

Electron Magnetic Resonance of Diluted Solid Solutions of Gd³⁺ in BaTiO₃

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Electron magnetic resonance (EMR) spectra of gadolinium-doped barium titanate (BaTiO₃) have been studied at room temperature for gadolinium concentrations between 0.20 and 2.00 mol%. The results suggest that the Gd³⁺ ions occupy substitutional sites, replacing the Ba²⁺ ion, that the electron magnetic resonance linewidth increases with increasing gadolinium concentration, and that the range of the exchange interaction between Gd³⁺ ions is about 0.98 nm, of the same order as that of the same ion in other host lattices, such as strontium titanate (SrTiO₃), strontia (SrO), quicklime (CaO), magnesia (MgO) and zircon (ZrSiO₄). The fact that the electron magnetic resonance linewidth of the Gd³⁺ ion increases, regularly and predictably, with Gd concentration, shows that the Gd³⁺ ion can be used as a probe to study, rapidly and non-destructively, the crystallinity and degradation of BaTiO₃.

Keywords: ceramics, electron magnetic resonance, barium titanate, gadolinium

1. Introduction

Barium titanate (BaTiO₃) is a traditional piezoelectric material that has been proposed for use in the microelectronics industry after studies revealed that its properties can be changed by controlling grain size^{1,2} and by doping with rare earth ions³. EMR spectroscopy is a convenient method for studying these impurities within the BaTiO₃ structure. In this work, we study the effect of gadolinium concentration on the EMR spectrum of Gd³⁺ in polycrystalline BaTiO₃. The importance of this investigation is twofold. First, once the effects of gadolinium concentration on the spectrum are known, it becomes possible to use EMR results to study, rapidly and non-destructively, the crystallinity and degradation of BaTiO₃. Second, knowledge of the range of the exchange interaction between Gd³⁺ ions is essential for a better understanding of the magnetic properties of gadolinium-doped barium titanate.

1.1. Crystal structure of strontium titanate

At room temperature, barium titanate (BaTiO₃) crystallizes in the perovskite structure⁴ conforming to the space group P4mm(99). There are two distinct cation sites, one with twelve nearest neighbor oxygen ions, occupied by Ba atoms, and one with six nearest neighbor oxygen atoms, occupied by Ti atoms.

1.2. EMR of barium doped barium titanate

Analysis of the EMR spectrum of single-crystal gadolinium doped barium titanate⁵ shows that trivalent gadolinium ions substitutionally replace strontium ions in the lattice. The spectrum can be fitted to the Hamiltonian

$$\mathcal{H} = g\beta H.S + b_{2,0}Y_{2,0} + b_{4,0}Y_{4,0} \quad (1)$$

with $g = 1.995$, $b_{2,0} = -293,6 \times 10^{-4} \text{cm}^{-1}$ and $b_{4,0} = 4.0 \times 10^{-4} \text{cm}^{-1}$.

1.3. EMR of dilute solid solutions

The theory of dipolar broadening in diluted solid solutions was developed in Kittel & Abrahams⁶ and extended in de Biasi & Fernandes⁷ to take exchange interactions into account. The main results of the theory can be summarized as follows:

- (I) the lineshape is a truncated Lorentzian;
- (II) the peak-to-peak first derivative linewidth may be expressed as

$$\Delta H_{pp} = \Delta H_0 + \Delta H_d = \Delta H_0 + C_1 f_e \quad (2)$$

where ΔH_0 is the intrinsic linewidth, ΔH_d is the dipolar broadening, C_1 is a constant and f_e is the concentration of substitutional ions of the paramagnetic impurity not coupled by the exchange interaction, which can be expressed as

$$f_e = f(1-f)^{z(r_c)} \quad (3)$$

where f is the impurity concentration, $z(r_c)$ the number of cation sites included in a sphere of radius r_c , and r_c the effective range of the exchange interaction.

- (III) the intensity of the absorption line is

$$I = C_2 f_e \quad (4)$$

where C_2 is a constant.

The analysis above is based on the assumption of two ion populations, one with no exchange, which is responsible for the normal paramagnetic line, and another which, due to exchange, is either EPR silent (if the coupling is antiferromagnetic) or gives rise to a much broader line (if the coupling is ferromagnetic).

