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Communication

Better Resolution of High-Spin Cobalt Hyperfine at Low Frequency: Co-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ as a Model Complex

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Abstract: Low-frequency electron paramagnetic resonance (EPR) is used to extract the EPR parameter A-mid and support the approximate X-band value of g-mid for $Ba(Co_yZn_{1/3-y}Ta_{2/3})O_3$. Although cobalt hyperfine structure for the [+/-1/2> state is often unresolved at X-band or S-band, it is resolved in measurements on this compound. This allows for detailed analysis of the molecular orbital for the [+/-1/2> state, which is often the ground state. Moreover, this work shows that the EPR parameters for Co substituted into Zn compounds gives important insight into the properties of zinc binding sites.

Keywords: electron paramagnetic resonance; EPR; multi-frequency EPR; high-spin cobalt complex; resolution of A-mid

1. Introduction

The electron paramagnetic resonance (EPR) parameters of high-spin cobalt(II) [Co(II)] complexes in small molecules and enzymes consist of g-values, zero field splitting parameters D and E/D, and sometimes resolution of the Co hyperfine for the [+/-3/2> doublet; most often, they do not include resolution of the Co hyperfine for the [+/-1/2> doublet [1-3]. Copper hyperfine and superhyperfine lines, particularly the hyperfine lines about g-parallel, are better resolved at low frequencies due to less g- and A-strain [4-7]. To the best of our knowledge, this is the first paper to show that the hyperfine lines for high-spin Co for the Co site in Co-doped barium zirconate titanate (BZT) are resolved for the [+/-1/2> doublet at low frequencies. The determination of Co A-mid provides an EPR parameter that is more sensitive to adduct formation and the electron density distribution in the [+/-1/2> state. A-mid for Co is also a sensitive parameter to characterize zinc (Zn) sites, where Co is substituted for Zn.

2. Results and Discussion

2.1. No Resolvable Hyperfine Structure at X-band

EPR spectra are obtained for $Ba(Co_yZn_{1/3-y}Ta_{2/3})O_3$. The X-band spectrum gives a central g_{eff}-value of 4.76 and possibly exchange, narrowed, and/or dipolar broadened lines for the interaction of the nearest neighbors, but the Co hyperfine structure is unresolved (Figure 1) [8].

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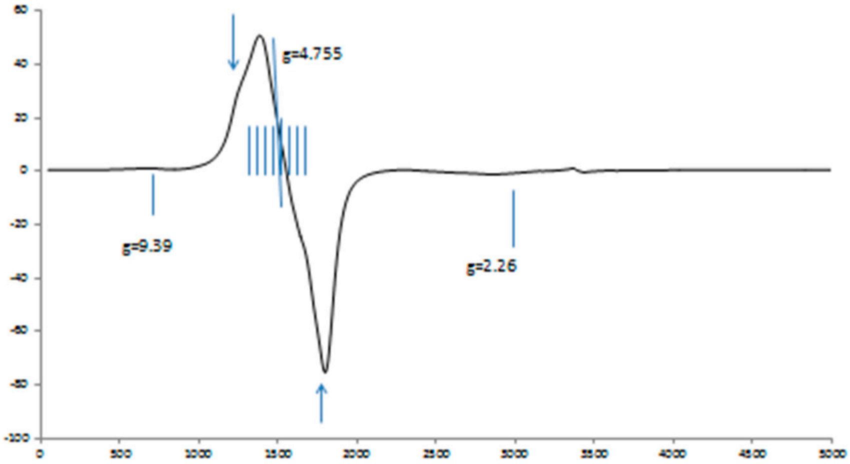

Figure 1. X-band (9.488 GHz) spectrum at 12 K for Co-doped BZT; eight short vertical lines for expected but unresolved Co hyperfine lines; vertical lines with arrows may depict exchange narrowed and/or dipolar broadened lines for the interaction of the nearest neighbors. Weak lines at g=9.39 and 2.26 are not assigned.

