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A space group assignment of ZrP_2O_7 obtained by ^{31}P solid state NMR

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2-D ^{31}P dipolar recoupling magic angle spinning NMR has been used to determine the true symmetry of the low temperature structure of ZrP_2O_7 for the first time.

ZrP_2O_7 is often considered to be the parent of the AM_2O_7 family of compounds (A = Sn, Ti, Zr *etc.*; M = P, V, As), which are of interest as several members of the family show low or even negative coefficients of thermal expansion.[1–3] A detailed knowledge of the structure of these materials is of vital importance in understanding this unusual property. The approximate structure of ZrP_2O_7 was reported as being cubic with an ~8.25 Å cell edge as long ago as 1935 by Levi and Peyronel.[4] It can be described as a network of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra, the PO_4 tetrahedra themselves sharing corners to form $P_2O_7^{4-}$ pyrophosphate groups (Fig. 1). It has long been realised, however, that there are problems associated with this simple structure in that the space group symmetry requires linear P–O–P bonds, whereas the energetically preferred bond angle for these linkages is in the region 130–160°. The bending of these linear bonds (and the concomitant lowering of symmetry) is believed to be the driving force behind the phase transition to a low temperature 3 × 3 × 3 superstructure which has been observed for ZrP_2O_7 (and other members of the AM_2O_7 family) by a variety of experimental techniques.[5–9]

The exact nature of these low temperature superstructures is a matter of some debate. Good quality single crystals of these materials can be hard to obtain, and the structural complexity makes detailed interpretation of powder diffraction data difficult. Symmetry considerations show that a 3 × 3 × 3 material can adopt one of 12 possible space groups, containing between 11 ($Pa\bar{3}$) and 216 ($P1$) different unique P sites.[3] Several members of this family have been shown to adopt space group $Pa\bar{3}$; others are known to have lower symmetry.[10,11] In the case of ZrP_2O_7 there has been one previous NMR study, which interpreted the 12 resonances observed in terms of the 11 ^{31}P sites expected for space group $Pa\bar{3}$ and a peak due to an unspecified impurity phase.[3] However, the observation of the same impurity peak by several groups has cast some doubt on this interpretation.[12] Electron diffraction studies[13] have shown extinction conditions consistent with the presence of an a-glide, suggesting that the space group is either cubic $Pa\bar{3}$ or orthorhombic $Pbca$. In the former possibility the 11 crystallographically independent P sites give rise to 6 independent $P_2O_7^{4-}$ groups, 4 in general positions, 1 on a 3-fold axis and 1 on an inversion centre (such that the P atoms of the P–O–P linkage are crystallographically equivalent and the bond angle is required to be 180°). For $Pbca$ one would expect 27 P sites giving rise to 13 $P_2O_7^{4-}$ groups in general positions and one on a centre of inversion. In the case of SiP_2O_7[14] and TiP_2O_7,[15] two-dimensional (2-D) homonuclear correlation NMR techniques have been shown to be very useful in assigning the space group of these 3 × 3 × 3 superstructures, since they allow the phosphorus connectivity scheme to be probed[16] and give evidence of the presence of different phases in a sample.[17] In this work, we have used various 2-D ^{31}P dipolar recoupling MAS NMR experiments to characterize the ZrP_2O_7 structure.

^{31}P NMR experiments on ZrP_2O_7† were carried out on a Bruker DSX 300 spectrometer operating at a Larmor frequency of 121.48 MHz, using a standard 4 mm Bruker MAS probe. One dimensional (1-D) single-pulse MAS NMR spectra were recorded at spinning speeds of 3, 5, and 10 kHz using a small pulse angle ($\pi/8$) and recycle delay of 80 s to prevent saturation. ^{31}P 2-D MAS exchange NMR experiments were obtained at 10 kHz spinning rate using the RFDR sequence[18] during the mixing time. ^{31}P 2-D MAS double quantum spectra were recorded at a 10 kHz spinning rate using the POSTC7 sequence[19] for excitation and reconversion of double quantum coherences under MAS. The hypercomplex acquisition method[20] was used to obtain pure absorption phase 2-D spectra and the t_1 time increment was synchronised with the rotor period to avoid sidebands in the ω_1 dimension. 160 t_1 increments with 8 and 16 transients per increment were recorded for the MAS exchange NMR spectra and for the MAS double quantum experiment, respectively. The ^{31}P chemical shifts were referenced relative to a 85% H_3PO_4 solution at 0 ppm.

