Nuclear Magnetic Resonances of $BaTiO_3$

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At temperatures greater than the Curie point (135 °C), narrow ^{137}Ba and $^{47,49}Ti$ nuclear magnetic resonances (static conditions) have been observed for the cubic phase of polycrystalline $BaTiO_3$; additionally, ^{137}Ba and ^{93}Nb resonances have been detected at elevated temperatures for $BaTiO_3$-based ceramics doped with Nb.

Of all the piezoelectric and ferroelectric materials studied to date, barium titanate remains the most thoroughly studied compound of this class.[1] Polarized $BaTiO_3$-based ceramics have also been of commercial importance owing to their unique electrical and dielectric characteristics.[2] The lattice can accommodate a wide variety of inorganic dopants which can substitute at the Ti^{4+} (six-co-ordinate) or the Ba^{2+} (twelve-co-ordinate) sites and fundamentally alter the electrical properties of the host.

Above the Curie point (135 °C), the $BaTiO_3$ unit cell is cubic[3] (a = 4.002 Å at 140 °C) with barium atoms on the cell corners, a titanium atom at the centre, and oxygen atoms on the cube faces. It is well known that on lowering the temperature through the Curie point, $BaTiO_3$ undergoes a first-order phase transition from a cubic to a tetragonal structure. This crystallographic change represents only a modest change in the unit cell associated with a distortion about the TiO_6 octahedron. In view of the wide body of information available concerning the n.m.r. of quadrupole nuclei in crystals of cubic symmetry,[4] it is surprising to us that there are no reports of the magnetic resonance of $BaTiO_3$. The related perovskites, $KNbO_3$[5] and $LiNbO_3$,[6] have been studied by both n.m.r. and pure quadrupole resonance techniques. We report the first n.m.r. observations concerning the cubic phase of $BaTiO_3$. These studies grew out of our interest in these materials for applications to positive temperature coefficient of electrical resistivity (PTC) devices.[7]

The n.m.r. study of quadrupole nuclei in solids with nominally cubic symmetry has received considerable attention since a large body of information is available from such studies concerning the distribution of dislocations, strains, and defects within the lattice.[8] The most commonly observed feature in the n.m.r. of half-integral quadrupole spins in cubic crystals (such as KBr, KI, and AgBr) is the ($\frac{1}{2}$, $-\frac{1}{2}$) transition which is usually broadened by dipole and second-order quadrupole interactions. The satellite lines for a poly-

