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Prospects for ^{137}Ba MAS NMR spectroscopy of ceramics and related inorganic materials

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Abstract

The 11.7T ^{137}Ba MAS NMR spectra are presented for 10 ceramic materials and related inorganic compounds. The spectra of compounds in which Ba occurs in highly symmetric sites ($BaZrO_3$, $BaTiO_3$, BaO) show sharp resonances, with a well-resolved quadrupolar lineshape in the case of $BaTiO_3$. In other Ba-containing ceramics and ceramic precursor compounds (e.g. $BaAl_2Si_2O_8$, $BaAl_2O_4$, Ba_2SiO_4, $BaCO_3$), the Ba typically occurs in irregular polyhedral sites, giving spectra which are considerably broader. Some of the present spectra show evidence of an expected negative trend in the resonance positions with increasing Ba coordination number. The results suggest that ^{137}Ba MAS NMR spectroscopy has potential value for studying some types of Ba-containing ceramics and ceramic precursors. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: ^{137}Ba MAS NMR; Ceramics; Inorganic materials

1. Introduction

The usefulness of solid state NMR spectroscopy with magic-angle spinning (MAS NMR) in providing unique structural information about ceramic materials is well known and continues to be widely exploited for nuclei such as ^{27}Al and ^{29}Si, which are readily detected. Other nuclei which pose greater experimental difficulties have nevertheless been used in NMR studies of ceramics; these include ^{25}Mg studies of silicates [1], catalysts [2] and sialons [3], ^{47,49}Ti and ^{15}N studies of titanium carbide, nitride and carbonitrides [4] and ^{89}Y studies of sialons [3] and related oxynitrides [5]. MAS NMR is particularly appropriate for investigations of the thermal evolution of ceramics derived from gels [6], or materials which pass through an amorphous stage in their synthesis [7]; information about these amorphous intermediates must be obtained by techniques which do not depend on the presence of long-range atomic order in the samples.

Barium is an important constituent of a number of different ceramics for applications ranging from electronics (piezoelectrics, pyroelectrics and ferroelectrics such as $BaTiO_3$, $BaZrO_3$), through glasses and glass-ceramics based on celsian ($BaAl_2Si_2O_8$) to high-T_c superconductors (e.g. $YBa_2Cu_3O_7$). Since these materials may be synthesised by sol–gel routes, it was of interest to investigate the possibilities and limitations of ^{137}Ba MAS NMR spectroscopy for the study of Ba-containing ceramics and some of the inorganic materials from which these ceramics are derived.

^{137}Ba is an NMR-active quadrupolar nucleus with a spin of 3/2 but its low natural abundance (11.32%) and small gyromagnetic ratio (4.731 MHz/T) suggest that ^{137}Ba NMR spectroscopy may be difficult except for compounds in which the Ba is in highly symmetric sites. The only solid-state ^{137}Ba NMR spectra reported to date are for compounds containing Ba in sites of high symmetry, namely, $BaTiO_3$ [8–10], $BaZrO_3$ [8], BaO [8], and $YBa_2Cu_3O_y$ [11,12]. A ^{135}Ba field-sweep NMR spectrum of isotopically-enriched $YBa_2Cu_3O_y$ has also been reported [13].

In this paper we report the ^{127}Ba MAS NMR spectra of a number of additional compounds of particular interest as ceramic materials and their precursors, with the aim of constructing a systematic ^{137}Ba database of materials relevant to ceramic systems. For comparison purposes, and to confirm the validity of our experimental procedures, we have also included the spectra of the four compounds already reported, re-determined under our conditions.

