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Pulse-based electron spin transient nutation measurement of BaTiO₃ fine particle: Identification of controversial signal around $g = 2.00$

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Two dimensional pulse-based electron spin transient nutation (2D-ESTN) spectroscopy is a powerful tool for determining the spin quantum number and has been applied to BaTiO₃ fine powder in order to identify the origin of the continuous wave electron spin resonance (CW-ESR) signal around $g = 2.00$. The signal is frequently observed in BaTiO₃ ceramics, and the correlation between the signal intensity and positive temperature coefficient of resistivity (PTCR) properties has been reported to date. The CW-ESR spectrum of BaTiO₃ fine particles synthesized by the sol-gel method shows a typical asymmetric signal at $g = 2.004$. The 2D-ESTN measurements of the sample clearly reveal that the signal belongs to the $S = 5/2$ high spin state, indicating that the signal is not due to a point defect as suggested by a number of researchers but rather to a transition metal ion. Our elemental analysis, as well as previous studies, indicates that the origin of the $g = 2.004$ signal is due to the presence of an Fe^{3+} impurity. The D value (second-order fine structure parameter) reveals that the origin of the signal is an Fe^{3+} center with distant charge compensation. In addition, we show a peculiar temperature dependence of the CW-ESR spectrum, suggesting that the phase transition behavior of a BaTiO₃ fine particle is quite different from that of a bulk single crystal. Our identification does not contradict a vacancy-mediated mechanism for PTCR. However, it is incorrect to use the signal at $g = 2.00$ as evidence to support the vacancy-mediated mechanism. *Published by AIP Publishing.* https://doi.org/10.1063/1.5020675

Barium titanate (BaTiO₃) has attracted great interest for its ferroelectric, piezoelectric, and positive temperature coefficient of resistivity (PTCR) properties.[1] These electronic properties are affected by doping with various kinds of metal ions and the formation of defects, such as oxygen vacancies.[2,3] Continuous wave electron spin resonance (CW-ESR) spectroscopy is a unique and powerful tool for detecting paramagnetic metal ions and vacancies,[4] and a number of researchers have discussed the relationship between the paramagnetic origin and the electronic properties. In particular, the ESR signal around $g = 2.00$ is frequently observed in BaTiO₃ ceramics and has been believed to reflect a quite important origin that is closely related to PTCR phenomena[5,6,8,11,12] although different interpretations have been suggested by many researchers for the assignment of the signal.[5–14] Kutty *et al.*[5] assigned the signal to V_{Ba} by using starting materials with high purity, and Lu *et al.*[14] subsequently supported the assignment. Jida and Miki[6] also used starting materials with high purity and considered that the signal stems from V_{Ba}-V_O at the grain boundary based on stoichiometry. Kolodiazhny and Petric[8] ascribed the $g = 2.00$ signal to V_{Ti} because other signals to be assigned to Fe^{3+}-related species, such as Fe^{3+} and Fe^{3+}-V_O in the tetragonal phase, are also observed in addition to the $g = 2.00$ signal at room temperature. Contrary to the argument by Kolodiazhny and Petric, Dunbar *et al.*[9] assigned the $g = 2.00$ signal to V_{Ti}

because they did not observe Fe^{3+}-related signals; they thought that additional Fe^{3+}-related signals would appear if the $g = 2.00$ signal stemmed from Fe^{3+}. Er *et al.*[11] reported that the signal intensity of $g = 2.00$ increases with the amount of Fe intentionally incorporated into BaTiO₃, and they temporarily assigned the signal to Fe^{3+}. It seems that the main origin of these different assignments is the purity of the starting materials, which leads to the presence or the absence of Fe^{3+}-related signals. All these reports contain much speculation based on insufficient spectroscopic data. Schwartz and Wechsler[7] reported clear signals of Fe^{3+} in the rhombohedral phase, i.e., the $g = 2.00$ signal accompanied by other weak signals at both sides of the central $g = 2.00$ signal, which correspond to the transitions of $|5/2, 5/2> \leftrightarrow |5/2, 3/2>$ and $|5/2, -5/2> \leftrightarrow |5/2, -3/2>$. However, such weak signals and a discussion of a correlation between the signal intensity at $g = 2.00$ and PTCR phenomena were never reported in the literature (not in the literature regarding single crystals).[5,6,8,11,12] In the argument that the signal is assigned to vacancies, an explanation has been offered that the vacancies capture conduction electrons above the Curie temperature (T_C), leading to a change in the potential barrier at the grain boundary, which assists the PTCR phenomena.