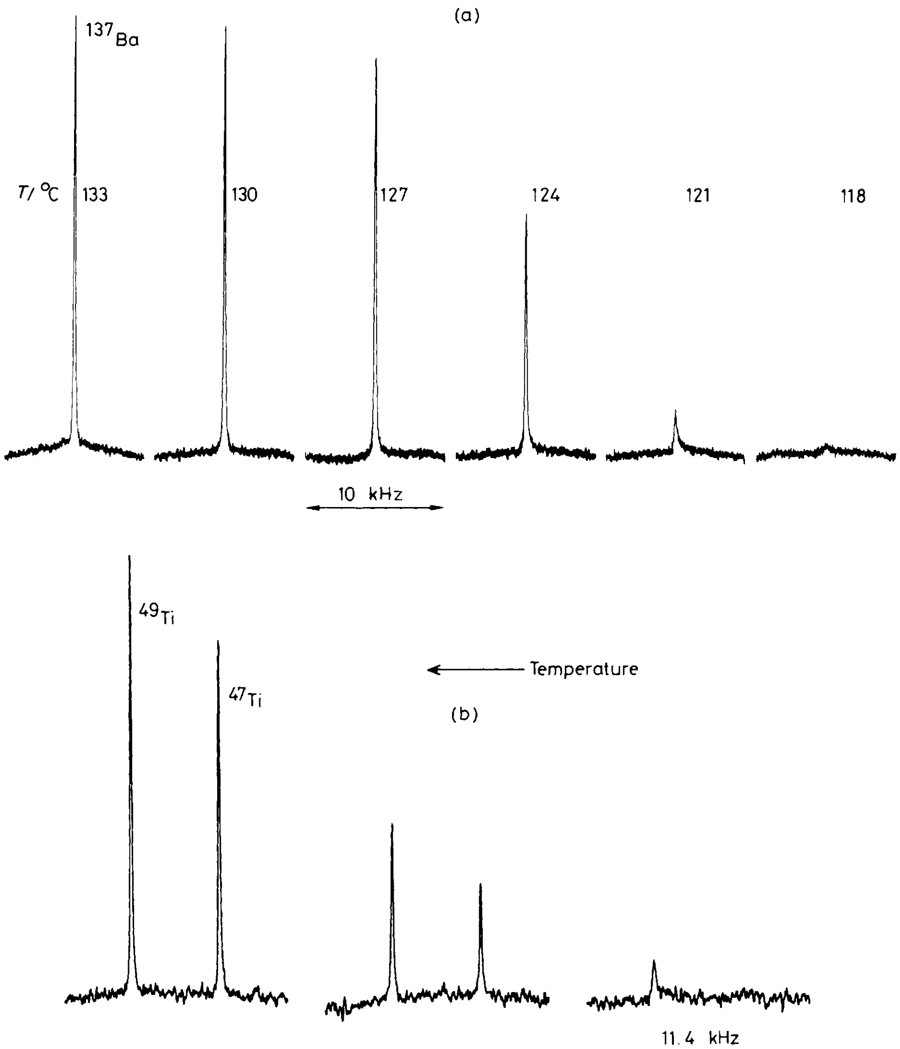

Figure 1. Temperature dependence of the ^{137}Ba (a) and ^{47,49}Ti (b) resonances near the Curie point of pure polycrystalline $BaTiO_3$. The ^{137}Ba spectra (4.7 T) were acquired with 2 000 transients at each temperature using a 0.4 s acquisition time and no delay between pulses. The ^{47,49}Ti spectra (7.05 T) were taken at 2—3 °C intervals with an uncalibrated variable temperature probe. At each temperature 64 transients were taken with a delay time of 1 s between pulses.

crystalline cubic sample are usually spread over a very large frequency interval owing to first-order quadrupole interactions caused by strains and dislocations within the lattice. The central ($\frac{1}{2}$, $-\frac{1}{2}$) transition is unaffected by first-order quadrupole interactions, and for some cubic environments, can be narrowed by magic angle spinning (m.a.s.).[9]

For $BaTiO_3$, reasonably narrow lines can be expected based on the theoretical dipolar linewidths[10] for this lattice. The relatively low natural abundance of the magnetically active nuclei, their low gyromagnetic ratios, and their relatively large interatomic distances (Ba–Ti distance 3.46 Å) should keep the dipolar contribution to the linewidths to less than 150 Hz for both the ^{137}Ba and ^{47,49}Ti resonances.† Outside of the usual dislocations and strains expected for $BaTiO_3$, there are expected to be a number of other centres associated with cationic and oxygen vacancies, such as F centres,[11] which are of fundamental interest. Defects, foreign atoms, and vacancies which create electric field gradients at the site of the nuclei are likely to have a considerable influence on the shape of the resonance line.[8] The dependence of the electrical and structural properties of barium titanate on the defect distributions opens the possibility of modifying the host in a controlled manner to enhance desired properties.

The static ^{137}Ba (I = 3/2, 11.32% natural abundance) Fourier transform n.m.r. signal at 140 °C of reagent grade $BaTiO_3$‡ at 4.7 T consists of a narrow single line with linewidth at half-height of 120 Hz, located 395 p.p.m. downfield (deshielded) from an external standard of aqueous $BaCl_2$ (linewidth of 1 500 Hz at 140 °C§). A comparison of the

† The calculated second moments σ^2 for the dipolar broadening of the central component of a first-order quadrupole line (assuming interactions with both unlike and semi-like spins; see ref. 10) for the ^{137}Ba, ^{47}Ti, and ^{49}Ti resonances are 9.22 × 10^4, 2.53 × 10^4, and 2.62 × 10^4 s^{-2}, respectively.

‡ Reagent grade $BaTiO_3$ was obtained from Johnson Matthey Chemical Ltd.

§ An aqueous sample of (0.14 g/0.2 ml) 2.8 M $BaCl_2$ in a sealed capillary was used as reference and calibration standard. The capillary was covered with a mixture of $BaTiO_3$ diluted with Al_2O_3 powder that acted as a sand bath at 140 °C preventing phase separation in the capillary.