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2. Experimental

The compounds $BaTiO_3$, $BaZrO_3$, $BaAl_2O_4$, Ba_2SiO_4 and $YBa_2Cu_2O_7$ were synthesised by solid state reaction from mixtures of the oxides with $BaCO_3$. $BaAl_2Si_2O_8$ (celsian) was synthesised by the hybrid gel method of Tredway and Risbud [14], taking into account the most recent solubility data [15]. Celsian was crystallised from the gel by thermal treatment at 1300°C for 15 min. BaO was prepared by thermal decarboxylation of $BaCO_3$ at 1300°C and because of its extreme tendency to rehydration and recarbonation, was crushed, loaded into the NMR rotor and tightly capped immediately on removal from the furnace. The other Ba compounds were of analytical grade (BDH). The composition and phase purity of all the Ba compounds was confirmed by X-ray powder diffraction.

The ^{137}Ba MAS NMR spectra were acquired at 11.7T using a Varian Unity 500 spectrometer operating at 55.541 MHz with a 5 mm Doty MAS probe spun at 10 kHz. The Hahn spin echo pulse sequence utilised 16-step phase cycling [16] with a refocusing interval of 20 µs, pulse recycle times of 0.03–0.1 s and a spectral width of 400 kHz. Typically 500,000 transients were acquired, and the shifts were referenced to 1 M aqueous $BaCl_2$ solution. Spectral processing of the broader, weaker spectra was complicated by effects such as probe ringdown, pulse breakthrough, etc. As was previously found for ^{25}Mg spectra [1], these effects can be minimised by left-shifting the free induction decay (FID), in this case by two points. For comparability, all the present spectra, including those with narrow resonances, were processed in this way. In most instances the spectra were baseline-corrected. The spectra of several of the samples were also acquired using a Bloch decay pulse sequence with a recycle delay of 0.1 s; these spectra confirmed the features of the Hahn spin echo spectra.

3. Results and discussion

The ^{137}Ba NMR spectra of the 10 ceramic materials and related precursors are shown in Fig. 1.

3.1. $BaZrO_3$ (Fig. 1A)

This narrow, single-line spectrum is as expected from Ba in the single extremely symmetrical site of cubic $BaZrO_3$ [17] and is also consistent with the spectrum reported by Dec et al. [18] at a field strength of 14.7T for the same compound. The sharpness of this resonance led Dec et al. [8] to adopt it as their ^{137}Ba calibration standard; our spectra which are referenced to aqueous $BaCl_2$ will thus appear downfield of the spectra of Dec et al. [8] by 279 ppm.

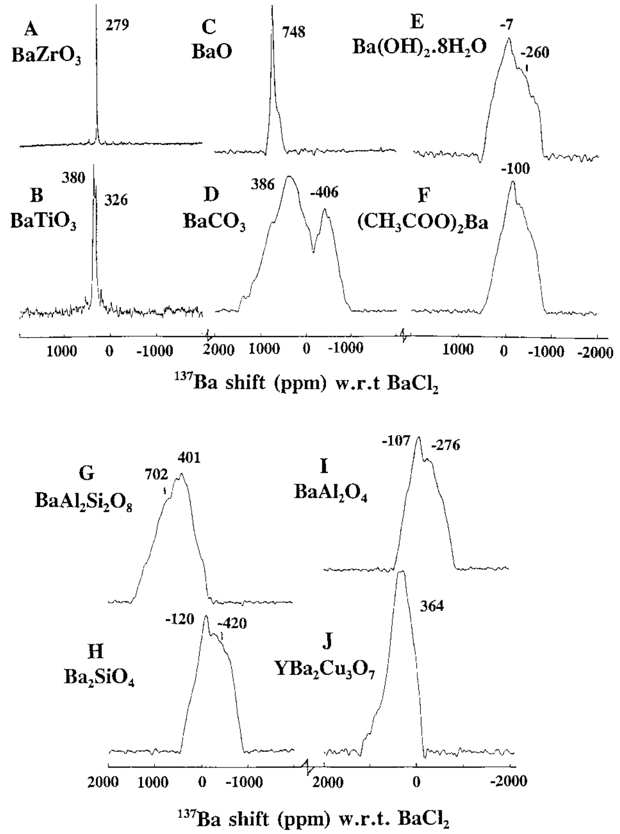

Fig. 1. 11.7T ^{137}Ba MAS NMR spectra of inorganic compounds and ceramics.

