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# Framework Stability of Nanoporous Inorganic Structures upon Template Extraction and Calcination: A Theoretical Study of Gallophosphate Polymorphs

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***Abstract:*** A systematic computational study of gallophosphates was undertaken. First, lattice energy minimization calculations using a formal-charge shell model potential have been carried out on a series of hypothetical gallium phosphates derived from their metallogallophosphate, aluminophosphate, or aluminosilicate analogues through atomic substitution. The minimized structures show the typical features in terms of bond angles and distances as expected in zeolitic gallophosphates. Second, the crystal structures of several gallophosphates in their calcined forms have been predicted, using for each compound lattice energy minimization and an initial model derived from its as-synthesized templated form. All the modified structures thus have the same $GaPO_4$ composition. The lattice energies of all the simulated gallophosphate structures were compared to that of $GaPO_4$-quartz as a reference structure. Interestingly, among all predicted calcined structures, various zeolitic topologies were found. The study of the energetics of these zeotypic structures showed a linear dependence of lattice energy upon density. Strikingly, a few simulated structures showed unrealistic structural features, such as important framework distortions, often associated with the occurrence of a hexameric unit in the original as-synthesized structures. Also, those gallophosphates with structural faults were found in the upper part of the energy/density plot. To address the validity of our force field calculations in these special cases, first principles calculations were undertaken on ULM-4, chosen as a typical representative structure. Indeed, the qualitative agreement found between our results and those obtained with the nonlocal density functional theory demonstrates the robustness of our force field. Further minimizations also showed that the inclusion of polarizability is crucial for yielding results comparable with those obtained using first principles methods.

## Introduction

Over the past decades, there has been a tremendous extension of the chemical and architectural diversity of open-framework inorganic structures. Following the development of synthetic aluminosilicate zeolites and the discovery of their aluminophosphate analogues, new families of compounds and new architectures have been explored on the basis of metal substitution of the framework atoms.[1] In this context, since the first structures synthesized by Parise,[2] the exploration of gallophosphates, and the introduction of the fluoride method by Kessler[3] have led to the discovery of a whole series of fluorinated three-dimensional structures including the extra-large-pore cloverite structure,[4] the Mu-*n*,[5] and the ULM-*n*[6] series of compounds. Also, the incorporation of gallium in zeolites has recently been reviewed in ref 7. Gallophosphates are of interest as compared to aluminophosphates and aluminosilicates because of the diversity of architectures which have been obtained, including novel and very open ones, with potential catalysis or adsorption properties, for example. This abundance is due to the proclivity of gallium atoms to adopt high coordination environments in comparison to aluminum.

A large number of open-framework materials are synthesized using organic amines. When incorporated in the final structure, the amine molecules act as compensating charges or allow the production of micropores with tailored size and shape. For a number of silicates or AlPOs, the extra-coordinated species in the as-synthesized structures (template, water, hydroxy groups, fluorine atoms, etc.) may be partially or totally removed upon

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careful thermal treatment, leaving behind open-framework materials with potential adsorption or catalytic properties. However, it appears that, in contrast with silicates and AlPOs, the removal of the template from GaPOs is most often a critical step and the production of the related stable microporous materials cannot be easily anticipated. In most cases, authors report that the removal of the template leads to the collapse of the inorganic framework. As far as we are aware, only a few crystal structures of stable calcined GaPOs obtained from their as-synthesized forms have been reported so far, including the cloverite structure,[4] $GaPO_4$-triclinic CHA,[8] $GaPO_4$-21,[9] and a member of the ULM-*n* family, ULM-6.[10]

Unlike the situation with silicates and aluminophosphates, there is a dearth of both experimental and simulation information relating to the thermodynamical stability of GaPOs. While both the synthesis and the characterization of GaPOs have been extensively studied by a number of groups, there is no systematic understanding of how the organic molecules act as structure-directing agents in the formation of the open-framework GaPOs and, more especially, how the structural features of the as-synthesized compound may determine the stability of the related template-free material. Indeed, there has been only one such experimental study exploring the energetics of a series of ULM-*n* ($n = 3, 4, 5$) relative to the dense polymorph $GaPO_4$-quartz using high-temperature calorimetry,[11] which revealed negative heats of formation (relative to standard components such as dense $GaPO_4$, HF, water, and amine) and thus an increased stability as compared to that of the dense phase. Topological relationships between a whole series of as-synthesized ULM-*n*, which have been identified on the basis of, on one hand, their common secondary building units (SBUs) and relationships between the organic agent and the synthesis conditions and, on the other hand, the final as-synthesized structure, have been proposed.[6,12] Nevertheless, there is still a lack of systematic investigation concerning the viability of the formation of GaPOs upon thermal treatment and template extraction.

The main reason systematic studies of GaPOs are nearly nonexistent is certainly the complexity of these systems. In contrast with zeolites that are made exclusively of tetrahedra, the major feature of these compounds is the general trend for the gallium atoms to adopt coordinations higher than those of aluminum, so that Ga atoms may be found in tetrahedral, bipyramidal, or octahedral coordinations. Also, the GaPO family shows a great structural and chemical diversity, due to the occurrence of charged template molecules, extra-framework cations, hydroxy groups, bridging/terminal/encapsulated fluorine atoms, and structural or adsorbed water molecules, some of them participating directly in the coordination sphere of Ga atoms. In addition, GaPOs cover a wide range of structures with a variable P/Ga ratio (ranging from 4/5 to 3) as well as metal-substituted gallophosphates with known, or new, topologies. Such diversity is illustrated for selected GaPOs in Figure 1, where different fragments extracted from various existing solids are represented.

As a consequence, a series of issues is left opened for questions. In view of the scarce number of existing template-free microporous GaPOs, one may wonder whether there are intrinsic reasons preventing Ga atoms from being part of stable microporous edifices. Is the production of the calcined materials discouraged by the low thermodynamic stability of the related template-free materials? Are there criteria allowing the anticipation as to whether an as-synthesized structure may be found to have stable/unstable thermal behavior upon template extraction or calcination treatment? What kind of structure may form? May we identify foreseeable and systematic relationships between the structural features of as-synthesized GaPOs and those of their possible related template-free forms?

Simulation tools have played a crucial role in materials science.[13] Considering the growing range of existing structures, one of the challenges for simulation is to provide a means of predicting the behavior of materials with a view to facilitating the identification of interesting systems. For example, simulation tools have played a key role during the past few years in the study of the structures and energetics of silicates and AlPOs. Formal-charge shell model force fields were derived that can reproduce a whole series of experimentally determined structures of silicates[14] and AlPOs.[15] Interestingly, these studies have permitted an estimation of the relative stabilities of these template-free framework compounds that are consistent with thermodynamic data for both families of compounds[16] and with recent extension to families of iron-,[17] cobalt-,[18] and vanadium-substituted AlPOs.[19]

The present theoretical study is part of our goal to systematically investigate open-framework gallophosphates and their behavior upon template extraction or calcination treatment. We use here lattice energy minimization to anticipate the calcined crystal structures of a whole series of both experimentally known as-synthesized GaPOs and model materials. Our main interest is to predict the energetics and the crystal structures of the inorganic frameworks in the absence of the structure-directing agents or templates, with the aim of identifying criteria for stability. For this purpose, we use our recently developed simulation approach,[20] that is, lattice energy minimization, to anticipate the template-free structures of compounds starting from the knowledge of their as-synthesized crystal structures exclusively. This method has allowed us to successfully predict the calcined crystal structures of three as-synthesized aluminophosphates, $AlPO_4$-14,[20] MIL-34,[21] and UT-6,[22] in excellent agreement with experimental structure determinations. Also, the

