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Site discrimination in the crystalline borophosphate $Na_5B_2P_3O_{13}$ using advanced solid-state NMR techniques

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Abstract

A comprehensive solid-state NMR investigation on crystalline $Na_5B_2P_3O_{13}$ is presented. Triple-quantum magic angle spinning (TQMAS) and rotational echo double resonance (REDOR) studies are used for accurate determinations of the ^{11}B, ^{23}Na and ^{31}P interaction parameters. Based on these results and complementary quantum mechnical calculations, plausible site assignments can be derived. Generally, the results show that detailed, quantitative information about structures in borophosphate compunds can be obtained by investigating both the local site environments characterized by chemical shift and quadrupolar interaction parameters and the correlated dipolar interactions to atoms in the second coordination sphere.

Keywords: Dipolar coupling; Rotational echo double resonance; Borophosphates

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1. Introduction

The interest in crystalline [1–4] and glassy [5–8] borophosphate compounds of the general composition xM$_2$O–y-B$_2$O$_3$–zP$_2$O$_5$(mH$_2$O) has increased dramatically in recent years due to the large structural diversity that can be found in these systems. The structures of the crystalline as well as the amorphous materials are built up of BO_3, BO_4^- and PO_4^- units that are interconnected to each other and can form complex networks with one-, two-, and three-dimensional topologies [2,4]. While the structures of the crystalline phases can be analyzed using X-ray diffraction, the most valuable information regarding the structures of amorphous phases today comes from solid-state NMR investigations [5–8]. Most recent studies have focused on extracting information about internuclear distances and network connectivities, based on the precise measurement of magnetic dipole–dipole couplings [5,6]. Such work requires careful validation (and/or calibration) studies on crystalline model compounds, in which the internuclear distance distributions are well known. In this study, we focus on the crystalline penta-sodium-catenadiborotriphosphate $Na_5B_2P_3O_{13}$ [9] which crystallizes in the monoclinic space group $P2_1$ (lattice parameters $a = 6.711$ Å, $b = 11.618$ Å, $c = 7.868$ Å, $\beta = 115.2°$) with two formula units per unit cell. The asymmetric unit contains five crystallographically distinguishable sodium sites, two boron sites and three phosphorus sites. All of the phosphorus atoms are four-fold coordinated by oxygen atoms (distorted PO_4^- tetrahedra). Two of these oxygen atoms are non-bridging, and two are connected to adjacent boron atoms ($P^{(2)}_{2B}$ unit with no P–O–P linking). The boron atoms are located at the center of distorted BO_4^- tetrahedra which are connected to three PO_4^- units and one BO_4^- unit ($B^{(4)}_{3P}$ unit, Fig. 1). The sodium ions are located between the phosphate and borate chains and each of them is coordinated by five or six oxygen atoms in distorted coordination polyhedra. $Na_5B_2P_3O_{13}$ was first synthesized by heating a stoichiometric mixture of $NaH_2PO_4 \cdot H_2O$ and $NaBO_2 \cdot 4H_2O$ at high temperatures, later a hydrothermal and a microwave-assisted synthesis was developed starting from the same precursors [10].

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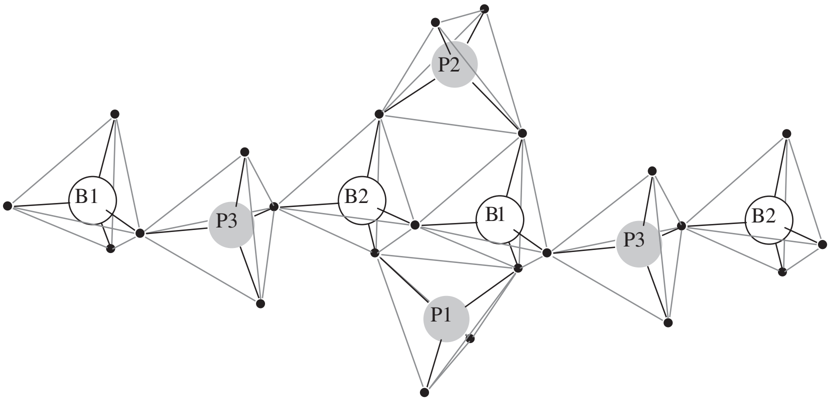

Fig. 1. Sketch of the borate–phosphate chain structure in $Na_5B_2P_3O_{13}$.

