Evidence of crystalline/glassy intermediates in bismuth phosphates

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^{31}P and ^{17}O NMR investigations have been achieved on bismuth oxide phosphates by a comparison between ordered and semi-ordered reference compounds; the wide chemical shift range for ^{17}O is revealed to be a profitable source of information about partially ordered materials.

Bi_2O_3–MO–P_2O_5, (M = Co, Cu, Cd, Zn, Mn...) ternary systems have been well investigated, leading to the characterization of new bismuth oxide phosphates having particular structural relationships.[1–8] As intensively detailed,[9] the rigid frameworks of these materials can be considered as an assembly by the edge sharing of $O(Bi,M)_4$ polyhedra, leading to infinite polycationic ribbons of variable width: one, two, three, ... tetrahedra wide, surrounded by isolated PO_4 groups. From XRD/ND crystal structure studies, we classified these compounds as "disordered" or "ordered", depending on the competition (or not) between several O_4 configurations around the central P sites. Indeed, in ordered compounds such as BiM_2PO_6,[3,4,10,11] the Bi^{3+} cations strictly sit in the middle of ribbons, whereas the M^{2+} cations are located at their edges. Similarly, in disordered compounds, *e.g.* $Bi_{1.2}M_{1.2}PO_{5.5}$,[7] Bi^{3+} cations still occupy the middle of the ribbons, whereas the edges of the ribbons are filled by mixed site Bi^{3+}/M^{2+}. This statistical distribution leads to a variable orientation of the PO_4 groups, depending on the local nature of its first (Bi, M) cationic shell. The disorder is all the more important because it also affects partially filled cationic channels (so-called *tunnels* hereafter) surrounded by PO_4 groups in between pairs of ribbons. Of course, the notion of disorder is inexact because of the existence at the microscopic scale of incommensurate modulated phenomena (mainly along b*) in most of the disordered compounds.[12–14] This extra information does not survive over long range scales, *e.g.*, it is not observed in the XRD of single crystals. Therefore, sometimes only ordered fragments of the disordered PO_4/tunnel interstitial areas can be assumed from the average crystal structure, on the basis of plausible interatomic distances.[13] However, structural interactions between the edges of the ribbons, PO_4 groups and the tunnel is far from being fully established, probably due to various phenomena, including anti-phase boundary defects within tunnels and the probable semi-ordered zones in these materials. In view of a complementary approach to these fascinating series and by an easy extension to different compounds, ^{31}P and ^{17}O NMR spectroscopy have been used as local probes. Indeed, recent technical advances in solid state NMR has led to the emergence of this technique by adapting it for use with low natural abundance nuclei having relatively small gyromagnetic ratios, such as ^{17}O. In addition, it is worth mentioning that impedance spectroscopy measurements on all of these materials (ordered and disordered) show low ionic mobilities due to the strong P–O bonds involved for most of the oxygen ions. Therefore, only the static aspect is considered hereafter.

Thus, the present work focuses on a comparison between a typical ordered and disordered compound, with the aim of establishing the pertinence, complementarities, and limits of both ^{31}P and ^{17}O nuclei as probes with regard to the structural aspects of ordered *vs.* semi-ordered materials. With that aim in mind, two compounds have been selected from among the series:

(i) $BiCd_2PO_6$ was chosen as the archetype of ordered compounds. Its structure is isostructural to $BiZn_2PO_6$,[15,16] and it is interesting because it crystallizes in the *Bbmm* space group, while many members of the BiM_2PO_6 class (including the M = Zn term) adopt the less symmetrical *Pnma* space group. The coordination around its unique phosphorus position is constituted by two independent O2 (2×) and O3 (2×) atoms, while O1 is located in the two tetrahedra-wide ribbons at the center of a OBi_2Cd_2 tetrahedron (Fig. 1(a)).