Thus, the assignment of the $g = 2.00$ signal is a controversial issue, and the clarification is important in order to completely understand the PTCR mechanism and to improve the electronic properties of BaTiO₃. For that purpose, we have applied pulse ESR-based nutation spectroscopy to the $g = 2.00$ signal observed in BaTiO₃. Nutation spectroscopy

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gives us straightforward information on the spin quantum number even if a high spin system in the non-orientation is characterized by small fine structure parameters, and it cannot be derived by CW-ESR spectroscopy.[15,16]

In this study, we focus on $BaTiO_3$ fine particles synthesized by the sol-gel method.[1] It is well known that a fine particle of $BaTiO_3$ (< about 200 nm) often shows a cubic phase or a core-shell structure (tetragonal core and cubic shell) at room temperature, in stark contrast to the bulk $BaTiO_3$ single crystal,[18–20] and it has been suggested that the phase transition behavior is quite different from that of a single crystal.[21] In the literature related to the signal at $g = 2.00$, XRD data have not been shown, particularly those of fine particles with low tetragonality, but it is known that doping of $BaTiO_3$ induces the PTCR effect and reduces tetragonality. From room temperature X-ray diffraction (XRD) analysis, our sample is found to be composed of a mixture of tetragonal and cubic phases (the ratio of the tetragonal phase to the cubic phase is 37:13), suggesting a core-shell structure. The crystalline size is derived to be about 44 nm. Figure 1 shows the CW-ESR spectrum from a $BaTiO_3$ fine particle observed at 40 K. A typical signal is slightly asymmetric at $g = 2.004$ and occurs due to the superposition of six weak lines from an unintentional Mn^{2+} impurity. To identify the spin quantum number of the signal at $g = 2.004$, two dimensional electron spin transient nutation (2D-ESTN) measurements were carried out (Fig. 2). An echo-detected field swept spectrum is presented on the right hand side in Fig. 2. The echo-detected field swept spectrum indicates that there is only the $g = 2.004$ signal without hyperfine splitting, and the sextet of Mn^{2+} observed in the CW-ESR spectrum is not detected because the intensity is very low compared with the intense $g = 2.004$ signal. The nutation frequency ω_n is defined as a resonant oscillation frequency of the spin magnetization in the rotating frame of pulsed microwave irradiation. Quantum mechanical treatments of the spin nutation dynamics show that the relative nutation frequency ω_n is given up to first-order

$$\omega_n = \sqrt{S(S+1) - M_S(M_S+1)} \times \omega_1. \quad (1)$$

Equation (1) describes the allowed transition between $|S, M_S>$ and $|S, M_S+1>$ sublevels in the extremely weak limit ($H_1 \ll H_D$) of microwave irradiation H_1.[15,16] Here, ω_1

FIG. 2. 2D-ESTN spectrum of $BaTiO_3$ observed at 10 K. The nutation pulse-$\pi/2$ (16 ns)-*tau*-π (32 ns)-*tau*-echo detection sequence was applied.

denotes the microwave irradiation field strength, and H_D stands for the second-order fine structure terms in the spin Hamiltonian. In Eq. (1), an isotropic g tensor is assumed for simplicity because anisotropic g-values seem to be relatively small from the CW-ESR spectrum. The frequency ω_n depends on the spin quantum number S, and thus, we can determine S in a straightforward manner.