3.2. $BaTiO_3$ (Fig. 1B)

Three ^{137}Ba spectra have been previously reported for this material. Dec et al. [8], working at a field strength of 14.1 T, observed a single line, broadened by significant contributions from second-order quadrupole effects arising from displacement of the Ba from the centre of its 12 nearest neighbours in the tetragonal structure [18]. Forbes et al. [9] reported that when this structure becomes cubic above the Curie point (135°C), the resonance becomes a single narrow line 395 ppm downfield from aqueous $BaCl_2$. The lineshape of the present spectrum (Fig. 1B) is as expected for tetragonal $BaTiO_3$ at room temperature, i.e. below the Curie point; its more pronounced quadrupolar character by comparison with the spectrum of Dec et al. [8] results from the the lower field strength (11.7 T) at which the present spectrum was acquired.

Simulations of this quadrupolar lineshape made using our own computer program (R.H. Meinhold, unpublished) indicate values for the nuclear quadrupole coupling constant χ and the asymmetry parameter η of 2.8 Mhz and 0.3, respectively. The simulated spectrum shown in Fig. 2A was produced using 10 ppm of line broadening. This value of χ is satisfactorily similar to

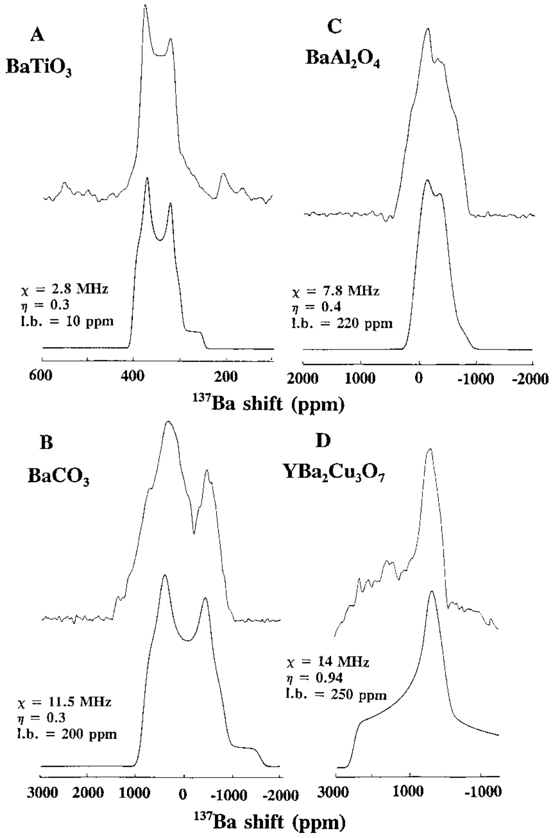

Fig. 2. Quadrupolar lineshapes of four resolved ^{137}Ba MAS NMR spectra with simulated spectra below. Simulation parameters as indicated. Baseline correction not applied to spectrum D.

the value of 2.90(3) Mhz determined by Bastow [10] in a single-crystal study of ^{137}Ba in ferroelectric BaTiO$_3$, and leads to an isotropic chemical shift δ_{iso} (the chemical shift in the absence of an electric field gradient) of 417 ppm.

3.3. *BaO (Fig. 1C)*

The ^{137}Ba spectrum of BaO consists of a single line at 748 ppm, broadened somewhat at its base by a small upfield shoulder probably indicating the occurrence of slight rehydration or carbonation in this extremely atmosphere-sensitive material. The single narrow resonance is consistent with the known lack of distortion of the octahedral Ba site in cubic BaO [19], and is in agreement with the single-line spectrum of Dec et al. [8] at 481 ppm with respect to BaZrO$_3$ (760 ppm with respect to BaCl$_2$).