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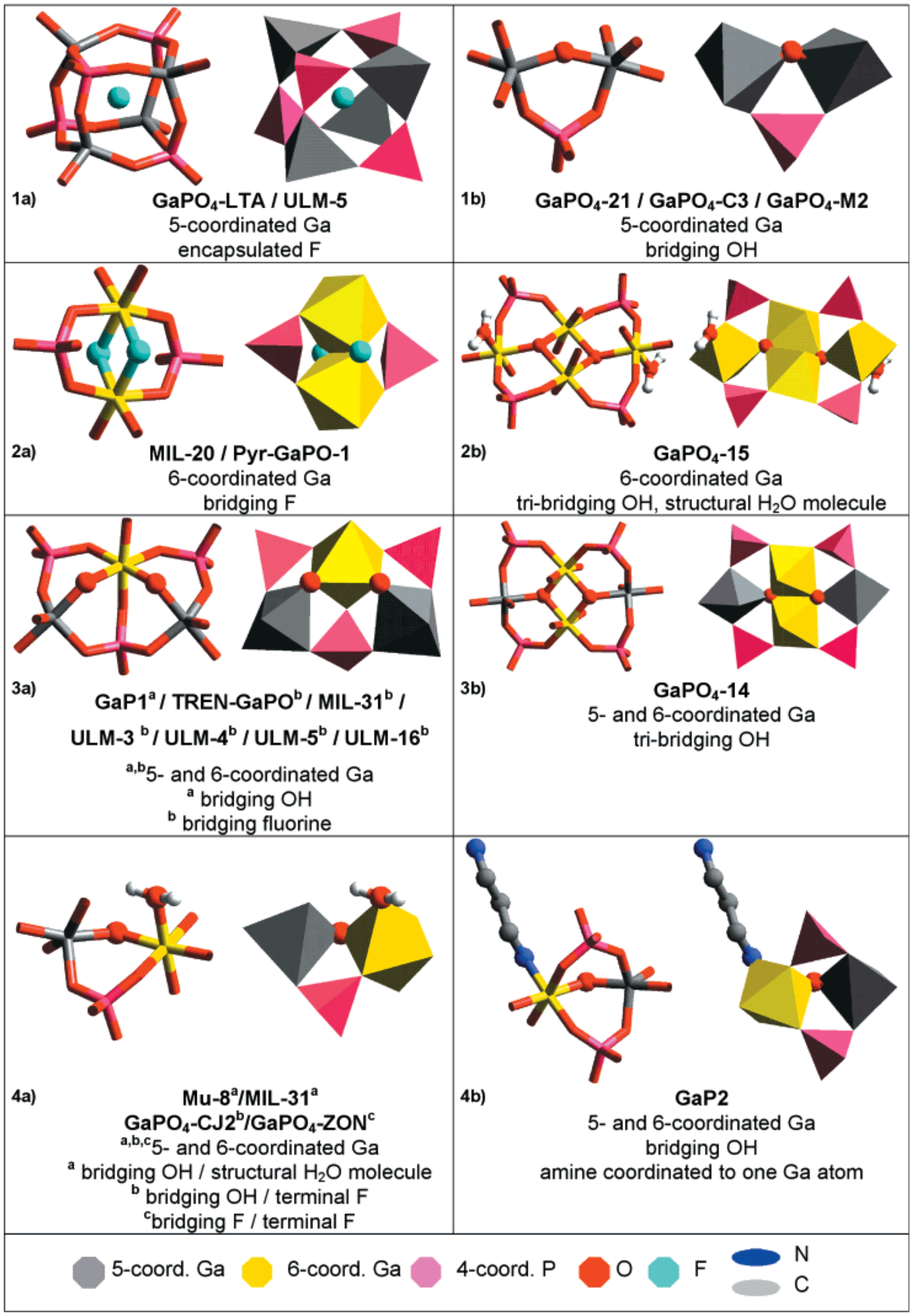

***Figure 1.*** Fragments of inorganic frameworks extracted from various existing gallophosphates, showing the chemical and structural diversity of the gallophosphate system.

validity of this approach in the realm of gallophosphates has recently been demonstrated through the structure solution of the calcined form of the as-synthesized compound $Ga_6P_6O_{24}F_2(C_4N_2H_6)_2$, namely the zeotype structure $GaPO_4$-tricl.CHA, as a result of a template extraction together with a dehydrofluorination process.[22]

With this intention of systematically applying lattice energy minimizations to gallophosphates, we have recently extended the force field initiated by Sanders[14] and Henson et al.[15] for silicates and AlPOs, respectively, to GaPOs.[23] This new force field for gallium atoms in microporous frameworks was built by deriving parameters empirically fitted to the structure and physical properties of $GaPO_4$-quartz, the polymorph of highest density. Its transferability to gallosilicates and zeotype gallophosphates derived from their metallogallophosphate analogues was then also demonstrated.

Equipped with both an appropriate force field and a "calcination" simulation method, we use energy minimizations to explore about 40 microporous GaPOs structures all with the $GaPO_4$ composition. They include hypothetical gallophosphate analogues of many zeolitic aluminophosphate[24] or metallogal-

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lophosphate structures,[25−30] together with models derived from existing as-synthesized possibly fluorinated gallophosphates.[2,8,31−48]

We present the results of our systematic computational study in terms of structures and energetics predictions. In the first section, we discuss the crystal structures of the various simulated $GaPO_4$ models. In the second section, since all minimized structures have identical $GaPO_4$ chemical composition, lattice energies relative to the $GaPO_4$-quartz structure, the highest-density gallophosphate polymorph, are discussed and compared to one another. On the basis of structures and energetics, the viability of gallophosphates upon template extraction and calcination treatment is discussed.

## Computational Section

**Interatomic Potentials.** The force field used here for gallophosphates is based on a formal-charge shell model. The form of the interatomic potential chosen to describe the interaction between two ions, *i* and *j*, is a Buckingham potential combined with a Coulombic term:

$$E_{ij} = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij} r_{ij}^{-6} + q_i q_j / r_{ij} \tag{1}$$

where $q_i$ and $q_j$ refer to the charges of the ions, and $A_{ij}$, $\rho_{ij}$, and $C_{ij}$ are short-range potential parameters. The electrostatic energy is calculated using an Ewald summation[49] with the cutoff radii for the real and reciprocal space chosen to minimize the number of terms to be evaluated. The cutoffs are chosen to give a precision on the order of 12 significant figures in the lattice energy. The short-range energies are evaluated directly in real space with a cutoff of 12 Å. Ionic polarizability of the oxygen atoms is incorporated using the shell model of Dick and Overhauser[50] in which an ion is represented by a core and a shell coupled by a harmonic spring:

$$E_{\text{core-shell}} = {}^{1}/_{2} k_{\text{O}} (r_{\text{core-shell}})^2 \tag{2}$$

where $k_O$ is the core−shell spring constant. The shell model is primarily intended to simulate the dielectric properties of a material, especially those at high frequency, as well as the phonon dispersion.

**Table 1.** Interatomic Potential Parameters

| | *A* (eV) | *ρ* (Å) | *C* (eV Å$^6$) |
|---|---|---|---|
| Ga−$O_{shell}$ | 1950.797 | 0.2870 | 0.000 |
| P−$O_{shell}$ | 877.340 | 0.3594 | 0.000 |
| $O_{shell}$−$O_{shell}$ | 22 764.000 | 0.1490 | 27.879 |
| Ga−P[a] | | | 20.346 |
| core−shell potential | | $k_O = 74.92$ eV Å$^{-2}$ | |

| atomic charges | P | Ga | $O_{core}$ | $O_{shell}$ |
|---|---|---|---|---|
| | +5 | +3 | + 0.86902 | −2.86902 |

[a] Regarding Ga−P interaction, *A* and *ρ* are not given since this potential term, which proved to be necessary when we derived the force field, is purely attractive.