From the observed nutation spectra in Fig. 2, the nutation frequency of the signal at $g = 2.004$ is determined to be 6.7 MHz. The value of ω_1 is 2.2 MHz under our experimental conditions, which is derived from the measurement in coal ($S = 1/2$) as a reference. The observed ω_n (6.7 MHz) at $g = 2.004$ is close to $3\omega_1$. Therefore, the signal should be ascribed to the transition between $|5/2, -1/2>$ and $|5/2, +1/2>$, indicating that S is equal to 5/2. Other transitions ($|5/2, -5/2> \leftrightarrow |5/2, -3/2>$, …., and $|5/2, 3/2> \leftrightarrow |5/2, 5/2>$, except for $|5/2, -1/2> \leftrightarrow |5/2, +1/2>$), cannot be observed. It is probably due to both a distribution of fine structure parameters (D and E strain) and their essentially low intensities in a powder pattern spectrum compared to the transition between $|5/2, -1/2>$ and $|5/2, +1/2>$. It is difficult to assign the $S = 5/2$ signal for $g = 2.004$ to vacancies such as V_{Ba}, V_{Ba}-V_O, and V_{Ti}, which should have the $S = 1/2$ state (doublet). The assignment to a paramagnetic metal cation is suitable, i.e., Fe^{3+} (high spin sextet state). Basically, nutation spectroscopy cannot distinguish between $S = 1/2$ and a high spin system in a perfectly cubic coordination field when the fine structure term (D value) is *exactly* zero (not for the case of the non-negligible D value).[16] If the high spin system is characterized by an exactly zero D value, then the nutation frequency must be the same as that of the $S = 1/2$ system because the condition of $H_1 \ll H_D$ in Eq. (1) is not satisfied. Because the nutation frequency observed at 10 K is well explained by Eq. (1), the D value at 10 K of our sample should be larger than 2.2 MHz, but the value is not so large, as justified from the CW-ESR line shape. The amplitude of D and the g-value obtained by the present study seem to be consistent with those reported previously ($D \approx 60$ MHz and $g = 2.0036$ in the rhombohedral phase).[7,27] To confirm that our $BaTiO_3$ sample includes Fe impurities, the elemental analysis by GD-MS (glow discharge mass spectrometry) was performed. The results are summarized in Table S1 in the supplementary material, where the concentrations of Cr, Mn, and Fe are shown. The amount of detected Fe is 66 ppm, which is larger than those of Cr and Mn, supporting our assignment of the ESR signal to Fe^{3+}.
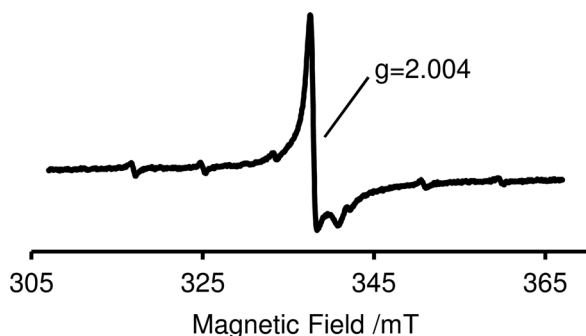

FIG. 1. CW-ESR spectrum from a $BaTiO_3$ fine particle observed at 40 K. The microwave frequency is 9.4788 GHz, the microwave power is 0.1 mW, and the modulation amplitude is 0.5 mT. Based on the sextet hyperfine splitting parameter ($|A| = 8.6$ mT), we assigned the signals to Mn^{2+} rather than Mn^{4+} because $|A|$ is too large to be assigned to Mn^{4+}.[7,31]
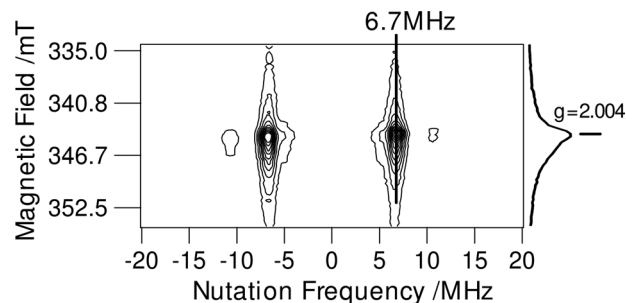
Generally, Fe^{3+} with a strong axial crystal field gives rise to an ESR signal at $g \sim 6$ due to large zero-field splitting $(D \gg h\nu)$.[17] Such a strong crystal field would be observed for Fe^{3+}-V_O with nearest-neighbor charge compensation. The spin Hamiltonian parameters for Fe^{3+}-V_O are known to occur in the rhombohedral phase of $BaTiO_3$,[22,23] the cubic phase of $SrTiO_3$,[24] and the tetragonal phase of $PbTiO_3$.[25] All these D values satisfy the condition $D \gg h\nu$ and show a signal at $g \sim 6$. Apparently, our signal at $g = 2.004$ is different from that of Fe^{3+}-V_O. Thus, the origin of the signal at $g = 2.004$ should be Fe^{3+} with distant charge compensation in $BaTiO_3$.[30] The spin Hamiltonian parameters for Fe^{3+} with distant charge compensation are also well known.[26–29] By using the reported parameters, we simulated the CW-ESR spectra for each phase (cubic, tetragonal, orthorhombic, and rhombohedral) and compared them with the observed spectra. The results are illustrated in the supplementary material. The observed spectrum is similar to those of the cubic and rhombohedral phases. It is noted that the D value for the perfect cubic phase is essentially zero,[29] and thus, we conclude that the phase of our sample at 10 K is rhombohedral or pseudo-cubic, where the non-zero D value from Fe^{3+} is expected by the distorted crystal field. Room temperature ESR investigation of a Mn^{2+}-doped $BaTiO_3$ fine particle revealed that the non-zero D value was observed, even in $BaTiO_3$ with small crystalline size, suggesting that Mn^{2+} is present in the pseudo-cubic phase.[31]