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2. Experimental Procedure and Results

2.1. Sample preparation

The gadolinium doped samples used in this study were prepared from high purity BaTiO₃ (Aldrich, 99,9%) and Gd₂O₃ (Reacton, 99.99%) powders by grinding them together and then firing the mixture for 24 h at 1200 °C in air. The gadolinium concentrations and reagent masses are shown in Table 1. Actual Gd concentrations were determined using the Inductively Coupled Plasma (ICP) technique. Room temperature X-ray diffraction patterns (Figure 1) of the samples matched, within experimental error, the pattern⁸ of BaTiO₃. No other phases were detected.

2.2. Magnetic resonance measurements

All magnetic resonance measurements were performed at room temperature and 9.50 GHz using a Varian E-12 spectrometer with 100 kHz field modulation. The microwave power was 10mW and the modulation amplitude was 1 mT. The magnetic field was calibrated with an NMR gaussmeter.

The spectrum of a sample of BaTiO₃ doped with 0.6 mol% Gd is shown in Figure 2. It closely matches the spectrum reported by Takeda & Watanabe⁹ for powdered Gd-doped BaTiO₃. In principle, linewidth data can be extracted from any of the lines in the powder spectrum. We chose the line indicated by an arrow in Figure 2. The results are shown in Table 2 for several gadolinium concentrations.

3. Discussion

The theoretical concentration dependence of the peak-to-peak linewidth ΔH_{pp} , given by Equation 2, is shown in Figure 3 for $\Delta H_0 = 3.3$ mT and eight different ranges of the exchange interaction. The values of r_c and $z(r_c)$ for the first eight coordinate spheres are listed in Table 3, where n is the number of the order of each coordinate sphere ($n = 1$ includes no neighboring sites, and so on). The values of $z(r_c)$ are those appropriate to the lattice of BaTiO₃; the values of r_c were calculated from the lattice constants at room temperature as measured by X-ray diffraction⁸, $a = 0.3990$ nm, $c = 0.4035$ nm. The experimental data are also shown in

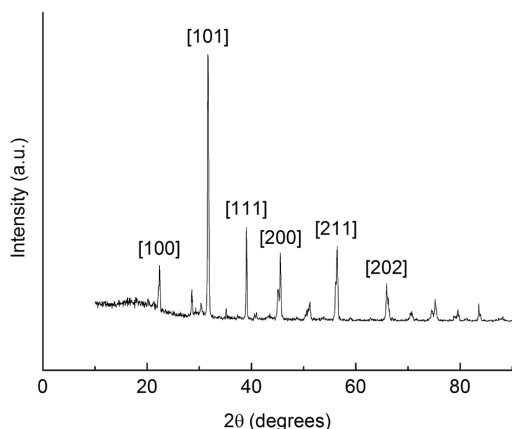


Figure 1. X-ray diffraction pattern of a BaTiO₃ sample doped with 0.2 mol% Gd. The indices were taken from JCPDS no. 81-2203.

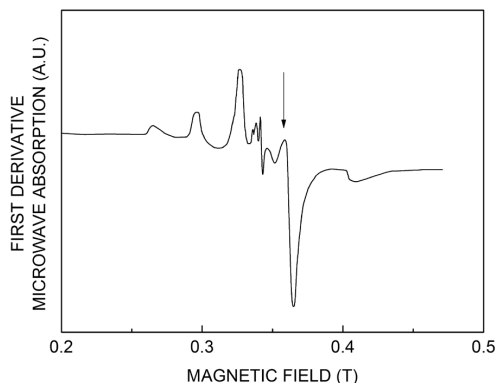


Figure 2. EMR spectrum of a BaTiO₃ sample doped with 0.6 mol% Gd.

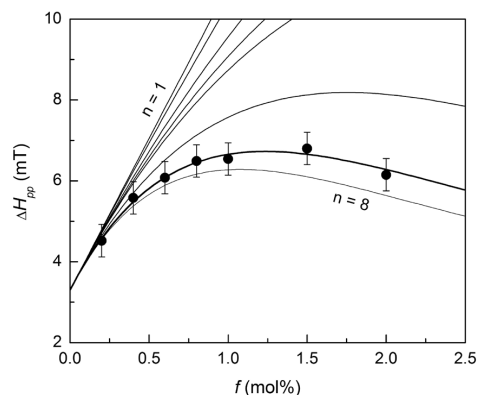


Figure 3. Concentration dependence of the peak-to-peak linewidth, ΔH_{pp} , in Gd-doped BaTiO₃. The circles are experimental points; the curves represent results of calculations for eight different ranges of the exchange interaction.

