

## A combined $^{135/137}\text{Ba}$ solid-state NMR and computational study of $\beta$ -Barium Borate

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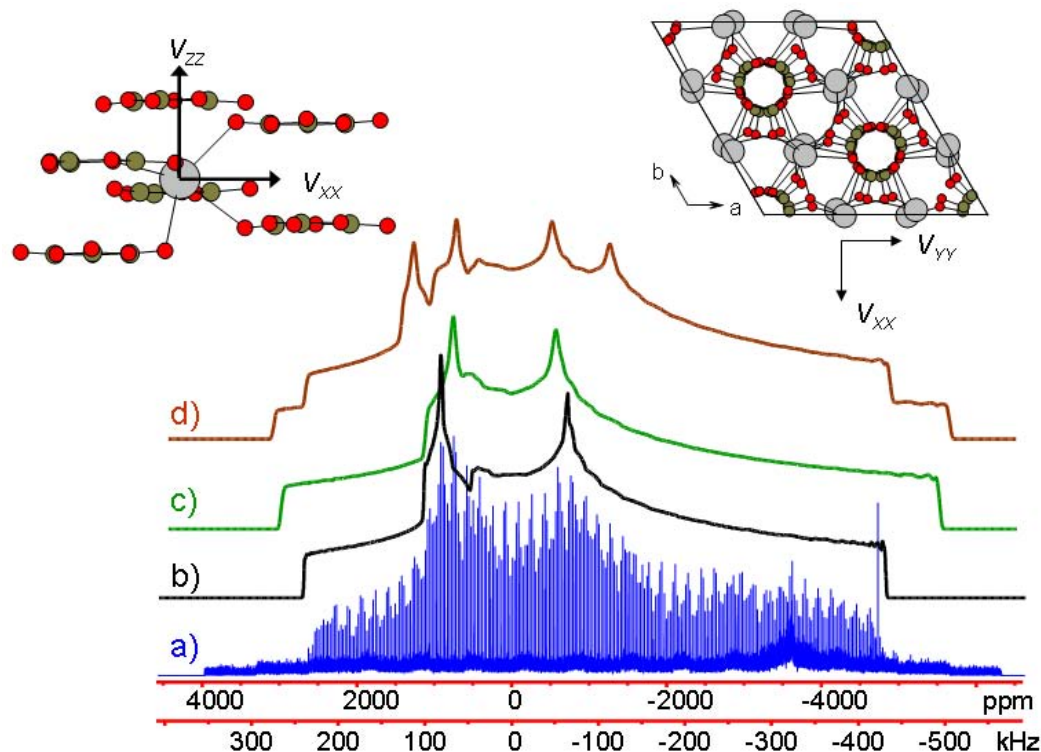
$\beta$ -Barium Borate ( $\beta$ -BBO or  $\beta$ -BaB<sub>2</sub>O<sub>4</sub>) is an important nonlinear optical (NLO) material with many practical applications. The relationship between the structure of  $\beta$ -BBO and its NLO properties has been the subject of numerous studies over the last two decades. Despite many structural studies, the exact space group of  $\beta$ -BBO still remains controversial. Although most of the studies support space group  $R3c$  [1-4], some work does prefer  $R3$  as the true space group [5,6]. The Ba local environment has never been probed directly by Ba SSNMR. Barium has two NMR-active isotopes,  $^{135}\text{Ba}$  and  $^{137}\text{Ba}$ . Both are quadrupolar nuclei with spin  $I = 3/2$ . They have relatively low natural abundances (6.59% for  $^{135}\text{Ba}$  and 11.32% for  $^{137}\text{Ba}$ ) and small gyromagnetic ratios ( $\gamma$ ) [ $\gamma(^{135}\text{Ba}) = 2.675 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ;  $\gamma(^{137}\text{Ba}) = 2.993 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ]. They also have relatively large quadrupole moments ( $Q$ ) [ $Q(^{135}\text{Ba}) = 0.160 \times 10^{-28} \text{ m}^2$ ,  $Q(^{137}\text{Ba}) = 0.245 \times 10^{-28} \text{ m}^2$ ], which more often than not leads to very broad lines when an appreciable electric field gradient (EFG) is present. These unfavourable NMR characteristics make the observation of  $^{135/137}\text{Ba}$  spectra difficult. Herein, we have directly probed the local environment of  $\text{Ba}^{2+}$  in  $\beta$ -BBO by acquiring  $^{135/137}\text{Ba}$  SSNMR spectra at an ultrahigh magnetic field of 21.1 T [7].