Furthermore, we investigated the temperature dependence of the CW-ESR spectrum (77–300 K, Fig. 3). Interestingly, we cannot see any other signals except for $g = 2.004$ at any temperature. The intensity of the signal at $g = 2.004$ simply changes depending on the Boltzmann distribution. Signals of Fe^{3+} in the tetragonal and orthorhombic phases could not be detected. These signals should appear as multiple lines extending into a wide field range in the case of a single crystal. It is assumed that such a peculiar behavior arises from the crystalline size effect of $BaTiO_3$, in stark contrast to a bulk $BaTiO_3$ single crystal.[18–21] Based on the results of XRD analysis and the ESR line shape, it is concluded that our sample contains Fe^{3+} placed in the pseudo-cubic phase.

Jida and Miki[6] prepared $BaTiO_3$ ceramics from high purity $BaCO_3$ and TiO_2 (less than 3 ppm impurity concentration), but
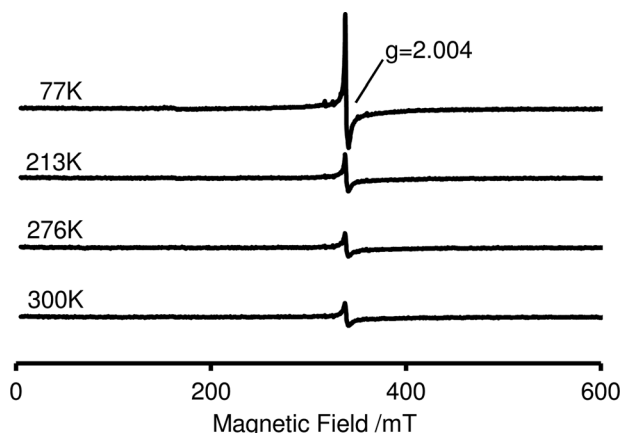
the resultant $BaTiO_3$ manifested an intense $g = 2.00$ signal. This may result from contamination during synthesis or sintering. Kolodiazhny *et al.*[8] suggested that accidental Fe contamination observed in their samples comes from the steel die utilized in the synthesis process. Er *et al.*[11] reported that the $g = 2.00$ signal intensity increases with the amount of Fe intentionally incorporated into $BaTiO_3$, as mentioned above. This behavior is coincident with our present results. We think that the observation of the $g = 2.00$ signal at room temperature also confused researchers because Fe^{3+} signals would appear as multiple lines as stated above, considering that the $BaTiO_3$ crystal typically has the tetragonal phase at room temperature.[8] The observation of the signal at $g = 2.00$ reported in the literature suggests that their samples are composed of some $BaTiO_3$ fine particles, similar to our sample.[8,10,11] It is important to suggest that our identification does not contradict a vacancy-mediated mechanism for PTCR. It is possible that vacancies act as non-paramagnetic centers. However, the use of the $g = 2.00$ signal as evidence to support a vacancy-mediated mechanism seems to be incorrect.

In summary, we clearly identified the controversial ESR signal around $g = 2.00$ which is often observed in $BaTiO_3$ samples associated with Fe^{3+} with distant charge compensation, which is a well-known center in a $BaTiO_3$ single crystal. In stark contrast to bulk $BaTiO_3$ single crystals, the temperature dependence of the CW-ESR spectrum shows peculiar behavior, suggesting that the phase transition behavior is quite different from that of the single crystal. We think that the knowledge derived from the present study will drive further ESR investigations into $BaTiO_3$ ceramics. However, from a methodological point of view, the present 2D-ESTN measurement illustrates its spectroscopic usefulness for identifying an arbitrary signal via spin quantum number information. We think that the measurement also serves to characterize other spin systems, particularly in non-orientated situations.

See supplementary material for information on XRD and GD-MS measurements, as well as some comments on Fig. 2, and details of the simulated CW-ESR spectra for each phase (cubic, tetragonal, orthorhombic, and rhombohedral) by using the parameters reported in the literature.

FIG. 3. Temperature dependence of the CW-ESR spectrum of a $BaTiO_3$ fine particle (wide ranged sweep).

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