The total energy of the system is therefore given by the following equation:

$$E_{\text{total}} = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij} r_{ij}^{-6} + q_i q_j / r_{ij} + {}^{1}/_{2} k_{\text{O}} (r_{\text{core-shell}})^2 \tag{3}$$

All the potential parameters are presented in Table 1. All calculations have been performed using the program GULP.[51]

**Construction of Hypothetical Gallophosphate Structures Derived from Zeotype Structures.** In a first step, the viability of template-free gallophosphates in terms of structures and energetics has been explored considering the gallophosphates' analogues of existing zeolites. Nineteen zeotype models with the $GaPO_4$ composition were derived from known template-free AlPOs[24] and aluminosilicates[24] or templated metallogallophosphates,[25−30] all having known zeotype architectures, simply by removing the template when needed and doing the appropriate substitutions, that is, $Al^{3+}$ (in AlPOs and AlSiOs) and $Co^{2+}$, $Zn^{2+}$ (in MeGaPOs) by $Ga^{3+}$ atoms, and Si by P atoms.

**Derivation of Template-Free $GaPO_4$ Models from As-Synthesized GaPOs.** In addition to the hypothetical frameworks presented in the previous paragraph, we include in this study models derived from experimental templated GaPOs (nine structures) together with templated oxyfluorinated GaPOs (11 structures). Their chemical characteristics in terms of gallium atom coordination and the presence of extra species, such as hydroxy groups, water molecules, or fluorine atoms, are shown in Tables 2 and 3, respectively. To generate template-free structures, we made the assumption that all as-synthesized GaPOs would undergo the same modifications that are known to occur upon calcination of as-synthesized AlPOs, that is, that structural or adsorbed water molecules, hydroxy groups, and template molecules are evacuated upon heating. Fluorine atoms are also assumed to be removed from the framework along with the other species, whether bridging, terminal, or encapsulated in the as-synthesized compound. Furthermore, the latter hypotheses were in accord with the recent study of the temperature behavior of the oxyfluorinated $GaPO_4$-tricl.CHA, where the loss of fluorine atoms, together with that of the above-mentioned species, was clearly experimentally evidenced.[8]

The modifications of all the as-synthesized structures resulted in neutral model frameworks with $GaPO_4$ compositions, where all Ga and P atoms have tetrahedral coordination. However, all the modified frameworks show very distorted environments around Ga metal atoms emanating from the removal of oxygen or fluorine atoms from their coordination spheres. A typical example of such distortions is shown in Figure 2 where the removal of F atoms from the as-synthesized

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***Table 2.*** Chemical and Structural Features of Various Existing Templated Gallophosphates

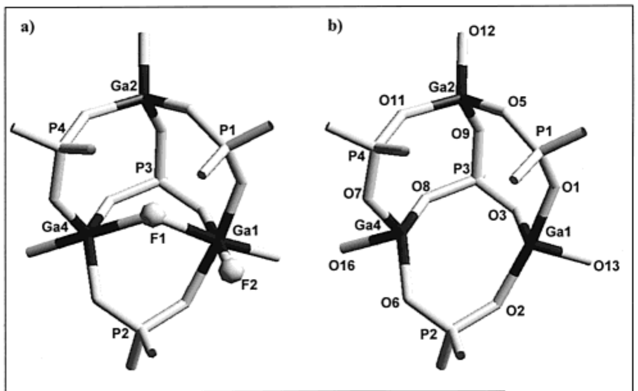
| formula | name | Ga coordination | hydroxy groups[a] | water molecules[a] | reference |
|---|---|---|---|---|---|
| $Ga_3(PO_4)_3(OH)\text{-}C_3H_{10}N$ | $GaPO_4$-21 | 4-5 | B | | 8 |
| $Ga_4(PO_4)_4(OH)\text{-}C_3H_{10}N\text{-}1.09H_2O$ | $GaPO_4$-14 | 4-5-6 | B | A | 31 |
| $Ga_3(PO_4)_3(H_2O)\text{-}NH_2(CH_2)_3NH_2$ | GaP2[c] | 4-5-6 | | S | 32 |
| $Ga_3(PO_4)_3(OH)\text{-}CH_3NH_3$ | $GaPO_4$-M2 | 4-5 | B | | 33 |
| $Ga_3(PO_4)_3(OH)_2\text{-}NH_3(CH_2)_3NH_3\text{-}H_2O$ | GaP1[b] | 5-6 | B | A | 32 |
| $Ga_2(PO_4)_2(OH)(H_2O)\text{-}NH_4\text{-}H_2O$ | $GaPO_4$-15 | 6 | B | S and A | 34 |
| $Ga_9(PO_4)_9(OH)\text{-}N(C_2H_5)_3H$ | $GaPO_4$-C3 | 4-5 | B | | 35 |
| $Ga_{12}(PO_4)_{12}(OH)_4\text{-}(C_6H_{18}N_2)_2\text{-}4H_2O$ | Mu-8 | 4-5-6 | B | S | 36 |

[a] B is the bridging group, S is the structural group, and A is the adsorbed species. [b] Structure containing the hexameric building unit. [c] In this structure, the amine molecule is unusually coordinated to a gallium atom.

***Table 3.*** Chemical and Structural Features of Various Existing Templated Fluorinated Gallophosphates

| formula | name | Ga coordination | F[a] atoms | OH[a] groups | $H_2O$[a] molecules | reference |
|---|---|---|---|---|---|---|
| $GaPO_4(OH)_{0.5}F_{0.5}(NH_4^+)_{0.93}(H_3O^+)_{0.07}$ | $GaPO_4$-CJ2 | 5-6 | T | B | | 37 |
| $Ga_4(PO_4)_4F_2\text{-}N_2C_6H_{14}$ | $GaPO_4$-ZON | 4-5-6 | B and T | | | 38 |
| $Ga_3(PO_4)_3F\text{-}0.5N_2C_6H_{18}$ | MIL-20 | 4-6 | B | | | 39 |
| $Ga_4(PO_4)_4F_2(H_2O)\text{-}N_2C_3H_{12}$ | ULM-6 | 4-6 | B | | | 40 |
| $Ga_6(PO_4)_6F_2\text{-}2NC_5H_6\text{-}H_2O$ | Pyr-GaPO-1 | 4-6 | B | | A | 41 |
| $Ga_4(PO_4)_4F\text{-}NC_6H_{16}\text{-}2H_2O$ | $GaPO_4$-LTA | 5 | E | | A | 42 |
| $Ga_3(PO_4)_3F_2\text{-}N_2C_3H_{12}\text{-}H_2O$ | ULM-3[b] | 5-6 | B | | | 43 |
| $Ga_3(PO_4)_3F_2\text{-}0.75N_2C_3H_{12}\text{-}0.5H_3O$ | ULM-4[b] | 5-6 | B | | | 44 |
| $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7\text{-}4N_2C_6H_{18}\text{-}6H_2O$ | ULM-5[b] | 4-5-6 | B and E | B | A | 45 |
| $Ga_4(PO_4)_4F_2\text{-}1.5NC_6H_{14}\text{-}0.5H_2O\text{-}0.5H_3O$ | ULM-16[b] | 4-5-6 | B | | A | 46 |
| $Ga_6(PO_4)_6F_4\text{-}N_4C_6H_{22}\text{-}NC_5H_5$ | TREN-GaPO[b] | 5-6 | B | | | 47 |
| $Ga_9(PO_4)_9(OH)_2F_3(H_2O)\text{-}2N_2C_{10}H_{26}\text{-}2H_2O$ | MIL-31[b] | 4-5-6 | B | B | A and S | 48 |

[a] B is the bridging group, S is the structural group, A is the adsorbed species, E is encapsulated, and T is terminal. [b] Structures containing the hexameric building unit (see Figures 1−3a)



| | |
|---|---|
| O6- Ga4- O8 = 128.3° | d(Ga1 O3) = 1.877 Å |
| O6- Ga4- O16 = 88.6° | d(Ga1 O2) = 1.994 Å |
| O3- Ga1- O13 = 85.0° | d(Ga2 O11) = 1.795 Å |
| O1- Ga1- O2 = 171.2° | d(Ga2 O5) = 1.843 Å |
| O9- Ga2- O5 = 109.3° | d(Ga4 O8) = 1.859 Å |
| O9- Ga2- O11 = 113.7° | d(Ga4 O16) = 1.975 Å |

***Figure 2.*** **(a)** Framework fragment extracted from the as-synthesized GaPO-ZON structure showing the various Ga atom environments due to bridging F atoms. **(b)** After removal of F atoms, in the initial model $GaPO_4$, all Ga atoms are in distorted tetrahedral environments, as shown by the list of bond lengths and angles.