The  $^{135}\text{Ba}$  central transition static QCPMG spectrum acquired at 21.1 T is shown in Figure 1a. It can be fitted by a single Ba site with the following EFG parameters:  $C_Q(^{135}\text{Ba}) = 14.9(5) \text{ MHz}$ ,  $\eta_Q = 0.70(5)$ ,  $\bar{\delta}_{\text{iso}} = 200(50) \text{ ppm}$  (Figure 1b). The large  $C_Q$  arises from the non-spherical electronic environment around the Ba atom. The  $\text{Ba}^{2+}$  ion is coordinated to eight oxygen atoms and the  $\text{BaO}_8$  unit has the geometry of a highly distorted square antiprism. The O-Ba-O bond angles are highly dispersed, varying between 49.14 and 96.83°. The variation of the Ba-O bond distances is also quite large, ranging from 2.638 to 3.050 Å. As mentioned earlier, the space group of  $\beta$ -BBO belongs to either  $R3$  or  $R3c$ . The difference between the two is subtle and lies in the fact that a  $c$ -glide plane is missing in space group  $R3$ , resulting in two crystallographically non-equivalent Ba sites. We have also conducted theoretical calculations of  $^{135}\text{Ba}$  EFG tensor of barium sites in both  $R3$  and  $R3c$  structures using the CASTEP, a program designed to compute the electronic properties of periodic structures. The calculated  $^{135}\text{Ba}$  EFG parameters of  $R3c$  structure are  $C_Q = 17.66 \text{ MHz}$ ,  $\eta_Q = 0.78$ , both of which are comparable to those measured experimentally. Figure 1 illustrates the Ba EFG tensor orientations of  $\beta$ -BBO within its structure. The largest component of the EFG tensor,  $V_{ZZ}$ , is oriented along the crystallographic  $c$ -axis and perpendicular to the plane of the anionic  $(\text{B}_3\text{O}_6)^{3-}$  ring. Consequently, both  $V_{YY}$  and  $V_{XX}$  are parallel to the plane of the anionic group with  $V_{YY}$  along the  $a$ -direction. Using the  $R3$  structure, the  $^{135}\text{Ba}$  EFG tensors of two Ba sites were also calculated: site 1:

$C_Q = 16.70$  MHz,  $\eta_Q = 0.77$ ; site 2:  $C_Q = 18.80$  MHz,  $\eta_Q = 0.61$ . The calculations clearly indicate that if the space group of  $\beta$ -BBO were  $R3$ , the two  $^{135}\text{Ba}$  sites would have a difference of 2.1 MHz in  $C_Q$  values. Such an appreciable difference would result in a  $^{135}\text{Ba}$  spectrum which is significantly different from that of space group  $R3c$ . Indeed, Figures 1c and d shows that the  $^{135}\text{Ba}$  spectra calculated from two space groups at 21.1 T look distinctly different. A comparison of these calculated spectra with the observed one clearly indicates that the calculated spectrum based on the space group  $R3c$  matches well with the measured one. Thus, our  $^{135/137}\text{Ba}$  SSNMR results indicate that the true space group of  $\beta$ -BBO is  $R3c$  with one unique crystallographic Ba site. The work demonstrates that a combination of  $^{135/137}\text{Ba}$  NMR and theoretical calculation is a useful tool for characterization of Ba-based materials with unknown or poorly described structures.

#### References

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**Figure 1:** (a) The observed  $^{135}\text{Ba}$  static QCPMG NMR spectrum of  $\beta$ -BBO at 21.1 T; (b) The simulated spectrum; (c) Theoretically calculated spectrum based on  $R3c$  structure (one Ba site),  $C_Q = 17.66$  MHz,  $\eta_Q = 0.78$ ; (d) Theoretically calculated spectrum based on  $R3$  structure (two Ba sites), site 1:  $C_Q = 16.70$  MHz,  $\eta_Q = 0.77$ ; site 2:  $C_Q = 18.80$  MHz,  $\eta_Q = 0.61$ . The calculations were performed using the CASTEP program.