After allowance is made for differences in magnetic field strength and referencing, the close agreement of the present spectra of BaZrO$_3$, BaTiO$_3$ and BaO with the few previously published spectra of these phases confirms the previous results and engenders confidence in the present pulse sequence and spectral processing methods. These were then applied to less tractable ceramic phases in which the Ba ions are located in sites of greater distortion, giving rise to much broader and weaker resonances.

3.4. *BaCO$_3$ (witherite, Fig. 1D)*

This spectrum is broad, as would be expected for the single Ba site of this orthorhombic aragonite-type structure, in which the Ba is surrounded by nine oxygens from the carbonate groups. Despite its broadness, the spectrum shows signs of quadrupolar lineshape, which was simulated using values for χ and η of 11.5 Mhz and 0.3, respectively, with line broadening of 200 ppm (Fig. 2B). The resulting isotropic chemical shift δ_{iso} is 1070 ppm.

3.5. *Ba(OH)$_2$·8H$_2$O (Fig. 1E)*

This compound contains Ba coordinated by eight water oxygens in the form of a slightly distorted Archimedean antiprism [20]; the hydroxyl groups are located too far away from the Ba to be coordinated by it. The ^{137}Ba spectrum represents a distorted single Ba site which is probably affected by the extensive hydrogen bonding present in the structure. The spectrum contains a hint of a possible quadrupolar lineshape, but this is too broad and poorly resolved to be meaningfully simulated.

3.6. *Ba(CH$_3$COO)$_2$ (barium acetate, Fig. 1F)*

Barium acetate was included in this study because of its use as a starting material for hybrid sol–gel synthesis of Ba-containing ceramics such as celsian (BaAl$_2$Si$_2$O$_8$) [14,15]. The present sample was shown by X-ray diffraction to be anhydrous. The Ba environment in anhydrous barium acetate has been determined in an X-ray structural study [24] to consist of nine oxygens from seven acetate groups. The Ba site consists of a very distorted monocapped square antiprism [21]. The ^{137}Ba spectrum (Fig. 1F) contains a suggestion of a quadrupolar lineshape as would be expected for such a distorted site, but is insufficiently resolved and too broadened to be readily simulated.

3.7. *BaAl$_2$Si$_2$O$_8$ (celsian, Fig. 1G)*

Celsian is a feldspar with the structure of the orthoclase sub-group, in which the irregular Ba site is located in a partly-ordered (Al,Si) tetrahedral network, with nine oxygen neighbours forming the Ba coordination polyhedron and another oxygen outside the bonding range [22]. The ^{137}Ba NMR spectrum (Fig. 1G) is broad and featureless, with a centre-of-gravity (COG) at about 550 ppm, suggesting that the Ba is considerably less shielded in this compound than in the aluminate or silicate (see below). The previously unreported ^{29}Si and ^{27}Al spectra of this phase were also recorded. The ^{29}Si spectrum is broad and poorly resolved, suggesting a degree of disorder in the tetrahedral aluminosilicate feldspar framework; nevertheless, three celsian resonances can be distinguished, at about −88 ppm [Q^4(4Al)], −101 ppm [Q^4(1Al)] and −113 ppm [Q4(0Al)] [referenced to tetramethylsilane (TMS)]. The ^{27}Al spectrum contains a single sharp tetrahedral resonance at 59.5 ppm, with respect to $Al(H_2O)_6{}^{3+}$.

3.8. Ba_2SiO_4 (Fig. 1H)

This compound contains two polyhedral Ba sites; in one, the Ba is surrounded by 10 nearest neighbour silicate oxygens has a slightly longer mean Ba–O bond length than in the other Ba site, in which the Ba is surrounded by nine silicate oxygens [23]. The presence of Ba in distorted polyhedral sites is consistent with the observed ^{137}Ba NMR spectrum (Fig. 1H), which is too broad however to allow the two sites to be resolved. The spectrum may suggest a quadrupolar lineshape, but the broadness due to site overlap and distortion rule out a meaningful simulation. The COG (−300 ppm) indicates Ba sites which are considerably more shielded than in celsian. The previously unreported ^{29}Si spectrum was also recorded; it contains a single sharp resonance at −69.5 ppm with respect to TMS.