GaPO-ZON structure generates neutral distorted tetrahedral configurations around Ga atoms.

It is important to note here that, though its calcined form is experimentally known, the cloverite structure was not included in the present study; the as-synthesized framework, $Ga_{96}P_{96}O_{372}(OH)_{24}(QF)_{24}(H_2O)_n$ (Q = quinuclidine), is interrupted with terminal oxygens[4] and cannot be submitted to the modifications described above as required to build a neutral model with the $GaPO_4$ composition. Furthermore, no neutral model could be derived from as-synthesized gallophosphates with a Ga/P ratio different from 1. Therefore all such gallophosphates were omitted from our study.

**Minimizations.** The ~40 model $GaPO_4$ structures were then submitted to constant pressure energy minimization (i.e., allowing both cell parameters and fractional coordinates to relax) in the space groups of the original compounds they are derived from, using the interatomic potentials given in Table 1. The phonon spectra at the Γ point of all the minimized structures were also calculated to check that the space groups used in the calculations are valid, as witnessed by the absence of imaginary modes.

The lattice energies yielded by minimization are dependent on the force field used, so the results given by these calculations are only meaningful when considered as relative to a reference structure. For this reason, $GaPO_4$-quartz was included in this study as the reference structure, being the simplest and highest-density experimental gallophosphate.[52]

**First Principles Calculations.** To validate some of the observations made in the results of the force field calculations, a small number of calculations have been carried out using nonlocal density functional theory, using the functional of Perdew−Burke−Ernzerhof (PBE),[53] within periodic boundary conditions. All quantum mechanical calculations have been performed using the program SIESTA,[54−56] which is specifically designed to make the study of complex materials with larger unit cells feasible. Optimizations were performed using the conjugate gradients algorithm based on analytical derivatives with respect to both internal degrees of freedom and stress.

In brief, the approach taken utilizes norm-conserving pseudopotentials of the Troullier−Martins[57] form in conjunction with numerical tabulations of the pseudoatomic orbitals as a basis set.[58] In the present study, a double-ζ basis set was used, with a radial confinement of the

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***Table 4.*** Selected Structural Features (Italic Characters, M = Ga) for the Minimized Gallophosphates Derived from Zeotypic Aluminophosphate or Aluminosilicate Analogues[a]

| zeotype | composition | space group | energy (kJ mol$^{-1}$/T) | volume (Å$^3$) | M–O bond (Å) | reference |
|---|---|---|---|---|---|---|
| AEI | $AlPO_4$ | $C2/c$ | | 3241.73 | 1.7277 | 24 |
| | $\mathit{GaPO}_4$ | $C2/c$ | *−12 913.39* | *3297.09* | *1.7512* | *simulated* |
| ATO | $AlPO_4$ | $R\bar{3}$ | | 1879.38 | 1.7330 | 24 |
| | $\mathit{GaPO}_4$ | $R\bar{3}$ | *−12 919.78* | *1888.38* | *1.7579* | *simulated* |
| AFS | $AlPO_4$ | $P\bar{3}c1$ | | 4073.38 | 1.7746 | 24 |
| | $\mathit{GaPO}_4$ | $P\bar{3}c1$ | *−12 912.09* | *4045.39* | *1.7550* | *simulated* |
| AFT | $AlPO_4$ | $P\bar{3}1c$ | | 4834.23 | 1.7242 | 24 |
| | $\mathit{GaPO}_4$ | $P\bar{3}1c$ | *−12 913.67* | *4927.49* | *1.7514* | *simulated* |
| APC | $AlPO_4$ | $Pbca$ | | 1778.88 | 1.7303 | 24 |
| | $\mathit{GaPO}_4$ | $Pbca$ | *−12 915.35* | *1814.28* | *1.7523* | *simulated* |
| APD | $AlPO_4$ | $Pca2_1$ | | 1613.22 | 1.7401 | 24 |
| | $\mathit{GaPO}_4$ | $Pca2_1$ | *−12 916.74* | *1742.24* | *1.7530* | *simulated* |
| DFO | $AlPO_4$ | $P6/mcc$ | | 18 064.96 | 1.7302 | 24 |
| | $\mathit{GaPO}_4$ | $P6/mcc$ | *−12 911.93* | *18 727.35* | *1.7577* | *simulated* |
| AEL | $AlPO_4$ | $Ibm2$ | | 2093.66 | 1.6693 | 24 |
| | $\mathit{GaPO}_4$ | $Ibm2$ | *−12 918.45* | *2167.13* | *1.7514* | *simulated* |
| AFO | $AlPO_4$ | $P112_1$ | | 1048.69 | 1.6983 | 24 |
| | $\mathit{GaPO}_4$ | $P112_1$ | *−12 918.71* | *1056.49* | *1.7544* | *simulated* |
| AFI | $AlPO_4$ | $Pcc2$ | | 2774.82 | 1.7070 | 24 |
| | $\mathit{GaPO}_4$ | $Pcc2$ | *−12 917.77* | *2872.45* | *1.7524* | *simulated* |
| OSI | $AlPO_4$ | $Imm2$ | | 1699.19 | 1.7575 | 24 |
| | $\mathit{GaPO}_4$ | $Imm2$ | *−12 918.85* | *1789.84* | *1.7533* | *simulated* |
| FAU[b] | $Al_xSi_yO_z$ | $Fd\bar{3}$ | | 15 677.56 | 1.7296 | 24 |
| | $\mathit{GaPO}_4$ | $Fd\bar{3}$ | *−12 911.44* | *15 304.56* | *1.7578* | *simulated* |

[a] The experimental values (normal characters, M = Al) found in the initial aluminophosphate or aluminosilicate compound are given when relevant. The calculated space group for a gallophosphate is given when different from that of its experimental aluminophosphate analogue. [b] The FAU compound was derived from its aluminosilicate analogue.

orbitals equivalent to an energy shift of 0.02 Ry.[55] The Hartree and exchange-correlation potentials were evaluated using a real-space mesh with a kinetic energy cutoff of 150 Ry, while the Brillouin zone was sampled only at the Γ point. These represent only moderately precise computational conditions. However, the aim of the calculations in the current context was to determine qualitative structural features, rather than precise absolute values, and thus they are sufficient.

## Results and Discussion

**Crystal Structures of Model Template-Free Gallophosphates. Hypothetical Gallophosphates Derived from Existing Zeotype Analogues.** The purpose of this section is to study the viability of existing and well-characterized zeotype architectures, known as AlPOs, aluminosilicates, or MeGaPOs, when transformed into their GaPO analogues, namely $GaPO_4$. Indeed, all minimizations converged rapidly, leading to zeotype GaPOs with realistic structural features.

The crystal structures derived from their MeGaPOs analogues have typical bond lengths and angles as expected in a gallophosphate. The zeotype topologies of the minimized structures with a $GaPO_4$ composition are thus viable. These model structures are discussed in more detail elsewhere.[23]

Table 4 shows selected structural features for the minimized GaPOs built from their zeolitic AlPO or aluminosilicate analogues and compares them with the experimental data of the original forms.