(ii) The simplest disordered compounds have the $Bi_{\sim 1.2}M_{\sim 1.2}PO_{5.5}$ general formula (M = Mn, Co, Zn). Their structure (space group *Icma*) is formed of triple ribbons with

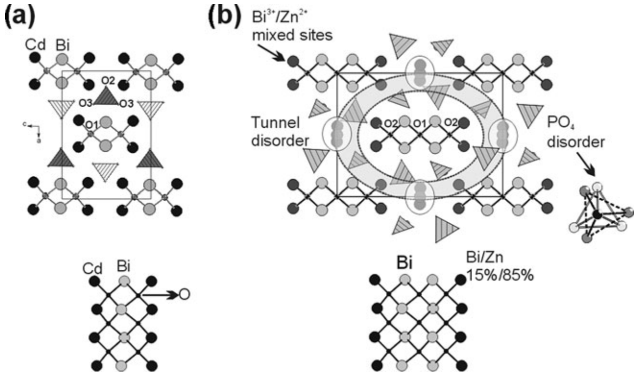

Fig. 1 The structures of (a) $BiCd_2PO_6$ and (b) $Bi_{1.2}Zn_{1.2}PO_{5.5}$. $BiCd_2PO_6$ consist of $[Cd_4Bi_2O_2]$-ordered double ribbons surrounded by six isolated ordered phosphates. $Bi_{1.2}Zn_{1.2}PO_{5.5}$ is disordered because of (1) the presence of mixed Bi^{3+}/Zn^{2+} sites at the edges of triple $[(Bi_{0.15}Zn_{0.85})_4Bi_4O_6]$ ribbons, (2) disordered tunnels, partially occupied by Zn^{2+}, and (3) multiple PO_4 configurations around the same phosphorus.

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mixed Bi/M edges (for M = Zn: 15% Bi^{3+}/85% Zn^{2+}). The partially M-filled tunnels and surrounding disordered PO_4 groups are shown in Fig. 1(b). Only one phosphorus position exists, even if it has finally been split into two close satellites, P1 (~50%) and P2 (~50%), in the published model. To avoid any paramagnetic perturbation, the M = Zn compound was selected. It is noteworthy that the influence of Cd^{2+} for Zn^{2+} replacement in BiM_2PO_6 on the ^{31}P NMR chemical shift has already been fully quantified on the basis of the empirical z/a^2 parameter,[15] and no additional contribution is expected between these two neighboring cations. The possibility of quantifying the local cationic environment of the PO_4 groups in a $Bi(M,M')PO_6$ statistical solid solution compounds has also been enhanced.

^{31}P MAS NMR: Fig. 2(a) and (b) show the ^{31}P NMR spectra of $BiCd_2PO_6$ against $Bi_{1.2}Zn_{1.2}PO_{5.5}$, which clearly reveals the broadening of the signal for the latter due to the multitude of individual resonances in the disordered compound. It is comparable to the IR spectra of ordered *vs.* disordered compounds presented elsewhere.[13] In that sense, the broad envelope does not show discrete contributions but rather a continuum. Here, in addition to the local distortion of each individual PO_4 group, the influence of the nature of the neighboring Zn/Bi cationic shell has to be considered.[15] Furthermore, the ^{31}P double quantum MAS-NMR spectrum shows no particular privileged out-of-diagonal correlations (Fig. 2(c)) reminiscent of a glass-like state from the ^{31}P NMR resolution.

Since oxygen occupies both the polycationic regular sublattice and the disordered interstitial regions, ^{17}O NMR analysis would be expected to give relevant information about disorder. Here, samples were enriched *via* the ^{17}O enrichment method developed by Flambard *et al.*[17] Due to the presence of water vapor, the sample was checked by ^{1}H NMR to ensure that all protons disappeared at the end of the enrichment. Another difficulty in obtaining ^{17}O NMR spectra is the presence of the quadrupolar interactions of the nuclei (spin $I = 5/2$) that largely broaden signals. This requires suitable techniques, such as double rotation (DOR),[18] multiple-quantum magic angle spinning (MQ-MAS)[19] or satellite transition magic angle spinning (ST-MAS),[20] in order to remove the anisotropic broadenings that remain under magic angle spinning conditions.