The ^{31}P 1-D MAS NMR spectra of ZrP_2O_7 obtained at different spinning rates are shown in Fig. 2 (centreband region only). These spectra can be seen to contain at least 13 partially overlapping ^{31}P isotropic resonances, corresponding to at least 13 different phosphorus sites. Assuming that these resonances belong to the same phase this is not consistent with space group $Pa\bar{3}$. It can be noted that the positions and linewidths of these resonances vary to different extents with the spinning fre-

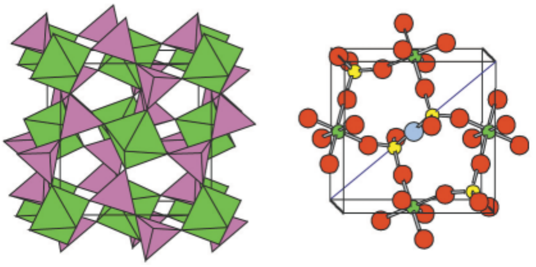

Fig. 1 The ideal cubic structure of ZrP_2O_7 containing ZrO_6 octahedra and PO_4 tetrahedra. A linear P_2O_7 group is emphasised on the right.

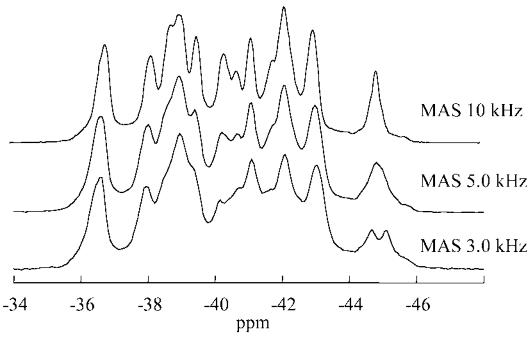

Fig. 2 ^{31}P 1-D MAS NMR spectra of ZrP_2O_7.

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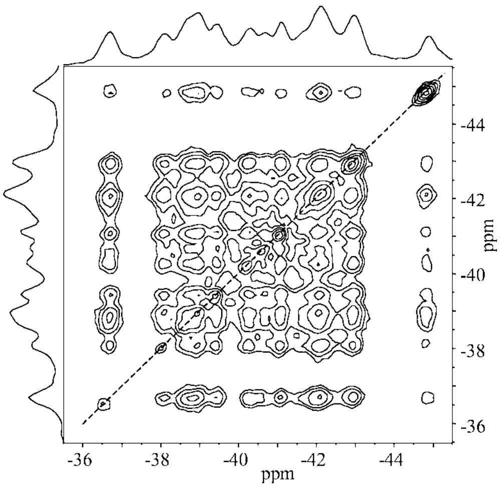

Fig. 3 ^{31}P 2-D exchange MAS spectrum of ZrP_2O_7 obtained with a mixing time of 40 ms at 10 kHz spinning rate, showing that all peaks belong to the same phase.

quency. These effects have also been reported for SiP_2O_7 and TiP_2O_7[15] and may be attributed to the presence of residual dipolar interactions under MAS conditions.

To investigate the possible presence of different phases in our ZrP_2O_7 sample, we have used 2D exchange MAS NMR spectroscopy. In this experiment, the polarisation transfer in the mixing time is driven by the dipolar interaction, allowing one to probe large intra-$P_2O_7^{4-}$ ^{31}P–^{31}P dipolar couplings at short mixing times and weaker long range dipolar couplings at long mixing times. As shown in Fig. 3, the 2-D exchange MAS spectrum of ZrP_2O_7 obtained with a mixing time of 40 ms shows cross-correlation peaks of various intensities between all the individual resonances displayed in the 1-D MAS spectrum reflecting their short and long range spatial proximities. This clearly indicates that our sample contains a single phase with at least 13 different crystallographic sites, ruling out the possibility of the $Pa\bar{3}$ space group to which the ZrP_2O_7 superstructure has previously been assigned.