Hypothetical structures derived from their AlPO analogues are correctly simulated, with the expected average ⟨Ga−O⟩ and ⟨P−O⟩ distances and O−M−O angles (M = Al or P). The elongation of M−O bond lengths upon Al/Ga substitution, owing to the difference between the effective ionic radii of Al (0.53 Å) and Ga (0.61 Å),[59] leads to a systematic increase in the cell volumes of $GaPO_4$ structures in comparison with those of $AlPO_4$.

Regarding the model derived from the aluminosilicate faujasite structure, the minimized $GaPO_4$-FAU shows ideal zeolitic features, with typical Ga−O and P−O bond lengths (1.76 and 1.52 Å respectively), leading to a decrease of the cell volume in comparison with that of its aluminosilicate analogue.

Interestingly, the calculation of the phonon modes at the Γ point shows imaginary frequencies for only four structures (AFI, AEL, AFO, OSI zeotypes), suggesting that the space groups used when minimizing these structures were incorrect. We performed additional calculations in which the symmetry of these structures was initially reduced to $P1$ with the structure being perturbed and reminimized to the point where no more imaginary frequencies were present. Such results indicate that the experimental space groups of the original structures were too high for describing their GaPOs analogues. A similar situation was reported by Henson et al. for some zeolitic AlPOs,[16] namely $AlPO_4$-5 (AFI) and $AlPO_4$-11 (AEL). Also, two structures (AFS, GIS) have a higher symmetry after the minimization in the experimental space group of their original AlPO form.

The above results partially address the viability of zeotypes' architectures in their gallophosphate form. Using starting geometries taken from existing zeotype structures shows that realistic zeolitic GaPOs may be generated without structural frustration.

**As-Synthesized Gallophosphates: Study of Their Related Template-Free Structures.** In this section, we intend to explore the structural viability of as-synthesized GaPOs when simulated in their calcined forms. The initial models were derived from the related experimental crystal data (see Computational Section). In contrast with the previous section where *existing* zeotype topologies were considered with *modified* chemical compositions emanating from in-framework gallium substitutions, we consider here *existing* gallium-containing frameworks and study virtually *modified* structures, especially regarding the Ga coordination.

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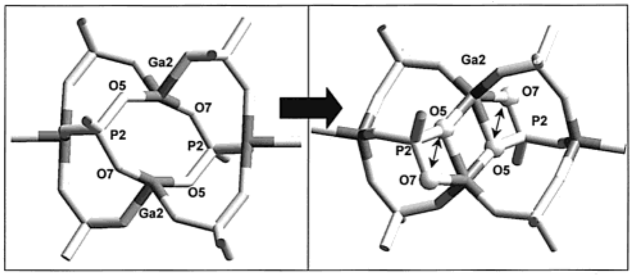

**a)** Initial model of calcined $GaPO_4$-15

**b)** Local distortion in calcined $GaPO_4$-15 after energy minimization

***Figure 3.*** (a) Framework fragment extracted from the initial model $GaPO_4$-15 after the removal of bridging OH groups. All Ga atoms are 4-fold coordinated before minimization. (b) Framework fragment extracted from the minimized $GaPO_4$-15. Oxygen atoms O5 and O7 (in white balls) have come close upon minimization at 2.24 Å from one another. Ga atoms are represented in dark.

As a consequence of preliminary modifications prior to minimization, the resulting $GaPO_4$ model structures show 4-fold Ga atoms with highly distorted environments. For example, the O−Ga−O angles before minimization span a large range from 82° to 178° due to the removal of oxygen or fluorine atoms that were linked to gallium atoms (Figure 2). An important feature of this section is therefore to check the capacity of our force field to deal with framework distortions.

As a result of lattice energy minimization, we can identify two groups of simulated structures. Ten $GaPO_4$ structures show unrealistic features, that is, important framework distortions, even after structure optimization. The 10 other structures show regular architectures after minimization with zeotype topologies. All the structures below were found to be phonon stable except $GaPO_4$-C3 and $GaPO_4$-LTA, for which additional simulations performed in *P*1 showed no imaginary frequencies after symmetry-breaking and further minimization, indicating that the symmetries of their experimental space groups were too high. These two groups of minimized model structures are discussed below.

**Distorted Models of Calcined $GaPO_4$ Frameworks: GaP1,[32] $GaPO_4$-15,[34] $GaPO_4$-C3,[35] Mu-8,[36] ULM-3,[43] ULM-4,[44] ULM-5,[45] ULM-16,[46] TREN-GaPO,[47] MIL-31.[48]** While showing regular structural features around P atoms (⟨P−O⟩ ≈ 1.53 Å and ⟨O−P−O⟩ ≈ 109.4°), all these minimized structures show unrealistic structural features regarding in-framework Ga atoms. The ⟨Ga−O⟩ distances vary between 1.79 and 1.89 Å, while O−Ga−O angles vary from 66° to 174°, both describing unrealistic ranges similar to those observed before minimizations. A striking feature is that oxygen atoms tend to get closer to Ga atoms upon lattice energy minimization. This systematically creates an extra O−Ga bond around the already 4-fold gallium, such that it adopts 5-fold coordination. This is illustrated in the case of $GaPO_4$-15 in Figure 3, where O5 has come close to Ga2 during minimization, creating a 5-fold coordination around Ga2. In this new geometry, each $GaO_5$ bipyramid shares an edge with a $PO_4$ tetrahedron, which generates close O5−O7 interatomic distances (2.24 Å in $GaPO_4$-15) incompatible with the van der Waals radius of framework oxygens in microporous solids (1.40 Å). Similar close O−O distances in the [2.19−2.26 Å] range are observed in the other structures.

In an attempt to explain the unrealistic features of these "calcined" $GaPO_4$ models, the original as-synthesized structures were reexamined carefully. A striking point is the presence in seven as-synthesized structures (GaP1, ULM-3,-4,-5,-16, TREN-GaPO, and MIL-31) out of 10 of the same hexamer consisting of three $PO_4$ tetrahedra, two $GaO_4X$ bipyramids, and one $GaO_4X_2$ octahedron sharing corners, with X being a hydroxy group in GaP1 and a fluorine atom in the fluorinated structures (Figure 4a). While the initial model contains all Ga atoms in 4-fold coordination (Figure 4b), the distortions induced by minimization precisely take place inside the hexamer for each of these structures (Figure 4c). This point will be further examined in this paper using first principles calculations in the case of ULM-4.

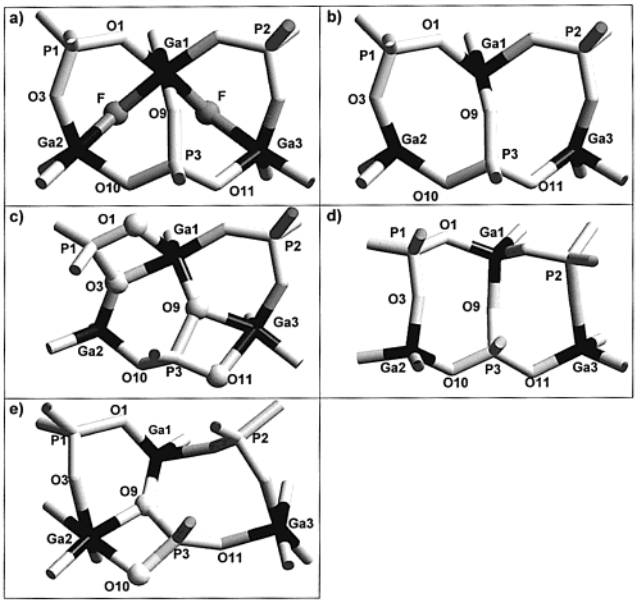

***Figure 4.*** Hexameric unit extracted from ULM-4. (a) As extracted from the as-synthesized structure, with two bridging F atoms (in gray balls). (b) Prior to minimization, but after the removal of bridging F atoms. (c) In the simulated $GaPO_4$-ULM-4 minimized with our force field. (d) In the simulated $GaPO_4$-ULM-4 minimized with Murashov's potential. (e) In the $GaPO_4$-ULM-4 minimized using first principles calculations. Ga atoms are represented in black; O atoms close within van der Waals contacts are represented in white balls.