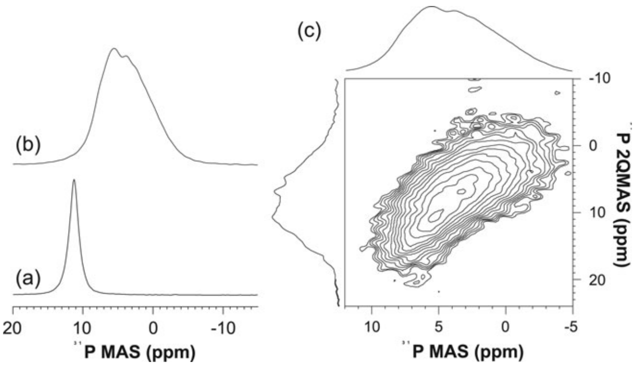

Fig. 2 ^{31}P MAS-NMR (9.4 T) spectra of (a) $BiCd_2PO_6$ and (b) $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The spectra were acquired at an MAS speed of 10 kHz, with a short pulse excitation of 1.5 μs (20°) and a recycling delay of 20 s. (c) ^{31}P double quantum MAS-NMR spectrum of $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The spinning frequency was 10 kHz. The excitation and reconversion period was composed of back-to-back 90° pulses[21] of 4 μs, which gave a total excitation/reconversion time of 400 μs. The repetition time was 30 s, preceded by a presaturation period. A total of 16 scans were used and 64 t1 increments were collected. The ^{31}P chemical shift was referenced externally to an 85% H_3PO_4 solution at 0 ppm.

^{17}O MAS NMR: Fig. 3 shows the high resolution MQ-MAS spectra of (a) $BiCd_2PO_6$ and (b) $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The horizontal projections (top) correspond to MAS spectra still broadened by the second order quadrupolar interaction. The vertical projections reveal ^{17}O isotropic spectra of the two compounds, where the quadrupolar broadening is removed, *i.e.*, each maximum peak corresponds to a given oxygen environment. The resonance at 90 ppm, marked with an asterisk, corresponds to a spinning sideband of site A on the isotropic dimension. The two spectra show two groups of resonances, around

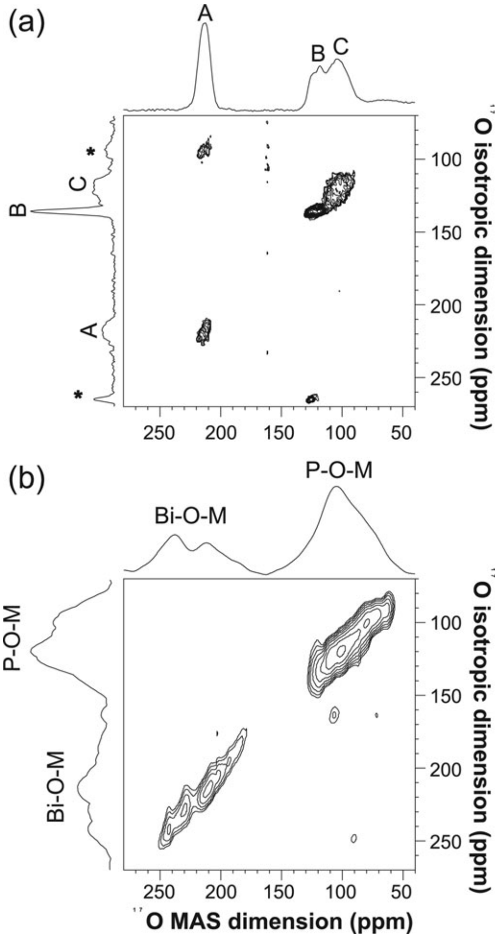

Fig. 3 ^{17}O MQ-MAS NMR (18.8 T) spectra of (a) $BiCd_2PO_6$ and (b) $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The spectra were acquired at an MAS speed of 20 kHz, with a recycling delay of 1 s, using the SPAM sequence.[24] The excitation and reconversion pulses were set to 3.75 μs and 1.20 μs, respectively, corresponding to an RF field strength of 80 kHz, followed by a selective 90° pulse of 11 μs (RF field of 8 kHz). For spectrum (a), each transient was accumulated with 72 scans, and 128 t1 data points were collected using the STATES method. For (b), a total of 4500 scans were needed and 30 t1 increments were collected. The ^{17}O chemical shift was referenced externally to tap water.

