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A coupled electron diffraction and rigid unit mode (RUM) study of the crystal chemistry of some zeotypic $AlPO_4$ compounds

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Abstract

Electron diffraction and lattice dynamical calculations are used to investigate the unit cells, space group symmetries and inherent displacive flexibility of the room-temperature average structures of $AlPO_4$-8, $AlPO_4$-16 and $AlPO_4$-tridymite. The zero-frequency rigid unit modes (RUMs) of the idealized high-symmetry polymorphs thereof are also investigated along with their relationship to the lower-temperature polymorphism of these zeotypic aluminophosphates. The clear presence of $\mathbf{G}\pm\frac{1}{2}\mathbf{c}^*$ satellite reflections in addition to the Bragg reflections (**G**) of the underlying $Cmc2_1$ parent structure in the case of $AlPO_4$-8 shows that the true unit cell of the room-temperature polymorph has a doubled *c*-axis due to a condensed RUM mode. Structured diffuse scattering is also observed which can be related to the thermal excitation of RUM modes. In the case of $AlPO_4$-tridymite, a complex $F1$ triclinic polymorph is observed and related to soft RUM modes while, in the case of $AlPO_4$-16, a soft $\mathbf{q}=\mathbf{0}$ RUM mode is shown to be responsible for an observed phase transition in the case of the all SiO_2 analogue of $AlPO_4$-16. A large number of additional zero-frequency RUM modes also exist in the case of $AlPO_4$-16.

Keywords: Microporous aluminophosphates; Characteristic diffuse distributions; Dynamical disorder; Correlated tetrahedral rotations

1. Introduction

The large family of zeotypic, tetrahedrally corner-connected, aluminophosphate framework structures have been intensively investigated ever since they were first discovered [1] as a result of their potential for use in catalysis, ion exchange and as molecular sieve materials [2–5]. Despite the rigidity of their tetrahedral building blocks as well as the fixed nature of their topological connectedness, many such aluminophosphates retain considerable inherent dynamic displacive flexibility [6,7]. This inherent flexibility arises from the often surprisingly large number of ways in which it is possible to change the relative orientation and positioning of neighbouring tetrahedral units without distorting the essentially rigid tetrahedral units themselves [8,9]. It manifests itself in sharp (in at least one local reciprocal space direction), highly structured, continuous diffuse intensity distributions which map out the 'zero-frequency' rigid unit mode (RUM) modes [8–12] characteristic of the particular framework structure. Structured diffuse intensity distributions of this type are most easily visible in electron diffraction patterns (EDPs) and have recently been shown to be characteristic of the room-temperature structures of both $AlPO_4$-5 [6] as well as $AlPO_4$-11 [7].

Conventional average structure refinements of such dynamically disordered framework structures almost invariably lead to chemically unsound crystal structures (with too short metal (*T*)–O distances within constituent tetrahedra, chemically unreasonable linear *T*–O–*T* angles along with large and/or strongly anisotropic thermal parameters [6,7,13,14]) as a result of the fact that the large amplitude excitation of RUM modes is typically ignored in such refinements. When this is the

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case, it is reflected in calculated bond valence sums, or apparent valences [15], which usually differ strongly from expected ideal valences when the reported average structure fractional co-ordinates are used [6,7]. Such a situation, e.g., occurs in the case of the reported *F*23 average structure refinement of $AlPO_4$-16 [16] where chemically unsound linear Al–O–P angles exist as well as metal–O distances within AlO_4 and PO_4 tetrahedra that are far too short and lead to heavily over-bonded Al, P and O ions (see Table 1). Clearly, this reported average structure does not give a good idea of the instantaneous local structure of $AlPO_4$-16.

One way to avoid such crystal chemically unreasonable resultant crystal structures is to undertake distance least squares (DLS) refinements (see e.g. Ref. [17] where a constrained DLS refinement of the structure of $AlPO_4$-8 has been reported) whereby the Al–O and P–O bond lengths are constrained to be reasonable. For such a refinement to reflect reality, however, it is essential that the appropriate average structure unit cell and space group symmetry is chosen. Otherwise, such a refinement is tantamount to making the assumption that only a very particular RUM mode of distortion (e.g., a $\mathbf{q} = \mathbf{0}$ RUM mode) has frozen in.