**Model Calcined Gallophosphates with Regular Zeotype Frameworks: $GaPO_4$-21,[8] $GaPO_4$-14,[31] GaP2,[32] $GaPO_4$-M2,[33] $GaPO_4$-CJ2,[37] $GaPO_4$-ZON,[38] MIL-20,[39] ULM-6,[40] Pyr-GaPO-1,[41] and $GaPO_4$-LTA.[42]** The prediction of the zeotype $GaPO_4$-tricl.CHA from its as-synthesized form ($Ga_6P_6O_{24}F_2(C_4N_2H_6)_2$) is not included here, while being part of this series of compounds. More details are given in ref 22. In this section, we further consider the interesting cases where zeotype calcined $GaPO_4$ structures were simulated starting from the related as-synthesized templated gallophosphates.

Typically, all these structures display a regular environment around the metal atoms (Ga, P) after minimization. Table 5 summarizes selected structural and energetics features of these minimized structures. The O−Ga−O angles now describe a much smaller range [102°−117°], with average O−M−O (M = Ga, P) angles of 109.46°. These values are close to those found in the minimized $GaPO_4$-quartz (⟨O−Ga−O⟩ = 110.66° and ⟨O−P−O⟩ = 109.58°). These results demonstrate that both Ga- and P-centered tetrahedra in these structures have become regular upon lattice energy minimization.

Also, Ga−O bond lengths systematically decrease during minimization. The average Ga−O bond length typically de-

***Table 5.*** Comparison of Experimental (Normal Type) and Calculated (Italic Characters) Average Bond Lengths/Angles for the Predicted Calcined Gallophosphates with Regular Zeolitic Environments[a]

| structure | ⟨Ga–O⟩ (Å) | ⟨O–Ga–O⟩ (°) | standard deviation O–Ga–O (°) | ⟨O–Ga–O⟩ range (°) | space group | energy per T atom (kJ mol$^{-1}$) | volume (Å$^3$) | reference |
|---|---|---|---|---|---|---|---|---|
| $GaPO_4$-quartz | 1.815 | 110.3 | 3.4 | 105.4−113.6 | | | | 52 |
| | *1.769* | *110.7* | *4.6* | *104.2−115.8* | $P3_121$ | *−12 925.56* | *230.83* | *simulated* |
| $GaPO_4$-21 | 1.865 | 107.2 | 20.7 | 84.9−172.4 | | | | 8 |
| | *1.753* | *109.5* | *2.8* | *103.7−113.2* | $P2_1/c$ | *−12 915.77* | *1359.86* | *simulated* |
| $GaPO_4$-14 | 1.855 | 107.9 | 15.5 | 91.2−165.3 | | | | 31 |
| | *1.758* | *109.5* | *2.9* | *104.2−115.4* | $P\bar{1}$ | *−12 913.03* | *946.98* | *simulated* |
| GaP2 | 1.889 | 105.8 | 21.5 | 82.0−175.7 | | | | 32 |
| | *1.756* | *109.5* | *2.8* | *103.2−113.6* | $Pbc2_1$ | *−12 914.54* | *1371.48* | *simulated* |
| $GaPO_4$-M2 | 1.875 | 107.4 | 20.2 | 85.4−175.6 | | | | 33 |
| | *1.756* | *109.5* | *3.0* | *102.4−115.0* | $Pbca$ | *−12 918.55* | *2459.52* | *simulated* |
| GaPO-CJ2 | 1.933 | 104.2 | 26.1 | 83.6−177.8 | | | | 37 |
| | *1.754* | *109.5* | *3.3* | *103.4−116.2* | $P2_12_12_1$ | *−12 915.37* | *888.22* | *simulated* |
| GaPO-ZON | 1.867 | 107.2 | 17.2 | 85.0−171.2 | | | | 38 |
| | *1.756* | *109.5* | *2.5* | *105.0−115.8* | $Pbca$ | *−12 913.94* | *3810.90* | *simulated* |
| MIL-20 | 1.849 | 108.4 | 15.6 | 91.5−165.6 | | | | 39 |
| | *1.757* | *109.5* | *2.1* | *105.7−113.9* | $P2_1/c$ | *−12 913.65* | *1399.18* | *simulated* |
| ULM-6 | 1.805 | 107.4 | 20.9 | 89.3−170.0 | | | | 40 |
| | *1.758* | *109.5* | *2.9* | *104.3−115.4* | $P\bar{1}$ | *−12 913.03* | *946.87* | *simulated* |
| Pyr-GaPO-1 | 1.852 | 108.5 | 16.3 | 91.0−168.0 | | | | 41 |
| | *1.751* | *109.5* | *1.0* | *107.8−110.3* | $R\bar{3}$ | *−12 913.72* | *2464.88* | *simulated* |
| $GaPO_4$-LTA | 1.852 | 108.4 | 9.6 | 92.6−120.5 | | | | 42 |
| | *1.751* | *109.5* | *1.2* | *107.9−111.4* | $Fm\bar{3}c$ | *−12 911.34* | *14 066.00* | *simulated* |
| $GaPO_4$-CHA | 1.850 | 108.5 | 15.9 | 92.0−166.6 | | | | 7 |
| | *1.751* | *109.5* | *1.0* | *107.8−110.3* | $R\bar{3}$ | *−12 913.72* | *2464.88* | 21 |

[a] The calculated cell volumes and lattice energies for the predicted calcined structures with zeolitic architectures are also given.

creases during minimization from 1.873 to 1.755 Å, which is again close to the value found in $GaPO_4$-quartz optimized with our force field (1.769 Å).[23] Indeed, it turns out that our force field encapsulated the following feature that the effective ionic radius[59] of gallium in 5-fold (0.69 Å) or 6-fold coordination (0.76 Å) is higher than that of gallium in a tetrahedral environment (0.61 Å). It is not surprising since our force field was precisely fitted to the structure and properties of $GaPO_4$-quartz.[23] However, this is an interesting result since it provides some evidence for the structural robustness of the force field when applied to initially highly distorted structural models.

While simulated calcined $GaPO_4$-M2, $GaPO_4$-ZON, Pyr-GaPO-1, $GaPO_4$-LTA, $GaPO_4$-14, and ULM-6 adopt known zeotype architectures (AEN, ZON, CHA, LTA, AFN, and AFN, respectively),[24] simulated calcined GaP2, $GaPO_4$-MIL-20, and $GaPO_4$-CJ2 correspond to new zeotypes. The latter are shown in Figure 5 together with the respective atomic coordinates of their T atoms. GaP2 (Figure 5a) contains rings delimited by 10, 6, and 4 tetrahedra. The edge sharing of six- and four-membered rings generates chains parallel to the *b* axis. These chains are connected to each other by oxygen atoms bridging a Ga atom in one chain to the P atom in the next chain, which generates layers parallel to the (001) plane. The layers are superimposed and linked together by oxygen atoms shared by both Ga and P atoms to form a 3-D microporous network.

The model for calcined MIL-20 (Figure 5b) is made up of similar chains to those of GaP2, parallel to the [101] direction. The chains are connected through bridging oxygen atoms to form sheets. The framework is built up from the stacking of these layers through bridging oxygen atoms along the *b* axis. This construction results in the formation of cross-linked channels, delimited by eight-membered rings, running along [100], [001], and [101].

Simulated calcined $GaPO_4$-CJ2 (Figure 5c) can be described as a stack of $4.8^2$ 2-D nets parallel to the (001) plane. Each layer is made up of alternating four- and eight-membered rings with UUUD and UUDDDUUD sequences, respectively, following Smith's description of such structures (U = up and D = down).[60] A layer derives from the one below it by a rotation of 180°. The framework delimits 8-membered ring channels along the *a* and *c* axis.