2.2. Cobalt Hyperfine Lines Resolved at Low Frequencies, S-band and L-band

The S-band spectrum (3.216 GHz) has four of eight resolved Co hyperfine lines, for which a g_{eff}-mid value of 4.76 and an A-mid of 65 G (432 MHz) are readily apparent (Figure 2). A simulation using Easyspin and a least squares fitting routine gives g_{eff}-values of 4.83, 4.56, and 2.14, and A-values of 432, 402, and 130 MHz (Figure 2). The simulation is consistent with, but not proof of, the parameters for the experimental spectrum, because other parameters such as line width variation, Euler angles, etc., are not included and the simulation may not be unique. The number of variables are underdetermined for three multifrequency spectra. Simulations suggest that the structure is slightly rhombic, but the g_{eff}-value of 4.76 confirms that E/D falls close to the tetragonal value. Nevertheless, clear values for g_{eff}-mid and A-mid are obtained. A g_{eff}-value of 4.8 suggests that the g-mid and A-mid are for the [+/-1/2> state from the rhombogram [8].

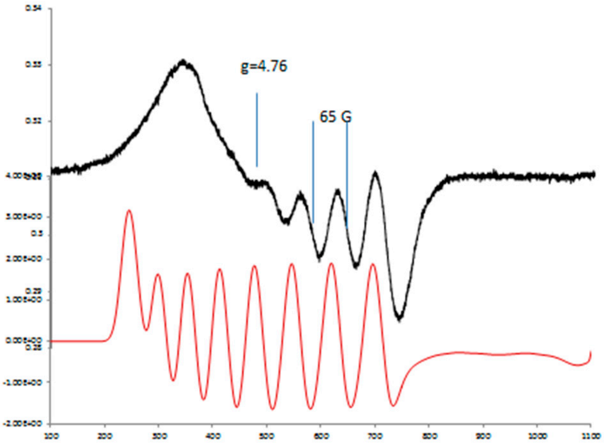

Figure 2. S-band (3.216 GHz) spectrum (black) for Co-doped BZT at 17 K. Exp: 28 dB, 5 G mod., time constant 0.1285 sec. Simulation (red): Easyspin, least squares, simplex, g_{eff}: 4.83, 4.56, 2.14; A: 432, 402, 130 (fixed) MHz, HStrain: 200, 200, 200 MHz.

The L-band spectrum is well resolved but complicated (Figure 3). None of the splittings between the resolved lines directly correspond to the 65 G for A-mid obtained at S-band, presumably from the overlap of lines. It is difficult to determine whether the resolved lines are S-shaped, as would be

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obtained for g_{eff}-mid and A-mid, or hills and valleys, as would be obtained for the low- and high-field EPR parameters. The second harmonic of the L-band spectrum was measured to accurately characterize the line shape (Figure 3), as it does very well for sharp lines. Starting with parameters from S-band, a simulation (red spectrum) is obtained using Easyspin with least squares fitting by Monte Carlo (Figure 3). The EPR parameters obtained are g_{eff}: 5.04, 4.01, 2.14, where 2.14 is arbitrarily fixed, i.e., set without resolved or even unresolved lines, and A: 472, 393, 130 (fixed) MHz. A-max from the simulation equals 67 G and A-mid equals 67 G, which are in good agreement with the S-band value of 65 G. The simulation is also consistent with the experimental parameters (Table 1). It is noted that the simulations come with a warning that there are looping transitions and possible discontinuities at the ends of the spectrum, but the agreement with the experimental spectrum is evidence that the simulated parameters are sensitive to g_{eff}- and A-values.

