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# Influence of Chromium Concentration on the Electron Magnetic Resonance Linewidth of $Cr^{3+}$ in $SrTiO_3$

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Electron magnetic resonance (EMR) spectra of $Cr^{3+}$ ions in samples of chromium-doped strontium titanate ($SrTiO_3$) have been studied at room temperature for chromium concentrations between 0.20 and 1.00 mol%. According to previous studies, chromium substitutes $Ti^{4+}$ sites in the lattice and its preferred valence state is $Cr^{4+}$, which is EMR silent in the X-band, but the trivalent state can be produced by illumination or codoping with Nb. In the present work, the codoping method was used; the results show the electron magnetic resonance linewidth of the $Cr^{3+}$ spectrum increases with increasing chromium concentration and that the range of the exchange interaction between $Cr^{3+}$ ions is about 0.96 nm.

**Keywords:** *ceramics, electron magnetic resonance, strontium titanate, chromium, niobium*

## 1. Introduction

Strontium titanate ($SrTiO_3$) is a high dielectric constant ceramic material with several industrial applications[1-4], such as memory devices, oxygen sensors, electro-optical devices and flexible dielectric waveguides, whose electrical properties can be changed by the presence of transition metal and rare earth impurities such as iron and gadolinium[5,6]. EMR spectroscopy is a convenient method for studying these impurities within the $SrTiO_3$ structure. In this work, we study the effect of chromium concentration on the EMR spectrum of $Cr^{3+}$ in polycrystalline $SrTiO_3$ codoped with chromium and niobium. The importance of this investigation is twofold. First, once the effects of chromium concentration on the spectrum are known, it becomes possible to use EMR results to study the effects of other impurities[7-9] on the valence state of the chromium ion in $SrTiO_3$. Second, knowledge of the range of the exchange interaction between $Cr^{3+}$ ions contributes to a better understanding of the electrical and magnetic properties[10,11] of doped strontium titanate.

## 2. Background

### 2.1. *Crystal structure of strontium titanate*

Strontium titanate ($SrTiO_3$) crystallizes in the perovskite structure[12] conforming to the space group $Pm\bar{3}m\left(O_h^1\right)$. There are two distinct cation sites, one with twelve nearest-neighbor oxygen ions, occupied by Sr atoms, and one with six nearest-neighbor oxygen atoms, occupied by Ti atoms.

### 2.2. *EMR of chromium-doped strontium titanate*

Analysis of the EMR spectrum of single-crystal chromium-doped strontium titanate[13] shows that $Cr^{4+}$ ions substitutionally replace titanium ions in the lattice. $Cr^{4+}$ ions cannot be observed at X band due to a high crystal field splitting, but the trivalent state can be produced under illumination[13] or by codoping with Nb[14]. The spectrum of $Cr^{3+}$ under illumination consists of a central line ($g \approx 1.978$) due to $^{50}Cr$, $^{52}Cr$ and $^{54}Cr$ and a hyperfine quartet due to the $^{53}Cr$ isotope[13].

### 2.3. *EMR of dilute solid solutions*

The theory of dipolar broadening in diluted solid solutions was developed in Kittel and Abrahams[15] and extended in de Biasi and Fernandes[16] to take exchange interactions into account. The main results of the theory can be summarized as follows:

The lineshape is a truncated Lorentzian;

The peak-to-peak first derivative linewidth may be expressed as

$$\Delta H_{pp} = \Delta H_0 + \Delta H_d = \Delta H_0 + C_1 f_e \quad (1)$$

where $\Delta H_0$ is the intrinsic linewidth, $\Delta H_d$ 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

$$f_e = f\left(1 - f\right)^{z(r_c)} \quad (2)$$

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.

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The intensity of the absorption line is

$$I = C_2 f_e \tag{3}$$

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).

## 3. Experimental Procedure and Results

### 3.1. *Sample preparation*

The chromium/niobium doped samples used in this study were prepared from high-purity $SrTiO_3$ (Aldrich, 99%), $Cr_2O_3$ (Aldrich, 99.9%) and $Nb_2O_5$ (Aldrich, 99.99%) powders by grinding them together and then firing the mixture for 24 hours at 1200 °C in air. Since niobium was intended to act as an electron donor, we used equal molar concentrations of Cr and Nb in each sample. The chromium concentrations and reagent masses are shown in Table 1. Room-temperature X-ray diffraction patterns (Figure 1) of the samples matched, within experimental error, the spectrum[17] of $SrTiO_3$. No other phases were detected.

### 3.2. *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 200 mW and the modulation amplitude was 0.1 mT. The magnetic field was calibrated with an NMR gaussmeter.