Also, the simulation of the calcined $GaPO_4$-21 failed to predict the expected structure, $GaPO_4$-25,[8] which adopts the ATV zeotype. Interestingly, the as-synthesized $AlPO_4$-21, which is isotypic of $GaPO_4$-21, is known experimentally to undergo a topotactic transformation into $AlPO_4$-25-ATV[61] upon calcination. Indeed, simulations of the calcined $AlPO_4$-21, using the appropriate force field,[14] also fail to predict the expected zeotype $AlPO_4$-25 and lead to the same framework as the calcined $GaPO_4$-21 predicted above. Both simulations on $AlPO_4$-21 and on $GaPO_4$-21 show that the respective force fields yield equivalent outcomes. Rather than modifying the force fields, these simulations suggest that more sophisticated calculations should be used to correctly capture such topotactic transformations.

**Energetics of the Template-Free Model Gallophosphates.** Our simulations not only yield candidates for the crystal structures of compounds upon metal substitution or calcination, but also predict their relative lattice energies. To this end, the minimized lattice energy for each structure was normalized relative to the number of metal atoms in the structure and compared to the normalized lattice energy of $GaPO_4$-quartz, which is considered as the reference structure.

In a fashion similar to what has been previously shown for silicates[15] and AlPOs,[16] the minimized lattice energies for model calcined GaPOs show a linear trend with density (Figure 6). The less dense structures have lower lattice energies and are to

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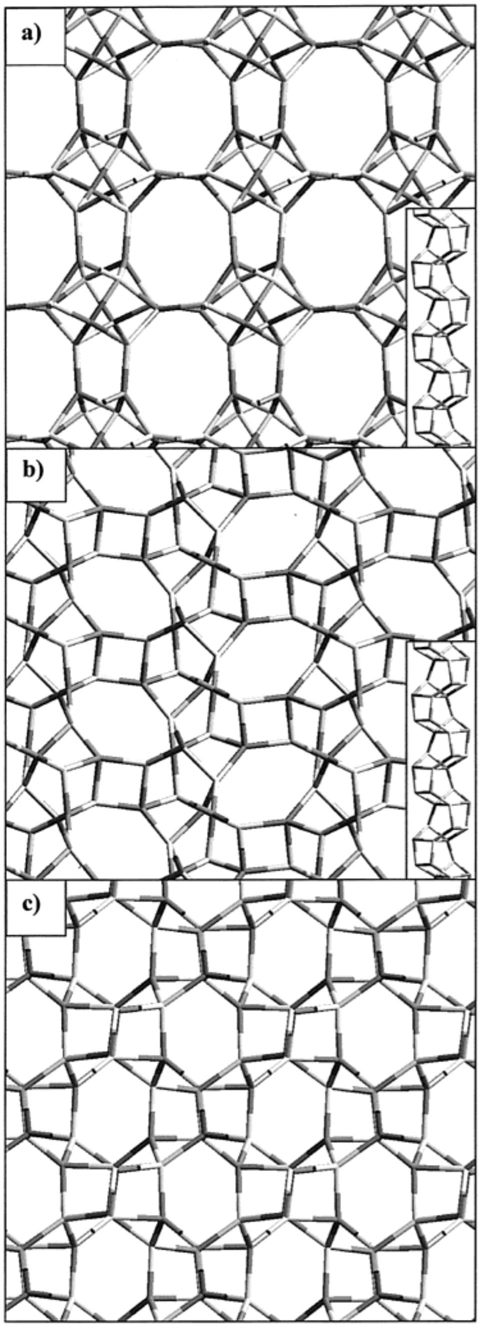

| **a)** | **GaP2** | | |
|---|---|---|---|
| | | $P$bc2$_1$ | |
| | a = 9.379Å | b = 9.065Å | c = 16.130Å |
| | α = 90° | β = 90° | γ = 90° |
| T1 | 0.86304 | 0.84329 | 0.39800 |
| T2 | 0.42437 | 0.81014 | 0.44750 |
| T3 | 0.64528 | 0.54147 | 0.21617 |
| T4 | 0.83208 | 0.49464 | 0.37642 |
| T5 | 0.66702 | 0.99762 | 0.52692 |
| T6 | 0.60667 | 0.85229 | 0.28334 |

| **b)** | **MIL-20** | | |
|---|---|---|---|
| | | $P$2$_1$/c | |
| | a = 9.019Å | b = 18.914Å | c = 9.428Å |
| | α = 90° | β = 119.54° | γ = 90° |
| T1 | 0.41928 | 0.21355 | 0.78896 |
| T2 | 0.83657 | 0.07367 | 0.29914 |
| T3 | 0.92685 | 0.18124 | 0.75815 |
| T4 | 0.15416 | 0.08939 | 0.65578 |
| T5 | 0.68883 | 0.19624 | 0.39415 |
| T6 | 0.81253 | 0.16992 | 0.02366 |

| **c)** | **GaPO$_4$-CJ2** | | |
|---|---|---|---|
| | | $P$2$_1$2$_1$2$_1$ | |
| | a = 9.229Å | b = 10.233Å | c = 9.406Å |
| | α = 90° | β = 90° | γ = 90° |
| T1 | 0.44512 | 0.23996 | 0.34338 |
| T2 | 0.90590 | 0.97646 | 0.33074 |
| T3 | 0.59765 | 0.27008 | 0.63612 |
| T4 | 0.61515 | 0.03485 | 0.16408 |

***Figure 5.*** Predicted calcined $GaPO_4$ compounds with new zeotype structures obtained from the related templated GaPOs. The predicted cell parameters and atomic coordinates of T atoms are given for completeness: (a) View of the predicted calcined GaP2 structure along the [010] direction, shown with chains extracted from the structure. (b) Projection of the predicted calcined MIL-20 structure along the [100] direction, shown with chains extracted from the structure. (c) View of the predicted calcined $GaPO_4$-CJ2 structure along the [100] direction.

be considered as metastable phases when compared to the $GaPO_4$-quartz dense polymorph.

Concerning the 19 $GaPO_4$ gallophosphates derived from their zeolitic analogues (AlPOs, aluminosilicate, MeGaPOs), the range of energies observed between UCSB-10, the least dense structure, and $GaPO_4$-quartz (14.4 kJ mol$^{-1}$ per T site) is larger than that for the aluminum analogues (11.7 kJ mol$^{-1}$ per T site relative to $AlPO_4$-berlinite). However, none of these structures have been synthesized directly in its template-free $GaPO_4$ form until now, which prevents us from drawing conclusions concerning their stability. Nevertheless, the template-free zeotype $GaPO_4$-CHA (which is obtained from the calcination of the as-synthesized form[22]) is known to exist in a stable form, yielding experimental evidence for the viability of a $GaPO_4$ compound with a zeotype architecture. This example provides a minimal range of lattice energies (as calculated with our force field) within which $GaPO_4$ zeotypes simulated here should be considered as thermodynamically viable. There is no thermodynamic reason these $GaPO_4$ zeotype structures should not be regarded as potentially accessible, for example, through direct synthesis or upon posttreatments of their as-synthesized forms. Most probably, the synthesis of these $GaPO_4$ zeolites in hydrothermal conditions may be hindered by the specific kinetics and reactivities of gallium-based precursors in solution.