High-resolution one-pulse MAS-NMR experiments contain valuable information about the local environment of the nuclei under consideration [11]. Nevertheless, in many cases the interpretation of different chemical shifts and/or quadrupolar couplings does not lead to an unambiguous assignment of the peaks to the structural groups. One way to solve this problem is to establish a correlation between NMR interaction parameters and structures by performing quantum mechanical calculations. Applying DFT methods, detailed information about chemical shielding tensors can be obtained [12], while the calculation of quadrupolar interaction parameters is mostly performed using the linear-augmented-plane-wave (LAPW) method implemented in the WIEN2k program code [13,14].

Yet another possibility of identifying and characterizing chemical sites in complex materials is to make use of differences in magnetic dipole–dipole coupling strengths of the different atomic sites which occur in crystalline as well as in glassy borophosphate materials [5,6]. The most prominent method for this purpose is the *r*otational *e*cho *do*uble *r*esonance (REDOR) experiment [15,16] which, as shown recently, is well suited for the quantification of dipole–dipole couplings in multispin systems such as they occur in inorganic solids [17], even when quadrupolar nuclei are involved [18,19].

In this study, we present a comprehensive approach for the assignment of solid-state NMR signals for the compound $Na_5B_2P_3O_{13}$, using results from single pulse MAS, triple-quantum (TQ) MAS experiments, WIEN2k calculations, as well as new REDOR experiments involving all of the NMR active nuclei in the sample.

2. NMR methodology

For quadrupolar nuclei, MAS/TQMAS NMR measurements are well-established methods in order to obtain high-resolution spectra and quadrupolar coupling parameters [20]. Here, results from these methods are complemented by results from REDOR measurements that are used to probe the heteronuclear dipole–dipole coupling between the NMR active nuclei in the sample. In these latter experiments, the signal of the observe-nucleus S is measured using a rotor-synchronized spin echo sequence yielding intensities S_0. Dipolar recoupling is performed by applying π-pulse(s) to the second spin species diminishing the full echo intensity S_0 to a reduced intensity S [16]. In principle, the dipolar coupling can be determined by plotting the normalized intensity difference $(S_0{-}S)/S_0 = \Delta S/S_0$ against the evolution time NT_r (the duration of one rotor period multiplied by the number of rotor cycles). The application of this technique to inorganic solids faces some complications: The internuclear distances and angles in multispin systems are subject to possibly wide distribution effects influencing strongly the obtained REDOR curves at longer evolution times [17]. A useful approach to overcome this difficulty is to restrict the analysis of REDOR curves to the initial regime ($0 \leqslant \Delta S/S_0 \leqslant 0.2$) where the dipolar evolution still proceeds independent on specific spin interaction geometries. In this limit, the dipolar coupling can be considered to result from a summation of pair-wise interactions, and the dipolar coupling can be quantified in terms of second moment (M_2) values, which represent a convolution of the number of interacting spins and their respective internuclear distances [17].

In the case of $S\{I = 1/2\}$ REDOR experiments, the corresponding M_2^{s-1} values can be directly obtained from a parabolic fit to the experimental REDOR curves [18]:

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2}(NT_r)^2 M_2^{S-I}. \tag{1}$$

The original REDOR pulse sequence [16] should be used and for a precise determination of M_2 values the experimental REDOR curve should be corrected for effects of pulse errors and radio frequency amplitude (B_1) inhomogeneities by compensation schemes as proposed in Ref. [18] (pulse sequence see Fig. 2a). In the case of $S\{^{31}P\}$ REDOR experiments, an additional attenuation of the REDOR dephasing can arise due to the substantial chemical shift anisotropy (CSA) of ^{31}P leading to a non-negligible underestimation of the experimental M_2 values even if the compensation strategy is used. In the present study, these effects are taken into account by explicitly