180–250 ppm and around 50–130 ppm (see the MAS projections). The region around 200 ppm (resonance A) is assigned to $O(Bi,M)_4$ tetrahedral sites in the polycationic ribbons. The value of the chemical shifts are close to those determined for OBi_4 tetrahedra in related compounds, 195 ppm in Bi_2O_3[22] and 265 ppm in α-$Bi_4V_2O_{11}$.[23] Our assignment was indirectly confirmed by a ^{17}O T_2 relaxation measurement (using a saturation recovery pulse sequence) performed on the $BiCd_2PO_6$ compound. The A site exhibited a short T_2 relaxation time of about 200 μs, maybe due to the presence of Bi quadrupolar nuclei in its first-neighbour cationic shell (^{111}Cd and ^{113}Cd are non-quadrupolar). A similar measurement was not possible for the disordered compound due to the low efficiency of the isotopic enrichment (probably because the ^{17}O-enriched water had already been used in previous experiments).

Ordered compound: The second region around 100–160 ppm is typically in the chemical shift range of oxygens involved in PO_4 groups.[25] In $BiCd_2PO_6$, it is composed of two resonances, B (120 ppm, T_2 = 5 ms) and C (100 ppm, T_2 = 500 μs), corresponding to O2 and O3. This assignment arises from their proximity or otherwise to quadrupolar Bi nuclei in their second cationic shell (Table 1). It was checked by a ^{31}P–^{17}O heteronuclear multiple quantum correlation (HMQC)[26] experiment that a correlation existed between the unique ^{31}P site and the ^{17}O–B sites (Fig. 4). However, no correlation signal was detected for the ^{17}O–C sites due to the very short T_2 relaxation time (500 μs). It is also noteworthy that both A and C showed broad isotropic resonances compared to B. So far, this is not understood in this "ordered" compound. Note the presence of a broad signal of low intensity in the ^{17}O dimension (Fig. 4), which is due to an impurity obtained after the process of enrichment and was not detected by XRD.

Semi-ordered compound: Next, we analyzed a semi-ordered compound, $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The ^{17}O MQ-MAS NMR spectrum is shown in Fig. 2(b). Two isolated regions are highlighted in the 2D spectrum. The broadness of the peaks seen in the isotropic projection is a signature of the high disorder present in this system, as discussed in the first part of this work. The assignment of both regions was deduced by analogy with the ^{17}O spectrum obtained for $BiCd_2PO_6$. One region corresponds to oxygen atoms linked to ribbons (resonance A) between 160 and 240 ppm. Referring to the structure presented in Fig. 1(b), two oxygen sites should be distinguishable in the isotropic dimension, whether they are at the center ($O1Bi_4$) or at the edge ($O2Bi_2Zn_2$) of the ribbon. A close look at the two-dimensional contours clearly suggests the presence of more than two sites, probably due to the high sensitivity of the ^{17}O NMR chemical shift to the cationic environment, even at a semi-local scale (second shell cationic neighbours). The presence of additional oxygen sites is easily explained by the existence of a mixed Bi/Zn cationic site at the edge of the ribbon. The assignment of each individual resonance is not yet possible due to the current absence of a large ^{17}O NMR chemical shift database for these systems. The development of such a database would require a series of model compounds to be isotopically enriched for further ^{17}O MAS NMR analysis. The second option available is to profit from the recent development of first principles calculations of NMR parameters using periodic boundary conditions.[27] The latter approach, which is beyond the scope of this Letter, is definitely more realistic at present.

The chemical shift region centred on 50–150 ppm exhibits two main resonances in the isotropic projection. These can be assigned to the oxygen atoms in the PO_4 groups. First, it should be noted that the ^{17}O resonances are spread over a large chemical shift range, especially in the isotropic dimension when the second order quadrupolar broadening is removed. This large distribution of chemical shift values with respect to the so-called ordered compound, $BiCd_2PO_6$, reveals the important disorder associated with the PO_4 groups in these systems. Nevertheless, some discontinuities associated with

