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^{93}Nb and ^{17}O NMR chemical shifts of niobiophosphate compounds

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Abstract

Niobiophosphate compounds with a large range of niobium and oxygen environments were studied with ^{93}Nb and ^{17}O solid-state NMR. ^{93}Nb isotropic chemical shift of pure niobate Nb(ONb)$_6$, pure phosphate Nb(OP)$_6$ and mixed phosphate–niobate Nb(OP)$_x$(ONb)$_{(6-x)}$ ($1 \leqslant x \leqslant 5$) sites were measured at a high magnetic field (18.8 T). ^{93}Nb chemical shifts were found to be sensitive to the variation of local charge on Nb, but not to the local bond geometry (i.e. crystallographic site and edge or corner connectivity). A systematic shift to high field of the ^{93}Nb chemical shift is measured when x increases. Then, ^{17}O NMR spectra of a series of enriched samples provided the chemical shift and quadrupolar parameters for 4 types of oxygen environment (P–O–P, P–O–Na, P–O–Nb and Nb–O–Nb). Finally, Nb–O–Nb sites were characterized by a large ^{17}O chemical shift anisotropy.
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1. Introduction

Transition metal ions with an empty d shell, such as Nb^{5+}, contribute to increase both linear and non-linear indexes in iono-covalent insulating materials [1]. Indeed, remarkable non-linear optical properties were obtained in xNb$_2$O$_5$–$(1-x)$ (0.95NaPO$_3$–0.05Na$_2$B$_4$O$_7$) glasses [2]. More generally, niobiophosphate glasses are known to have improved properties compared to phosphate glasses [3–6]. Therefore, they have been proposed as host matrix of rare-earth elements for optical applications [7–9] or as durable matrix for the immobilization of nuclear wastes [10]. A better knowledge of the influence of Nb$_2$O$_5$ on the phosphate glass network structure is thus important in order to improve the niobiophosphate glass properties [11].

Solid-state NMR is a powerful method for probing the local structure around nuclei in glasses [12], and recent developments now enable the measurement of the connectivities between nuclei [13]. However, the assignment of NMR resonances is difficult when chemical shift data of reference compounds are missing, and ab initio chemical shift calculations are complex for inorganic materials containing heavy elements like ^{93}Nb. 93-niobium is a 9/2 spin nucleus with 100% natural abundance and a relatively large gyromagnetic ratio. It is thus a relatively sensitive nucleus (its receptivity is 0.48 vs. ^{1}H). However, it suffers from a large nuclear quadruple moment ($Q = 32 \times 10^{-30}$ m^2) and in the solid state, ^{93}Nb NMR spectra are dominated by the second-order quadrupolar interaction. Thus, the resonance of the central transition ($-1/2 \leftrightarrow 1/2$) may be considerably broad. Lo et al. [14] indeed reported large Cq values, up to 54.4 MHz in Nb(V) complexes. This is probably the reason why only a few ^{93}Nb solid-state NMR analyses have been published [15,16]. Spectra obtained from static echoes on SiO$_2$–Nb$_2$O$_5$ gels were reported by Drake et al. [17], which exhibit featureless broad lineshapes. ^{93}Nb MAS-NMR [18,19] spectra were recorded on crystalline niobate compounds with structures that were simple enough to provide resolved spectra. ^{93}Nb MQ-MAS and ST-MAS NMR [16,18,20] spectra were furthermore recorded to increase the resolution.

An extensive study of ^{93}Nb NMR of niobate compounds was published recently by Lapina et al. [16]. They reported

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a chemical shift range from -600 to -2000 ppm, which is mostly influenced by the niobium coordination. Concerning the octahedral niobium coordination, which is expected in niobiophosphates, the chemical shift values are located between -900 and -1300 ppm [16] depending on the local symmetry and the ionic character of the niobium sublattice. However, no data were reported on niobiophosphate compounds in this study [16].

In glass systems, the spectral resolution is even worse than in crystals, owing to the distribution of chemical shift and quadrupolar constant inherent to the glassy state. Hart et al. [21] reported the presence of Te–O–Nb linkages between Te(IV) and Nb(V) in potassium niobate tellurite glass ceramics. In a preliminary study [11], we reported ^{93}Nb MAS NMR spectra of sodium niobiophosphate glasses. Two broad resonances could be observed with variable intensities when the Nb_2O_5 content increases in the glasses. However, the lack of chemical shift reference data prevented a definitive assignment of these resonances.