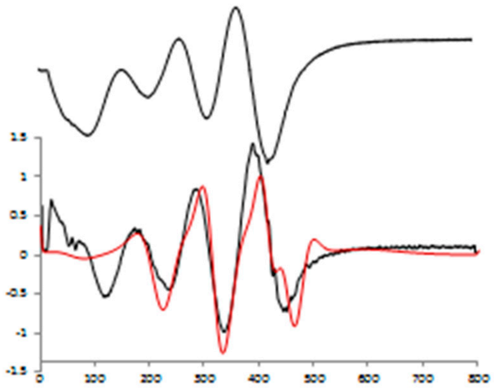

Figure 3. L-band (1.362 GHz) spectrum (black, top) at 16.7 K. Exp: 28 dB, 5 G mod., time constant 0.128 sec; second harmonic (black, bottom) 1% Bessel function using Sumspc, see Exp. Section for details; Simulation (red), Easyspin, least squares, Monte Carlo: g: 5.04, 4.01, 2.14 (fixed), A: 472, 393, 130 (fixed) MHz.

Table 1. EPR A-mid values and geff for Co-doped BZT from spectra and simulations.

	g-max	g-mid	A-max	A-mid
X-band (9.488 GHz, exp)	------	4.76	------	------
S-band (3.216 GHz, exp)	------	4.76	------	64.9 G
S-band (3.216 GHz, sim)	4.83	4.56	63.8 G	63.0 G
L-band (1.362 GHz, sim)	5.04	4.01	66.9 G	67.0 G

2.3. Summary

A-mid and g_{eff}-mid from low-frequency spectra for Co-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ were determined from the experimental S-band spectrum and from simulation of S-band and L-band EPR spectra. It is estimated that E/D from a rhombogram is less than or equal to 0.1, indicating the crystal field is tetragonal, almost octahedral. This study shows that the Co hyperfine value can be obtained for the [+/-1/2> ground state for high-spin Co(II) complexes. This is the first Co site for which we have resolved both S-band and L-band hyperfine spectra. Thus, these spectra for Co-doped BZT serve as a model for Co complexes where Co hyperfine is resolved at L-band but not S-band, as is usually found in other complexes [11, 12]. It is suggested that EPR values for A-mid will be a more sensitive parameter for determining the coordination of and differences in the coordination of high-spin Co complexes.

3. Materials and Methods

The methods to obtain the microwave ceramic, Co-doped BZT, Co-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ are given in ref. [8].

3.1 Molecular Structure

Co(2+) ions are substituted for Zn(2) in $Ba(Zn_{1/3}Ta_{2/3})O_3$ [8]. Co(2+) ions are in a slightly distorted octahedral crystal field and the ground state has symmetry T1g.

3.2 EPR Spectrometers

Data were obtained from a low-frequency spectrometer station assembled at the National Biomedical EPR Center at the Medical College of Wisconsin (Milwaukee, WI). The station incorporates an in-house built L-band (1–2 GHz) bridge, a Varian V-7200 Electromagnet, Varian V-7700 Magnet Power Supply, and a Bruker BH-15 Magnetic Field Controller. The 100 KHz field modulation and signal phase sensitive detection were provided by a Varian E-109 System EPR console. EPR signals from the phase sensitive detector were recorded on a PC with Windows 7 running a custom LabVIEW program. The program also controlled the BH-15 Field Controller, and perform multiple-scan signal averaging, when needed.

The L-band bridge in the spectrometer utilizes a low phase-noise mechanically and electronically tunable fundamental transistor oscillator capable of 50 mW power output to the sample resonator port at 0 dB main power attenuator setting. A loop-gap resonator was used to collect samples [6,7]. The oscillator microwave frequency is locked to the sample resonator frequency by a 70 KHz AFC system in the bridge, operating through the electronic tuning port of the oscillator. A low-noise amplifier in the microwave signal receiver prior to signal mixing improves the overall bridge sensitivity.

S-band spectra (3.2 GHz) were acquired using a loop-gap resonator, which is one of the spectrometers housed at the National Biomedical EPR Center at the Medical College of Wisconsin [6,7].

X-band spectra were obtained at Marquette University (Milwaukee, WI) using an updated EMX spectrometer and a Bruker cryogen-free system.

Simulations were completed using an online version of EasySpin [10].