Such a situation may well have happened in the case of $AlPO_4$-8 where the DLS determined room-temperature structure of Dessau et al. [17], as well as the subsequent refinement of Poojary and Clearfield [18], used an average structure unit cell and space group symmetry corresponding to the maximum topological symmetry of the $AlPO_4$-8 framework structure. A later neutron powder diffraction study [19] reported the existence of additional superlattice reflections not consistent with this unit cell and space group symmetry at room temperature and below which disappeared on heating to ~200 °C. Neither a supercell nor a space group symmetry for this room-temperature structure, however, were given. These authors [19] also reported the existence of a '…non-crystalline (background) component…' suggestive of the presence of a significant diffuse intensity component co-existing with the strong Bragg reflections of the underlying average structure [7]. Clearly, the room-temperature unit cell and space group symmetry of $AlPO_4$-8 need to be re-examined by a technique more sensitive to weak features of reciprocal space such as electron diffraction [6,7].

Table 1
Bond valence sums or apparent valences (AVs) calculated from the *F*23 average structure refinement of $AlPO_4$-16 reported in Ref. [16]

Structure	*F*23 [16]	Ideal
Bond valence parameter *R*	Al–O = 1.651 Å	Al–O = 1.7574 Å
	P–O = 1.604 Å	P–O = 1.5214 Å
	O–O = 1.480 Å	O–O = 2.4844 or 2.8698 Å
At Al(1)	2.917	3.000
At Al(2)	***3.342***	
At P(1)	***6.461***	5.000
At P(2)	***6.738***	
At O(1)	2.270	2.000
At O(2)	***2.543***	
At O(3)	***2.544***	

($V = \exp((R - d)/0.37$ Å, calculated using the bond valence parameters listed in Ref. [15]). Sites where the calculated AV deviates markedly from the expected ideal AV are highlighted in bold and italicized.

Given the existence of numerous potential RUM modes at higher temperatures, it should not be surprising that, on lowering of temperature, many of these dynamically disordered framework structures undergo polymorphic phase transitions involving condensation of one or more RUM modes of distortion. Polymorphic phase transitions of this sort occur, e.g., in the case of the tridymite forms of SiO_2 (see e.g. Refs. [20,21]) and $AlPO_4$ [22–24] as well as in the all silicon analogue of $AlPO_4$-5, SSZ-24 [25], etc. Given the sensitivity of electron diffraction to weak features of reciprocal space difficult to pick up by means of powder diffraction coupled with the absence of such a study in the case of $AlPO_4$-tridymite, it was decided to attempt to fill this gap. The purpose of the current paper then is to present the results of a combined room-temperature electron diffraction and RUM study of the crystal chemistry of the $AlPO_4$ compounds, $AlPO_4$-8, $AlPO_4$-16 and $AlPO_4$-tridymite.

2. Experimental

2.1. Synthesis

2.1.1. Preparation of $AlPO_4$-8, $AlPO_4$-16 and $AlPO_4$-tridymite

The three aluminium phosphates ($AlPO_4$-8, $AlPO_4$-16 and $AlPO_4$-tridymite) were synthesized using a three-step reaction procedure. The first step involved the formation of a gel, the second a hydrothermal treatment of the gel and the third the recovery of the product.

$AlPO_4$-8 powders were obtained from pre-synthesized $AlPO_4$-54, in turn prepared via the following hydrothermal reaction. A reaction mixture was obtained by slowly dropping the appropriate amount of orthophosphoric acid (H_3PO_4, 85 wt%, Univar) into distilled H_2O. A stoichiometric amount of *böhmite* alumina (HIQ-30, Alcoa, 75 wt% Al_2O_3) was then added. This resultant solution was then manually stirred until homogeneous and aged for 2 h with periodic stirring at 20 min intervals. A mixture of *N*-ethylbutylamine (used as a template *R*: $CH_3(CH_2)_3NHC_2H_5$, Aldrich) and distilled H_2O was then added into the aged solution and vigorously stirred. The mixture was then allowed to age