As well as the number of individual ^{31}P sites, the number of $P_2O_7^{4-}$ groups in the ZrP_2O_7 structure can be used for space group assignement. To characterize the number of $P_2O_7^{4-}$ groups in the $3 \times 3 \times 3$ superstructure, we have used the 2-D MAS double quantum experiment. As shown for other crystalline phosphates,[14,15] short double quantum excitation and reconversion periods of 600 μs allow us to differentiate dipolar coupling between chemically linked PO_4 tetrahedra (~ 750 Hz) and weaker long range dipolar interactions (~ 300 Hz) and thus to identify clearly the P–O–P connectivity scheme. As shown in Fig. 4, the 2-D MAS double quantum spectrum of ZrP_2O_7 exhibits one intense auto-correlation peak along the diagonal (L) and 11 pairs of intense resolved cross-correlation peaks (A–K) that reflect the dipolar connectivities between chemically bound PO_4 tetrahedra. The weaker correlation peaks (two lowest contour levels in Fig. 4) correspond to weaker longer range dipolar couplings in the structure. The diagonal auto-correlation peak (L) arises from a single $P_2O_7^{4-}$ group containing two crystallographically equivalent P sites; the remaining 11 paired cross-correlation correspond to $P_2O_7^{4-}$ dimers in which the two P sites are inequivalent. Analysis of the peak intensities in Fig. 4 shows that the paired cross-peaks A are about three times higher than the remaining resonances, suggesting the presence of three overlapping cross-correlation peaks corresponding to three $P_2O_7^{4-}$ groups. Good fits (not shown) of the 2-D double quantum and 1-D MAS spectra were thus obtained with 27 distinct ^{31}P resonances of equal intensity corresponding to 13 $P_2O_7^{4-}$ units (A–K) with two inequivalent P sites, and one $P_2O_7^{4-}$ group (L) with two equivalent P sites. This is entirely consistent with space group *Pbca*.

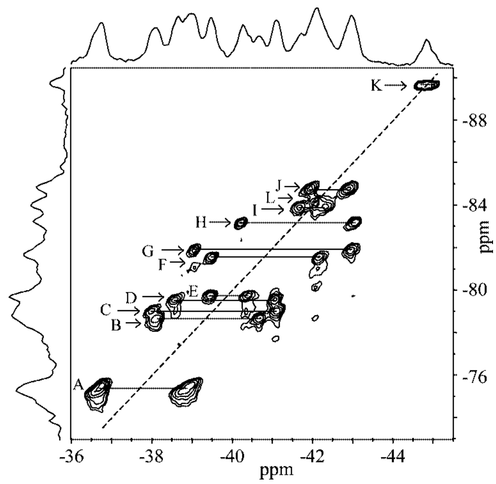

Fig. 4 ^{31}P 2-D MAS double quantum spectrum of ZrP_2O_7 at 10 kHz spinning rate. Cross-correlation peaks are labelled A–K; L is the single auto-correlation peak.

We therefore conclude that the previously assigned space group of $Pa\bar{3}$ for the ZrP_2O_7 superstructure is incorrect. From the analysis of ^{31}P double quantum MAS NMR spectra, we suggest that the true symmetry of ZrP_2O_7 is *Pbca*. Using this space group excellent agreement with powder X-ray and neutron diffraction data can be obtained.

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Notes and references

† High purity ZrP_2O_7 was prepared from $ZrOCl_2$ and H_3PO_4 (85%) which were mixed in a 1:2 molar ratio in a platinum crucible and heating to 350 °C for 1 h. The resultant powder was washed with distilled water, and heated to 750 °C then 1000 °C for 12 h periods. Powder X-ray and neutron diffraction measurements confirmed sample purity and the presence of $3 \times 3 \times 3$ superstructure reflections.

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