Author Contributions: Shengke Zhang synthesized Co-doped $Ba(Co_yZn_{1/3-y}Ta_{2/3})O_3$ using conventional ceramic powder processing methods at the Materials Program Lab at Arizona State University [8]. Justin Gonzales and Nathan Newman initiated the EPR studies by sending several transition metal ion doped microwave ceramics. William Antholine made the EPR measurements at low microwave frequencies and wrote the original draft of the manuscript. Justin Gonzales and Nathan Newman added insight, added details, and completed the writing of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Co	cobalt
EPR	electron paramagnetic resonance
Zn	zinc

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References

1. Krzystek, J.; Zvyagin, S.A.; Ozarowdki, A.; Fiedler, A.T.; Brunold, T.C.; and Telser, J. Definitive spectroscopic determination of zero-field splitting in high-spin cobalt(II). *J. Am. Chem. Soc*. **2004**, *126*, 2148-2155, 10.1021/ja039257y.
2. Bennett, B., EPR of cobalt-substituted zinc enzymes, in metals in biology: Applications of high-resolution EPR in metalloenzymes. In *Biological Magnetic Resonance*; Hanson, G. and Berliner, L., Eds.; Springer: New York, USA, **2010**; Volume 29, pp. 345-370, 978-1-4419-1139-1.
3. Marts, A.R.; Greer, S.M.; Whitehead, D.R.; Woodruff, T.M.; Breece, R.M.; Shim, S.W.; Oseback, S.N.; Papish, E.T.; Jacobsen, F.E.; Cohen, S.M.; Tierney, D.L. Dual mode EPR studies of a Kramers ion: high-spin Co(II) in 4-,5- and 6- coordination. *Appl. Magn. Reson*. **2011**, *40*, 501-511, 10.1007/s00723-011-0225-5.
4. Antholine, W. E.. Eaton S.S., Eaton G.R., and Berliner L.J., Eds.; Springer: New York, USA, **2005**; Volume 23, pp. 417-454, 978-0-306-48506-0.
5. Antholine, W.E.; Bennett, B.; Hanson, G. Copper coordination environments. In *Multifrequency Electron Paramagnetic Resonance: Theory and Applications*; Misra, S., Ed.; Wiley, Weinheim, Germany, **2011**; pp. 647-718, 9783527407798.
6. Froncisz, W.; Hyde, J.S. The loop-gap resonator: a new microwave lumped circuit ESR sample structure, *J. Magn. Reson*. **1982**, *47*, 515-521, 10.1016/0022-2364(82)90221-9.
7. Froncisz, W.; Hyde, J.S. Broadening by strains of lines in the g-parallel region of Cu2+ EPR spectra. *J. Chem. Phys*., **1980**, *73*, 3123-3131, 10.1063/1.440548.
8. Zhang, S.; Devonport, A.; Newman, N. Main source of microwave loss in transition-metal-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$ at cryogenic temperatures. *J. Am. Ceram. Soc*. **2015**, *98*, 1188-1194, 10.1111/jace.13419.
9. Hagen, W.R. EPR spectroscopy of iron sulfur proteins, *Adv. Inorg. Chem*. **1982**, *38*, 165-222, 10.1007/s00775-018-1543-y.
10. Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson*. **2006**, *178*, 42, 10.1016/j.jmr.2005.08.013.
11. Antholine, W.E.; Ross, M.O.; Hoffman, B.M.; Rosenzweig, A.C. Better Resolution at Low Frequency: CoEDTA, a Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest Like the Transmembrane Metal Binding Site for CzcP. American Chemical Society Meeting, Division of Inorganic Chemistry, Section: Bioinorganic Chemistry: Proteins and Enzymes and Model Systems, New Orleans, Louisiana, USA, 2018.
12. Antholine, W.E.; Mahim, A.; Petering, D.H. Better Resolution of High Spin Co Hyperfine at Low Frequency, L-band: Co-bovine Serum Albumin, A Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest. 59th Annual Rocky Mountain Conference on Magnetic Resonance, Snowbird, Utah, USA, 2018; Abstract Number 203.