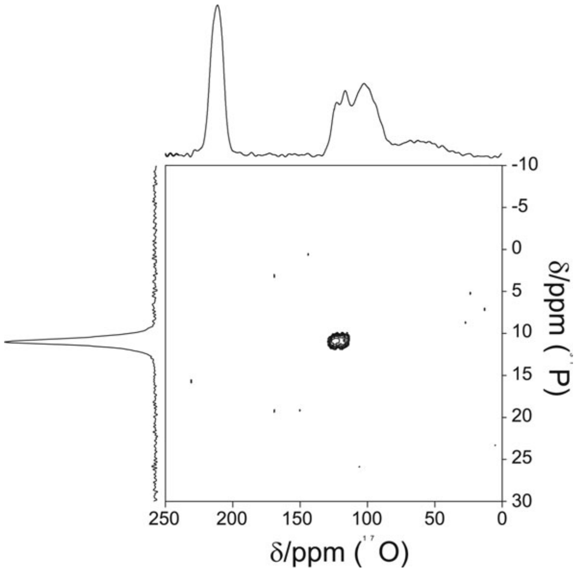

Fig. 4 The ^{31}P–^{17}O HMQC (18.8 T) spectrum of $BiCd_2PO_6$ was obtained at a MAS speed of 25 kHz by following the pulse sequence detailed by Massiot *et al.*[26] An echo was applied to the observed ^{17}O nuclei with respective 90° and 180° pulses of 10 and 20 μs. Two 90° pulses of 4.5 μs were then applied on either sides of the ^{17}O 180° pulse. The evolution delay was set to 3 ms for an evolution under *J*-coupling. A total of 512 scans were accumulated with a recycling delay of 1 s.

Table 1 The environment of the oxygen atoms (distances in Å) in $BiCd_2PO_6$ and $Bi_{1.2}Zn_{1.2}PO_{5.5}$. The first shell is given for the oxygen of the ribbons and the first two shells are presented for the oxygen of the PO_4 groups.[15,16]

	$BiCd_2PO_6$		$Bi_{1.2}Zn_{1.2}PO_{5.5}$[a]	
	1st shell	2nd shell	1st shell	
O1–Bi1	2 × 2.27(2)		O2–Bi1	2 × 2.243(1)
Cd2	2 × 2.18(2)		Bi/Zn2	2 × 2.159(9)
O2–P	1 × 1.43(3)		O1–Bi1	4 × 2.299(1)
Cd2	2 × 2.22(2)	2 × 3.41(3)		
Bi1		1 × 3.70(3)		
O3–P	1 × 1.51(4)			
Cd2	1 × 2.11(4)	2 × 3.29(2)		
Bi1		2 × 3.41(2)		
Bi1		1 × 3.65(4)		

[a] The coordination of the disordered PO_4 groups is not accurately known.

discrete chemical shift values appear in the isotropic dimension. This strongly suggests that some PO_4 positions are privileged, as observed from the single crystal X-ray diffraction data. For example, two major competing PO_4 positions have been located in $Bi_{1.2}M_{1.2}PO_{5.5}$, while residual electronic density on Fourier difference maps is reminiscent of a number of extra orientations. Again, the current ^{17}O NMR chemical shift database is not sufficient to fully interpret the spectrum in the P–^{17}O–M region.

This study highlights the informative data provided by ^{17}O NMR due to its broad range of chemical shifts compared to the ^{31}P nucleus. In disordered bismuth phosphates, ^{17}O NMR clearly provides evidence of preferential PO_4 orientations, in good agreement with the semi-ordering deduced from diffraction data, which shows modulated microdomains with loss of the order at long range scales. Of course, the methodology and conclusions developed here are not restricted to our particular chemical system, but can be generalized to other partially-ordered systems, solid solutions, composite structures and so on. Finally, it is worth stating that, to the best of our knowledge, a successful ^{31}P–^{17}O through-bond correlation has been presented here for the first time.

Experimental section

The different oxides reported in this Letter were prepared from stoichiometric mixtures of Bi_2O_3, MO (M = Cd, Zn) and $(NH_4)_2HPO_4$. To avoid the problem of volatile species, they were removed by solid state reparative methods, implying several heating–regrinding steps at temperatures from 200 to 700 °C. The purity of the samples was checked by powder X-ray diffraction using a Siemens D-5000 diffractometer with back-monochromatized Cu-K_α radiation. NMR experimental information is given in the Figure captions. ^{17}O enrichment was achieved by heating samples at 650 °C for 8 h under ^{17}O-enriched water vapor.[15]

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