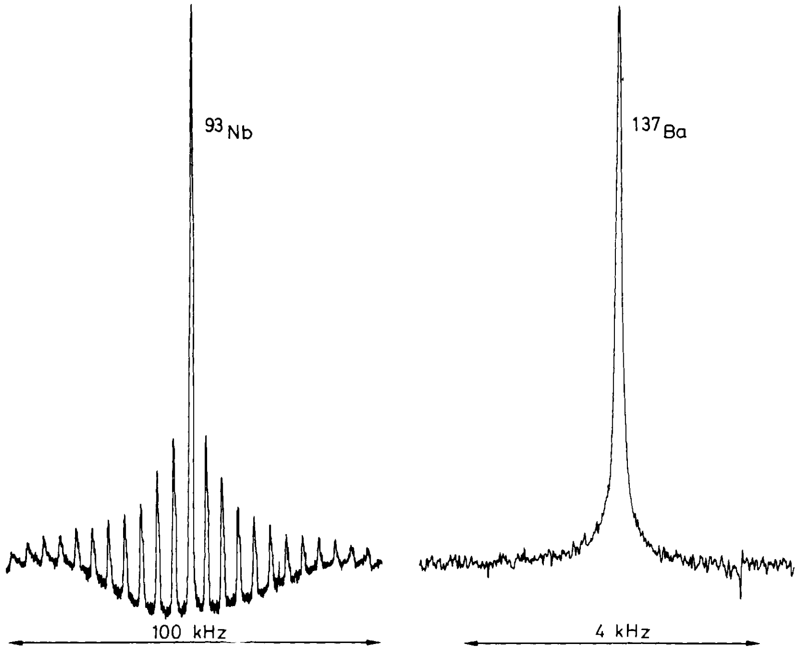

Figure 2. ^{137}Ba and ^{93}Nb m.a.s. n.m.r. spectra (4.7 T) for a $BaTiO_3$ ceramic doped with 0.2 atom% Nb at 130 °C. Spinning speed for both spectra was 4.3 kHz.

integrated intensity of this line, employing a simple one-pulse sequence with a small pulse angle, with that of the aqueous $BaCl_2$ solution indicated that only 45 ± 10% of the expected intensity was present. Additionally, the effective time for a 90° pulse for the $BaTiO_3$ signal was observed to be $\sim\frac{1}{2}$ that of the aqueous Ba^{2+} resonance. These observations indicate that only the central ($\frac{1}{2}$, $-\frac{1}{2}$) transition is observed; most probably the field gradients in the sample have a range of values and random orientations smearing out the satellite transitions. We have also observed the ^{47}Ti (I = 5/2, 7.71%) and ^{49}Ti (I = 7/2, 5.51%) resonances for polycrystalline $BaTiO_3$ at temperatures near 140 °C. The ^{47}Ti and ^{49}Ti resonances, separated by only 270 p.p.m. owing to their similar gyromagnetic ratios, were observed to have nearly identical linewidths (88 Hz). In Figure 1, we present the temperature behaviour of both the ^{137}Ba and ^{47,49}Ti signals as the sample is cycled through the cubic–tetragonal phase transition. As the temperature is lowered to the Curie point, the intensities of the ^{137}Ba and ^{47,49}Ti resonances drop precipitously as the phase transition from cubic to tetragonal sets in. Below the Curie point there is no observable n.m.r. intensity. These data suggest that the small change in symmetry in going to the tetragonal phase introduces further electric field gradients at the nuclear sites causing the central transition to broaden into the baseline by second-order quadrupole interactions.