**Table 1.** Chromium and niobium concentrations and reagent masses for the samples used in this work.

| $f_{Cr,Nb}$ (mol%) | $m_{Cr_2O_3}$ (g) | $m_{Nb_2O_5}$ (g) | $m_{SrTiO_3}$ (g) |
|---|---|---|---|
| 0.20 | 0.0017 | 0.0030 | 1.9953 |
| 0.40 | 0.0033 | 0.0058 | 1.9909 |
| 0.60 | 0.0050 | 0.0087 | 1.9863 |
| 0.80 | 0.0067 | 0.0117 | 1.9816 |
| 1.00 | 0.0083 | 0.0145 | 1.9772 |

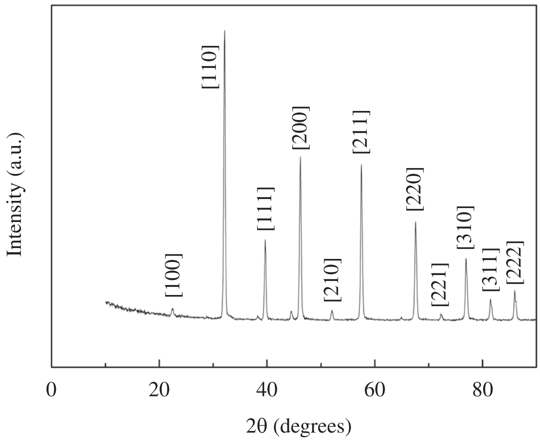

**Figure 1.** X-ray diffraction pattern of a $SrTiO_3$ sample doped with 1.0 mol% Cr and 1.0 mol% Nb. The indices were taken from JCPDS no. 86-0179.

Spectra of samples of $SrTiO_3$ doped with 0.2 and 1.0 mol% Cr and Nb are shown in Figures 2 and 3. Only the line due to the $Cr^{3+}$ $-1/2 \rightarrow 1/2$ transition is clearly seen; the *g*-value of this line is 1.978 ± 0.001, in good agreement with the value reported in Müller[13]. The lines due to the other transitions, like the $Gd^{3+}$ lines in the same compound[18], are broader because of lattice strain and are responsible, together with $Cr^{3+}$-$Cr^{3+}$ pairs within the range of the exchange interaction, for the feature near 0.34 T in Figures 2 and 3. Linewidth and intensity data for the $Cr^{3+}$ $-1/2 \rightarrow 1/2$ transition are shown in Table 2 for several chromium concentrations.

## 4. Discussion

The theoretical concentration dependence of the peak-to-peak linewidth $\Delta H_{pp}$, given by Equation 1, is shown in Figure 4 for $\Delta H_0$ = 0.6 mT and eight different ranges of