3.9. $BaAl_2O_4$ (Fig. 1I)

The ^{137}Ba NMR spectrum of this compound shows similarities with the other broad quadrupolar spectra, but with a slightly better resolved lineshape which allowed a simulation to be attempted. Values for χ and η of 7.8 MHz and 0.4, respectively, and line broadening of 220 ppm produced a reasonable simulation (Fig. 2C), and led to a value of δ_{iso} of 306 ppm. This compound contains two Ba sites, each in a coordination polyhedron of nine oxygen neighbours [24]. The principal difference between the two sites is the degree of distortion, Ba_I being less distorted than Ba_{II}, but the range of bond lengths in both sites is such that the broad observed Ba spectrum and the simulation probably represents the mean of both sites. The previously unreported ^{27}Al spectrum was found to contain a single sharp tetrahedral resonance at 75.4 ppm with respect to $Al(H_2O)^{63+}$.

3.10. $YBa_2Cu_3O_7$ (Fig. 1J)

High-T_c superconducting ceramics, of which $YBa_2Cu_3O_7$ is typical, have been the subject of intense investigation since their discovery, and several previous attempts at solid-state Ba NMR spectroscopy indicate that the spectra are dominated by quadrupolar effects [11]. The present sample, described here as $YBa_2Cu_3O_7$, has a T_c of 90–92 K, and an oxygen content of 6.9–7. Such a highly oxygenated compound is orthorhombic, with the Ba 10-coordinated [25]. Both ^{135}Ba and ^{137}Ba spectra have been previously reported for this compound, but these measurements tend to concentrate on the sub-RT region; the present ^{137}Ba spectrum (Fig. 1J) must be compared with the few available room-temperature data. Shore et al. [11] report a value of the quadrupole frequency ν_Q and the asymmetry parameter η for ^{137}Ba in $YBa_2Cu_3O_7$ at 300 K. This value of ν is in agreement with the NQR results of Yakubowskii et al. [12], and can be used to deduce a value for the nuclear quadrupole coupling constant χ (defined as e^2qQ/h), since for the spin = 3/2 ^{137}Ba system,

$$\nu_Q = e^2qQ/2h \tag{1}$$

The resulting values of χ and ν were used to simulate the MAS spectrum at 300 K (Fig. 2D), giving a reasonable approximation to the observed spectrum, and suggesting an isotropic chemical shift δ_{iso} of 2563 ppm (possibly including a Knight shift contribution).

These results indicate that ^{137}Ba spectra which are usefully narrow and well-resolved can be obtained from ceramic materials in which the Ba is located in well-defined and symmetrical crystal sites, as is the case for the cubic oxides BaO and $BaZrO_3$. Where a tetragonal distortion ocurs in the Ba site, as in $BaTiO_3$ below the Curie point, usefully sharp spectra can still be obtained, but these will show quadrupolar lineshapes which can be simulated, yielding structural information. However, in most of the other classes of Ba compounds of interest as ceramics or ceramic precursors, the Ba sites are irregular polyhedra with coordination numbers (CN) typically ranging from 8 to 10. The ^{137}Ba spectra of these compounds are generally very broad and poorly resolved, as has also been reported for ^{25}Mg [1], ^{47,49}Ti [4] and ^{91}Zr [26] in oxides and ceramic materials. In the case of Mg compounds of ceramic interest, the Mg is normally located in octahedral sites which differ in their degree of distortion from ideal octahedral symmetry; relationships have been demonstrated between the octahedral distortion index and the ^{25}Mg MAS NMR spectral parameters (notably the resonance COG position and width, and the nuclear quadrupolar coupling constant χ, where this could be estimated [1]). Such relationships are difficult to test for the present Ba results because the Ba coordination polyhedra are not comparable, and χ could be estimated in only a few compounds. The mean Ba–O bond length provides a simple geometrical distortion parameter which may be more appropriate for compounds of different coordination number, but no clear relationship can be detected in the present compounds between the mean bond length and the spectral parameters which should be