We have also examined a series of $BaTiO_3$-based ceramics by n.m.r. These ceramic materials were prepared by treating an aqueous slurry of $BaTiO_3$ (supplied from TAM) with Nb oxalate followed by precipitation as the hydroxide with NH_4OH. The resulting powder was air-dried and combined with a binder solution of a phenolic resin in acetone, pressed at 3.6×10^3 kPa, and fired at 1 300 °C for 2 h.[12]

The ^{137}Ba n.m.r. behaviour of these ceramic materials is similar to that observed for pure $BaTiO_3$ (see Figure 1) with the exception that the Curie point (by n.m.r. and electrical conductivity) occurs at slightly lower temperatures (the Curie point is altered by the dopants). The linewidths of the ^{137}Ba resonances for these ceramics are ~30% larger than for the pure polycrystalline powder. In addition to the ^{137}Ba resonance, we have also observed the ^{93}Nb (I = 9/2, 100%) resonance at 4.7 T in ceramic materials containing this ion. The static linewidth for the doped ^{93}Nb was observed to be 1.10 kHz, approximately ten times larger than either the Ba or Ti host resonances. The temperature behaviour of the Nb resonance near the Curie point parallels the ^{137}Ba signal in that both signals decay simultaneously and rapidly as the temperature is lowered through the Curie point of the ceramic.

In Figure 2 we present the ^{93}Nb and ^{137}Ba m.a.s. n.m.r. spectra for a ceramic doped with 0.2 atom% Nb. The sample spinning speed in this experiment (4 kHz) was considerably greater than the observable static linewidth, and the spectra show that for ^{93}Nb there is considerable intensity in the wings of the spectrum as shown by the presence of spinning sidebands spanning the spectral window. The ^{137}Ba resonance under m.a.s. conditions shows only a minor reduction in linewidth compared to static conditions and no detectable sideband intensity outside of the static breadth. The major contributions to the static linewidth of the ^{137}Ba signal are homogenous dipolar interactions,† which should not be amenable to narrowing by m.a.s. conditions.[13]

The ^{93}Nb static resonance is considerably broader than either the static Ti or Ba resonances of the host and is unsymmetrical with a shoulder at higher field. The linewidth for the ^{93}Nb resonance is likely to originate primarily from chemical shift dispersion since the observed linewidth increases by a factor of two at 9.4 T in comparison to the 4.7 T measurement. The linewidth for a second-order quadrupole broadened line should decrease at higher field strengths.

The facile observation of both the ^{137}Ba and ^{93}Nb static resonances in the ceramics studied is consistent with the known defect chemistry of donor-doped $BaTiO_3$. Since the expected valence of the Nb ions (5+) is greater than that of the host Ti^{4+} ions they replace, charge compensation should occur by introducing either free electrons [equation (1)] or vacancies [equations (2) and (3)].[14] For the temperatures and partial pressures of O_2 employed to prepare our ceramics, electron compensation is expected to be the predominant mechanism for accommodating Nb^{5+} into the ceramic. The observation of sharp and intense ^{93}Nb and ^{137}Ba signals is consistent with electron compensation. If vacancies were generated in the vicinity of the magnetically active nuclei, large electric field gradients should be generated, creating large intensity losses in the $(\frac{1}{2}, -\frac{1}{2})$ transition through second-order quadrupole broadening.

$$4BaO + 2Nb_2O_5 \rightarrow 4Ba_{Ba} + 4Nb^{\bullet}_{Ti} + 12O_O + O_2(g) + 4e' \quad (1)$$

$$BaO + Nb_2O_5 \rightarrow Ba_{Ba} + V''_{Ba} + 2Nb^{\bullet}_{Ti} + 6O_O \quad (2)$$

$$5BaO + 2Nb_2O_5 \rightarrow 5Ba_{Ba} + V''''_{Ti} + 4Nb^{\bullet}_{Ti} + 15O_O \quad (3)$$

$$O_O \rightarrow V_O^{\bullet\bullet} + \tfrac{1}{2}O_2(g) + 2e' \quad (4)$$

We have examined a sample of pure $BaTiO_3$ which had been sintered in a CO/CO_2 atmosphere at 1350 °C and have observed a significant reduction (greater than ten-fold) in the intensity of the ^{137}Ba $(\frac{1}{2}, -\frac{1}{2})$ resonance. It is generally accepted that treatment with low oxygen atmospheres, *e.g.* CO/CO_2, produces n-type conductivity by inducing a small number of oxygen vacancies[15] into the crystal lattice [(equation(4)]. The concentration of oxygen vacancies in this sample is sufficient to have a significant effect on the observable n.m.r. intensity through second-order quadrupole broadening. We would expect a similar sensitivity of either the ^{93}Nb, ^{137}Ba, or $^{47,49}Ti$ resonances to cationic vacancies [equations (2) and (3)].

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