17-oxygen NMR is attractive because it provides direct information about connectivities among those elements that are involved within the glass network. However, the natural abundance of ^{17}O is only 0.037%, its magnetogyric ratio ($\gamma/2\pi = 5.77 \times 10^6$ Hz T^{-1}) is small and it is a quadrupolar nucleus with spin 5/2. Solid-state ^{17}O NMR spectra generally require ^{17}O-enriched samples prior to recording, which limits the range and complexity of studied materials [15]. Thanks to high magnetic fields and high-resolution methods like DOR [22], DAS [23], MQMAS [24] or STMAS [25], many ^{17}O NMR spectra of inorganic materials have been published. However, only a few ^{17}O NMR studies are known for phosphate compounds [26–30] and none have been published for niobiophosphate compounds.

In this work, niobate and niobiophosphate compounds with well-known structures were prepared, isotopically ^{17}O-enriched and examined with ^{93}Nb and ^{17}O solid-state NMR at high magnetic field (18.8 T). The use of a high magnetic field enables to reduce the quadrupolar-induced broadening of ^{93}Nb and ^{17}O nuclei, which scales as the inverse of the magnetic field [31]. The aim is to measure chemical shift ranges for different niobium or oxygen environments in these materials. We first describe briefly the structure of the crystals and the local environment of Nb and O atoms. We assign the ^{93}Nb NMR spectra according to the structural data and discuss the limits of the assignments. Finally, we assign the ^{17}O NMR spectra, and propose chemical shift ranges for the different oxygen sites in niobiophosphate compounds.

2. Experimental procedures

2.1. Sample preparation

Crystalline samples were synthesized according to the published procedures using conventional solid-state chemistry methods. Details can be obtained in the references cited in the text. In the figures below, Nb atoms are drawn at the center of gray NbO$_6$ octahedra, P atoms are drawn at the

center of gray-striped PO$_4$ tetrahedra. The crystal structure and purity of all the prepared samples were checked with X-ray diffraction. The glasses were prepared by melting the laboratory-grade oxides in platinum crucible at a temperature high enough to obtain a homogeneous melt, and then quenched onto a brass plate. The ^{17}O-enriched samples were prepared using 40% enriched water through the use of a thermal treatment under ^{17}O-enriched water vapor [29].

2.2. NMR experiments

The ^{93}Nb MAS-NMR spectra were acquired at a static magnetic field of 18.8 T (Larmor frequency of 195.6 MHz) with a single pulse excitation of 1 μs at an RF field strength of ca. 80 kHz, a recycling delay of 1 s and 512 transients. A large spectral width of 2 MHz was used. A spinning frequency of 20 kHz (3.2 mm Bruker probe) was set. The ^{93}Nb echo/anti-echo SPAM-3QMAS spectrum was acquired with 12 anti-echo t_1 slices [24,32] at 18.8 T, using a 3.2 mm Bruker probe. The first 2 hard pulse lengths were 1 μs and the third soft 90° pulse length was 6 μs. The recycling time was 1 s with a spinning frequency of 20 kHz. A solution of NbCl$_5$ in acetonitrile has been used as a chemical shift reference ($\delta = 0$ ppm). A shearing transformation was performed on the MQMAS data and the scaling follows the convention proposed by Amoureux et al. [33].

The ^{17}O MAS spectra were recorded at 9.4 T (Larmor frequency 54.2 MHz) using a 4 mm Bruker probe at a spinning speed of 10 kHz, with a recycling time of 1 s at an RF field strength of 70 kHz. For $Nb_{1.91}P_{2.82}O_{12}$, the ^{17}O SPAM-DQF-STMAS spectrum [34] was recorded at 9.4 T (Larmor frequency 54.2 MHz) with a 4 mm Bruker probe without anti-echo signal. The spinning speed was 12 kHz, leading to increment times of 83.3 μs (for exact rotor synchronization). A total of 61 slices in t_1 dimension were sufficient. The pulse lengths were 2.25 and 1.8 μs for the first and the second pulses, respectively, at an RF field strength of 70 kHz. The selective pulse lengths were 16 μs ($\pi/2$) and 32 μs (π). The recycling time was 1 s. The ^{17}O chemical shift reference is tap water.

In the result section, chemical shift δ will refer to the peak maximum on the spectrum. However, NMR chemical shifts of quadrupolar nuclei are affected by a second-order quadrupolar-induced shift [31]. δ_{iso} will refer to the chemical shift that was discarded from the quadrupolar-induced shift, using the MQMAS spectra and the procedure as described in Ref. [33]. This procedure gives access to the $P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$ value which will be used in this article.

3. Results

3.1. ^{93}Nb NMR

Some niobate and niobiophosphate reference compounds have been selected to represent a range of niobium environments expected in glasses, i.e. pure niobate (Nb(ONb)$_6$), pure phosphate (Nb(OP)$_6$) and mixed niobiophosphate