Table 1. Gadolinium concentrations and reagent masses for the samples used in this work.

f (mol%)	$m_{\text{Gd}_2\text{O}_3}$ (g)	m_{BaTiO_3} (g)
0.20	0.0031	1.9969
0.40	0.0062	1.9938
0.60	0.0093	1.9907
0.80	0.0125	1.9875
1.00	0.0156	1.9844
1.50	0.0234	1.9766
2.00	0.0312	1.9688

Table 2. Experimental results for the Gd³⁺-BaTiO₃ system ($T = 300$ K, $\nu = 9.50$ GHz).

f (mol%)	ΔH_{pp} (mT)
0.20	4.52
0.40	5.58
0.60	6.08
0.80	6.49
1.00	6.54
1.50	6.80
2.00	6.15

Table 3. Values of r_c and $z(r_c)$ for BaTiO₃.

n	r_c (nm)	$z(r_c)$
1	0.00	0
2	0.40	6
3	0.56	18
4	0.69	26
5	0.80	32
6	0.89	56
7	0.98	80
8	1.13	92

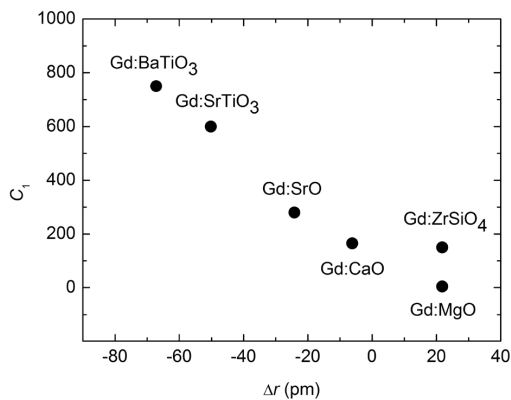
**Figure 4.** Dependence of the coefficient C_1 on the ionic radius misfit $\Delta r = r_{\text{Gd}} - r_{\text{h}}$. Gd:ZrSiO₄ data are from de Biasi & Grillo¹⁰; Gd:SrTiO₃ data are from de Biasi & Grillo¹¹; Gd:SrO data are from de Biasi & Grillo¹²; :CaO data are from de Biasi & Grillo¹³; Gd:MgO data are from de Biasi & Grillo¹⁴.

Figure 3. The experimental results fit the theoretical curve for $n = 7$, which corresponds, according to Table 3, to a range $r_c = 0.98$ nm for the exchange interaction.

In Table 4 we show the pertinent parameters for the dipolar broadening ΔH_D of the Gd³⁺ FMR spectrum in BaTiO₃ and in other host lattices. One can see that there is a large range of values for the rate of increase of the dipolar broadening with

Table 4. Values of n , r_c , $z(r_c)$, a , C_1 and Δr for the Gd³⁺ ion in several host lattices.

Host	n	r_c (nm)	$z(r_c)$	a (nm)	C_1	Δr (pm)	Reference
ZrSiO ₄	15	1.17	122	0.655	150	21.8	10
BaTiO ₃	7	0.98	80	0.399	750	-67.2	this work
SrTiO ₃	7	0.96	80	0.390	600	-50.2	11
SrO	7	0.89	86	0.516	280	-24.2	12
CaO	6	0.83	86	0.481	165	-6.2	13
MgO	5	0.60	54	0.421	4.5	21.8	14

concentration, expressed by the parameter C_1 , from 4.5 for MgO to 750 for BaTiO₃. In order to investigate the question further, we plot in Figure 4 the coefficient C_1 of Equation 2 as a function of the difference $\Delta r = r_{\text{Gd}} - r_{\text{h}}$, where r_{Gd} the ionic radius of Gd³⁺ and r_{h} is the ionic radius of the host lattice cation (the ionic radii were taken from Shannon¹⁵) for the Gd-doped compounds shown in Table 4. The results suggest that C_1 changes, in a systematic way, with the ionic radius misfit Δr .

4. Conclusions

The study of the EMR spectrum of Gd³⁺ in BaTiO₃ shows that the peak-to-peak linewidth increases with Gd concentration. This increase is attributed to dipolar broadening and is consistent with a model based on the exchange interaction and on the misfit between the ionic radii of the doping impurity and the host cation.

The fact that the linewidth increases in a predictable way with Gd concentration suggests that gadolinium can be used as a probe to study the crystallinity and degradation of barium titanate.

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