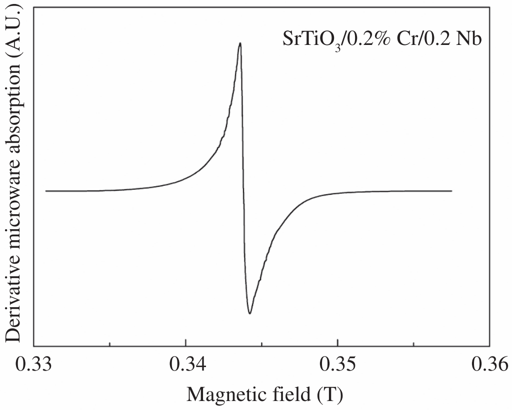

**Figure 2.** EMR spectrum of a $SrTiO_3$ sample doped with 0.2 mol% Cr and 0.2 mol% Nb.

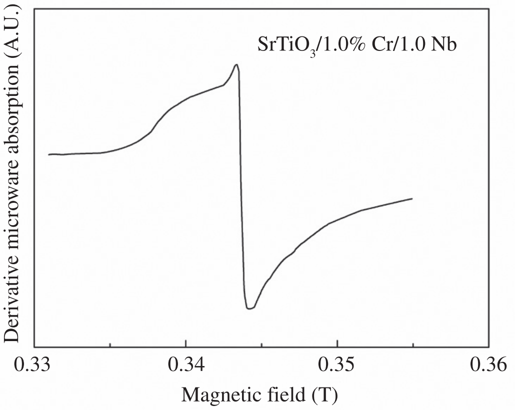

**Figure 3.** EMR spectrum of a $SrTiO_3$ sample doped with 1.0 mol% Cr and 1.0 mol% Nd.

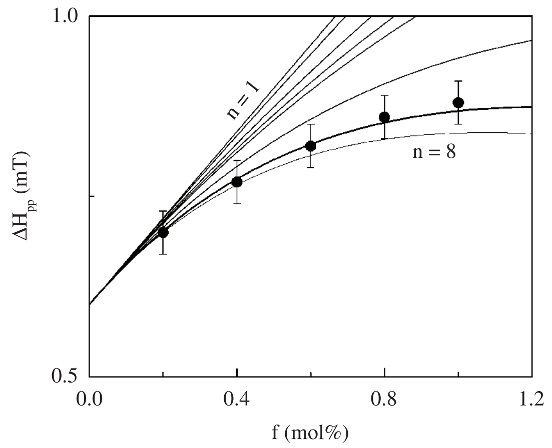

**Figure 4.** Concentration dependence of the peak-to-peak linewidth, $\Delta H_{pp}$, in Cr/Nb-doped $SrTiO_3$. The circles are experimental points; the curves represent results of calculations for eight different ranges of the exchange interaction.

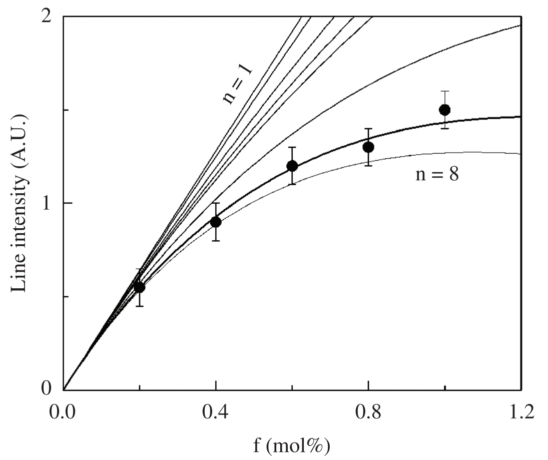

**Figure 5.** Concentration dependence of the line intensity in Cr/Nb-doped $SrTiO_3$. The circles are experimental points; the curves represent the results of calculations for eight different ranges of the exchange interaction.

**Table 2.** Experimental results for the $Cr^{3+}$-$SrTiO_3$ system (T = 300 K, ν = 9.50 GHz).

| $f_{Cr}$ (mol%) | $\Delta H_{pp}$ (mT) | $I$ (A.U.) |
|---|---|---|
| 0.20 | 0.70 | 0.55 |
| 0.40 | 0.77 | 0.90 |
| 0.60 | 0.82 | 1.20 |
| 0.80 | 0.86 | 1.30 |
| 1.00 | 0.88 | 1.50 |

**Table 3.** Values of $r_c$ and $z(r_c)$ for $SrTiO_3$

| $n$ | $r_c$ (nm) | $z(r_c)$ |
|---|---|---|
| 1 | 0.00 | 0 |
| 2 | 0.39 | 6 |
| 3 | 0.55 | 18 |
| 4 | 0.68 | 26 |
| 5 | 0.78 | 32 |
| 6 | 0.87 | 56 |
| 7 | 0.96 | 80 |
| 8 | 1.11 | 92 |

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 $SrTiO_3$; the values of $r_c$ were calculated from the lattice constant at room temperature as measured by X-ray diffraction[17], $a_o = 0.3901$ nm. The experimental data are also shown in Figure 4. The experimental results fit the theoretical curve for $n = 7$, which corresponds, according to Table 3, to a range $r_c = 0.96 \pm 0.10$ nm for the exchange interaction. Figure 5 shows the theoretical (Equation 3) and experimental (Table 2) intensity data, estimated using the expression $I = A(\Delta H_{pp})^2$, where $I$ is the line intensity, $A$ is the line amplitude and $\Delta H_{pp}$ is the peak-to-peak linewidth. The vertical scale is arbitrary and was chosen so as to provide the best fit of the experimental points to the theoretical curve for $n = 7$, or $z(r_c) = 80$. The agreement was found to be very good.

## 5. Conclusions

Since the linewidth and intensity of the EMR spectrum of $Cr^{3+}$ in $SrTiO_3$ increase with Cr concentration and the experimental results are fitted well by a theoretical model, niobium codoping seems to be a reliable way to change the valence state of the chromium ions from $Cr^{4+}$ to $Cr^{3+}$ in substitutional titanium sites of chromium-doped strontium titanate. The fact that the range of the exchange interaction of $Cr^{3+}$ in $SrTiO_3$ is much larger than in $Y_2O_3$[19] (0.96 and 0.64 nm, respectively) is probably due to a more favorable bonding angle in $SrTiO_3$, that favors indirect exchange[20].

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