

remarkable features that contrast to the spectrum of BaTiO_3 . First, the signal for BNT-15BT does not exhibit the steep singularities as those observed for BaTiO_3 and TiO_2 . Second, the high-field side of the signal is less steep than the low-field side. Both observations are a clear indication of a distribution of solid-state NMR parameters (especially C_Q and η), as reported for solid-solutions of $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$.²⁸ In addition to that, the distinct maxima expected for a quadrupolar nucleus in a single, well-defined EFG are not observed. Instead, one broad maximum at -880 ppm is present. Altogether, these features indicate a disordered local structure for the titanium site in BNT-15BT.

In order to investigate the effect of barium on the local structure of BNT-xBT ceramics, titanium NMR spectra were recorded for samples with different barium content, namely, for pure BNT, BNT-6BT, and BNT-15BT. Their static spectra are displayed in Figure 3(a). The same features described for the spectrum of BNT-15BT in Figure 2 can be observed in the spectra of pure BNT and BNT-6BT. From Figure 3, it is evident that the line-shape of the spectra and thus the local quadrupolar interaction and the local chemical environment of the titanium nuclei are practically independent of the amount of barium in the sample. The structural meaning of this independence is discussed below.

To gain further insight into the materials, the MAS spectra of the sample with the lowest (BNT-0BT) and highest (BNT-15BT) barium content were recorded (Figure 3(b)). Sample spinning under MAS induces a narrowing of the lines, due to partial averaging of the anisotropic NMR interactions between the nuclei and the local structure. The maximum exhibited by the static spectra is present as two peaks in the MAS spectra (Figure 3(b)), which occur at -920 ppm and -1170 ppm, respectively. The difference of approximately 250 ppm is close to the separation expected between the lines of both isotopes. Hence, these maxima can be attributed to the lines of both NMR-active titanium isotopes,

instead of a feature of the quadrupolar coupling 2nd order for a single isotope.

^{47,49}Ti NMR lines present approximately the same width for all three compositions. Under static conditions, the fwhm is approximately 770 ppm, whereas the spectra recorded under MAS exhibit a fwhm of 520 ppm. In addition, a broad hump between 0 and -2500 ppm (84 kHz broad) is present in the MAS spectra. The broader part of the MAS spectra is similar to the lower portion of the static spectra of BNT-xBT.

The comparison between static and MAS spectra indicates a distribution of both the quadrupolar coupling constant C_Q and the asymmetry parameter η and thus also the components of the EFG tensor. MAS will only effectively narrow the central transition lines in powder samples if the spinning frequency surpasses the width of the central transition (in frequency units) under static conditions.²⁹ The spectrum of a material for which a distribution of C_Q is present is the weighed sum of the lines for each value of C_Q in the distribution. If the spinning frequency is smaller than the width of the broadest line under the distribution, sites with different C_Q will behave differently under MAS. While the sites with C_Q smaller than the threshold value will be effectively narrowed, the sites with larger C_Q will remain with the same width as in the static spectrum, and result in a broad hump, as the one observed in Figure 3(b).

DISCUSSION

The results of our previous NMR investigation of BNT-xBT¹⁰ assume that oxygen octahedra tilt as rigid units, with tilting governed by the barium content. Based on this premise, the ^{47,49}Ti NMR spectra should remain unchanged for compositions with different barium content in the range from 0% to 15%. The ^{47,49}Ti NMR spectra of BNT-xBT samples, measured under static conditions (Figure 3(a)), do not present any significant changes as a function of barium content, indeed. Lines for BNT-0BT, BNT-6BT, and BNT-15BT all appeared in the same frequency range, revealing the same maximum position and a very similar line width.

The spectral features of the central transition of the titanium NMR lines are mainly determined by the chemical shift and the 2nd order quadrupolar interactions, which are expressed in terms of the isotropic chemical shift (δ_{ISO}) and the quadrupolar coupling constant (C_Q), respectively. These NMR parameters are associated with the local structure of the titanium site, with correlations to specific structural features being reported for ABO_3 oxides. The values of the isotropic chemical shift are related to mean Ti-O distances, whereas the shear strain in the TiO_6 octahedra (based on bond angle of O-Ti-O bonds) exhibits a strong correlation with the magnitude of the quadrupolar coupling.¹⁴ The shear strain is related to both titanium displacements and oxygen octahedra distortions, characterizing the C_Q as a spectral parameter sensitive to the local symmetry around this cation.

BNT-xBT samples with different barium content exhibit different symmetries for the average structure.^{3,20,21,30} Rhombohedral and tetragonal regions of its phase diagram are separated by a morphotropic phase boundary (MPB) around a barium content of 6%. Hence, one could expect

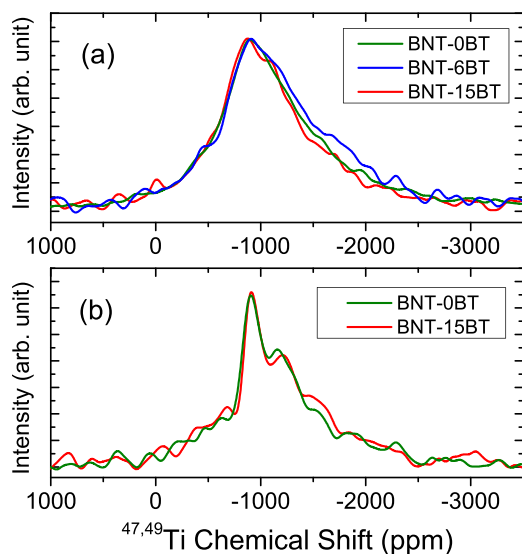


FIG. 3. ^{47,49}Ti NMR spectra of BNT-xBT. (a) Static and (b) under MAS (central region, spinning frequency of 10 kHz, corresponding to ca. 265 ppm).

- ²²D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, and G. Hoatson, *Magn. Reson. Chem.* **40**, 70 (2002).
- ²³D. G. Cory and W. M. Ritchey, *J. Magn. Reson.* (1969) **80**, 128 (1988).
- ²⁴T. Emmler, S. Gieschler, H. H. Limbach, and G. Buntkowsky, *J. Mol. Struct.* **700**, 29 (2004).
- ²⁵S. F. Dec, M. F. Davis, G. E. Maciel, C. E. Bronnimann, J. J. Fitzgerald, and S. S. Han, *Inorg. Chem.* **32**, 955 (1993).
- ²⁶A. Labouriau and W. L. Earl, *Chem. Phys. Lett.* **270**, 278 (1997).
- ²⁷T. J. Bastow, *J. Phys.: Condens. Matter* **1**, 4985 (1989).
- ²⁸C. Gervais, D. Veautier, M. E. Smith, F. Babonneau, P. Belleville, and C. Sanchez, *Solid State Nucl. Magn. Reson.* **26**, 147 (2004).
- ²⁹D. Freude, *Adv. Colloid Interface Sci.* **23**, 21 (1985).
- ³⁰R. Ranjan and A. Dviwedi, *Solid State Commun.* **135**, 394 (2005).
- ³¹V. A. Shuvaeva, D. Zekria, A. M. Glazer, Q. Jiang, S. M. Weber, P. Bhattacharya, and P. A. Thomas, *Phys. Rev. B* **71**, 174114 (2005).
- ³²B. N. Rao, L. Olivi, V. Sathe, and R. Ranjan, *Phys. Rev. B* **93**, 024106 (2016).

This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. This article appeared in *Journal of Applied Physics* 121 (2017) 11 and may be found at <https://tuprints.ulb.tu-darmstadt.de/19735>.

Available under only the rights of use according to UrhG.