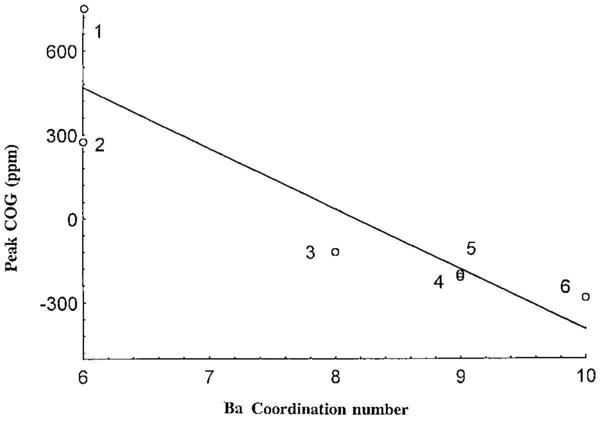

Fig. 3. Relationship between the position of the centre-of-gravity (COG) of the ^{137}Ba peaks in several ceramics and their Ba coordination number. Key: 1. BaO; 2. $BaZrO_3$; 3. $Ba(OH)_2{\cdot}8H_2O$; 4. $Ba(CH_3COO)_2$; 5. $BaAlO_4$; 6. Ba_2SiO_4.

sensitive to distortion (χ, δ_{iso} or COG). It should be noted however that no such simple relationship with mean Mg–O bond length was found for the ^{25}Mg spectra of Mg compounds [1].

On a more qualitative basis, changes in the chemical shift towards more negative values indicate increased shielding at the Ba nucleus, which can in turn be related to an increasing CN. A trend of this sort is shown by six of the present compounds (Fig. 3), but this effect appears to be masked by other factors in celsian, $BaCO_3$, $BaTiO_3$ and $YBa_2Cu_3O_7$, which also display more positive shifts than would be expected from simple CN considerations.

At present the usefulness of solid-state ^{137}Ba MAS NMR spectroscopy in the investigation of ceramic materials is limited (i) by the broadness of the spectra in all compounds except those in which the Ba site is extremely symmetrical, and (ii) by difficulties in interpreting the spectra and relating them to the structure. Both these drawbacks may eventually be overcome by improvements in experimental technique (new pulse sequences, higher field spectrometers and new MAS probes). However, the present results suggest that in its current state, ^{137}Ba MAS spectroscopy could be useful in studies of the synthesis and structure of compounds containing Ba in symmetrical sites (e.g. some types of electroceramics), and for monitoring changes in the Ba environment of systems such as sol–gel-derived ceramic precursors during the thermal evolution of crystalline structure.

4. Conclusions

The ^{137}Ba NMR spectra presented here for compounds containing Ba in a range of sites of differing symmetry are consistent with the behaviour of a quadrupolar nucleus. Where the Ba is located in sites of high symmetry (as in $BaZrO_3$, $BaTiO_3$ and BaO) the Ba resonance is very narrow, but at the present field strength (11.7T) shows a resolvable quadrupolar lineshape. Most of the other compounds of relevance to ceramics contain Ba in irregular polyhedral coordination, resulting in much broader spectra, some of which however show discernable quadrupolar features. The lineshapes and chemical shifts of the present spectra obtained using a Hahn echo pulse sequence are in agreement with the few ^{137}Ba spectra previously published for highly symmetrical compounds. Some evidence is presented for an expected trend in the ^{137}Ba peak positions with differences in the Ba coordination number, but other factors apparently dictate the spectral shape and position in several of these compounds.

Despite its limitations, the present results suggest that ^{137}Ba MAS NMR spectroscopy could be a potentially useful technique for studying some Ba-containing electroceramic materials and the thermal evolution of other Ba ceramics from amorphous gel-derived precursors.

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