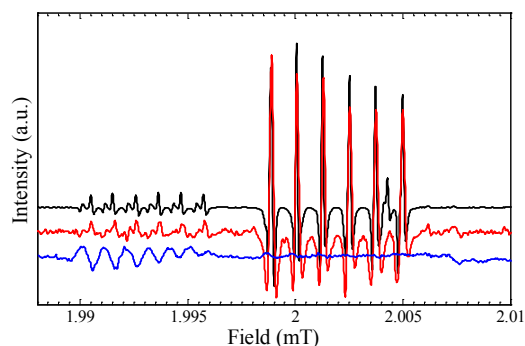
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### References

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- [2] Stoll, S., *et al.*, J. Magn. Reson., **178**, 42 (2006).



**Fig.1** X-band EPR spectrum for  $\text{CaTiO}_3$  with  $A/B = 1.000$ , as sintered (*black*) with the superimposed best fit (*red*) for samples (from top to bottom) with 0.05, 0.2, and 1 mol% Mn.



**Fig.2** HFEPR spectra for Mn-doped  $\text{CaTiO}_3$  ceramic samples measured at 400 GHz and 50 K on samples (from top to bottom): 0.05, 0.2, and 1 mol% Mn.