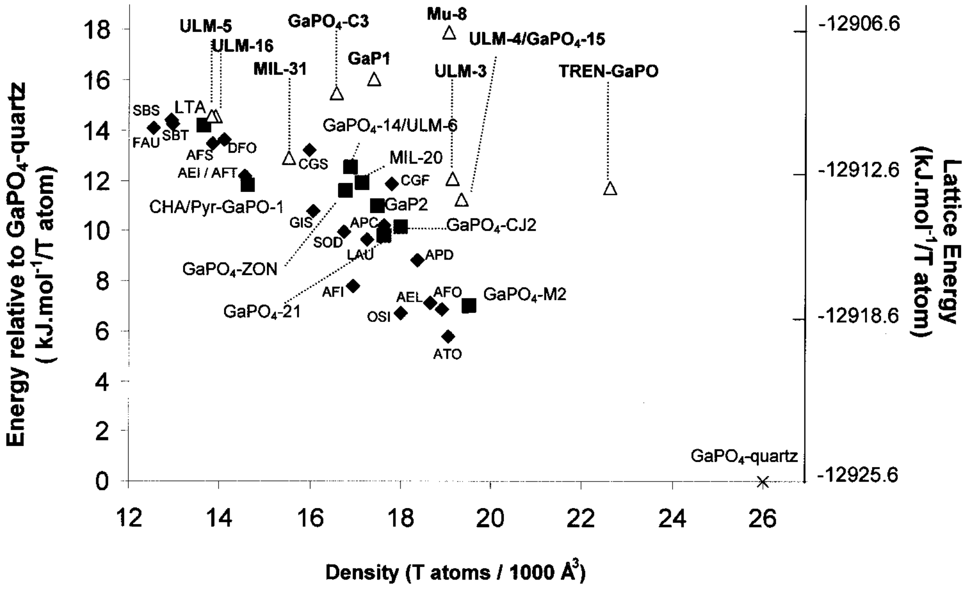

***Figure 6.*** Plot of calculated lattice energies as a function of density for gallophosphate structures. $GaPO_4$ structures directly built from their zeolitic analogues are shown with plain diamonds (◆). Predicted calcined GaPOs with zeolitic architectures derived from as-synthesized GaPOs are shown with plain rectangles (■). Predicted calcined GaPOs with highly distorted frameworks are shown with empty triangles (△).

If we examine now the simulated structures obtained upon calcination of their as-synthesized forms, two distinct groups of structures could be identified according to their structural features. The first one consists of zeotype structures ($GaPO_4$-21, $GaPO_4$-14, GaP2, $GaPO_4$-M2, $GaPO_4$-CJ2, $GaPO_4$-ZON, MIL-20, ULM-6, Pyr-GaPO-1, and $GaPO_4$-LTA), and the second one consists of distorted structures with unrealistically short oxygen−oxygen contacts (GaP1, $GaPO_4$-15, $GaPO_4$-C3, Mu-8, ULM-3,-4,-5,-16, TREN-GaPO, MIL-31). The zeotype structures span a range of energies (−12 918 to −12 911 kJ $mol^{-1}$ per T site) which is more favorable than the range covered by the distorted structures (−12 914 to −12 907 kJ $mol^{-1}$ per T site).

The relative lattice energies of the two groups of structures, for a given density, offer additional evidence for the instability of the distorted structures. Indeed, all predicted calcined gallophosphates displaying structural faults are found in the upper part of the energy/density plot. For a similar density, the zeolitic frameworks are found to be systematically more stable than the frameworks with structural faults. For example, the three structures $GaPO_4$-15, ULM-4, and $GaPO_4$-M2 have similar densities (~19.4 T atoms/1000 Å$^3$), while having significantly different lattice energies. On one hand, $GaPO_4$-M2 has a zeotypic architecture, with a lattice energy of 7 kJ $mol^{-1}$ per T site, having intermediate stability between $GaPO_4$-quartz and $GaPO_4$-CHA, as expected from the linear correlation of energy with density. In contrast, the two other structures, $GaPO_4$-15 and ULM-4, which both possess distorted frameworks, do not obey the linear energy/density dependence. They have far less favorable lattice energies in comparison with their zeotype polymorphs (11.2−11.3 kJ $mol^{-1}$ per T site), which further suggests their thermodynamic instability.

In the specific cases where structural faults are found in the simulated calcined GaPOs, it is noteworthy that none of the related as-synthesized structures have been experimentally reported to be stable upon calcination. In most cases, amorphization or collapse was reported.

Interestingly, among the viable zeotype structures simulated from as-synthesized GaPOs, that is, $GaPO_4$-21, $GaPO_4$-14, GaP2, $GaPO_4$-M2, $GaPO_4$-CJ2, $GaPO_4$-ZON, MIL-20, ULM-6, Pyr-GaPO-1, and $GaPO_4$-LTA, three related as-synthesized GaPOs have been reported to be experimentally stable upon template extraction, $GaPO_4$-21,[8] ULM-6,[9] and $GaPO_4$-LTA.[42] The lattice energies of these 10 structures approximately follow the linear energy/density trend, and this again suggests that they should be thermodynamically viable. It turns out that experimental template extraction from microporous GaPOs may yield stable phases and that, in such cases, their stability was correctly anticipated by the simulations. In light of such experimental and simulation results, we believe that special care should be taken regarding the experimental conditions of template extraction from as-synthesized GaPOs (gas atmosphere, speed of heating, etc.).

**Detailed Study of the Calcination of the Fluorinated Gallophosphate ULM-4.** As mentioned above, the as-synthesized frameworks (GaP1, $GaPO_4$-15, $GaPO_4$-C3, Mu-8, ULM-3,-4,-5,-16, TREN-GaPO, MIL-31) which lead to unrealistic calcined forms nearly all contain the same hexameric unit (Figure 4a). In our calculations, the occurrence of this hexamer in the as-synthesized structure seems to be correlated with systematic distortions in the related simulated calcined structure, leading to failure to predict zeotype structures. To test whether these distortions were specifically a consequence of our force field, or intrinsically related to the structures themselves, we performed energy minimizations with a different force field on the ULM-4 structure, chosen as a typical structure containing the hexameric unit. The force field used was developed by Murashov using ab initio methods,[62] and its performance has already been compared to those of our potential for the structural reproduction of various gallosilicate and gallophosphate structures.[23] Our force field was found to reproduce those structures more accurately, but we now have another opportunity to further test its quality.

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(62) Murashov, V. *Chem. Phys. Lett.* **1995**, *236*, 609−615.

To this end, the as-synthesized ULM-4 structure was modified exactly in the same way as described at the beginning of this paper, leading to a model with all Ga atoms in 4-fold coordination (Figure 4b). The initial neutral $GaPO_4$ model was then submitted to constant pressure lattice energy minimization using Murashov's potential. Surprisingly, the minimized structure has a quite regular zeotype architecture with O−Ga−O angles ranging from 101° to 122°. This contrasts with the unrealistic structure obtained with our force field, where O−Ga−O angles range from 70° to 170°, and close oxygen−oxygen contacts are obtained. From a structural point of view, this structure is more plausible than the one obtained with our potential. For comparison, the hexameric units extracted from the minimized structures as obtained with our force field and with that of Murashov's are compared in Figure 4c and d, respectively.

It clearly turns out here that the predicted calcined structure using force field methods is strongly dependent on the choice of the force field itself. To address the validity of our force field in regard to that of Murashov's, first principles calculations were performed on ULM-4, as described earlier, therefore circumventing the use of a parametrized force field. The same initial neutral $GaPO_4$ model was used as a starting point and subjected to geometry optimization. The striking feature of the quantum mechanical calculation is that it results in a distorted structure (Figure 4e) very similar to the one obtained with our force field; new Ga−O bonds have been created around some gallium atoms increasing their coordination to 5, along with the formation of short O−O distances. Indeed, the qualitative agreement between both structures, minimized with our force field and with nonlocal density functional theory, favors the robustness of our force field. However, it remains that the zeotype structure found with Murashov's force field may be a local minimum that was missed when performing our calculations, because the energy barrier between the initial model structure and the regular zeotype structure was too large for the minimization to overcome it. To address this issue, the regular zeotype structure obtained with Murashov's force field was then taken as a starting model for further energy minimizations, on one hand, with our force field and, on the other hand, with the first principles DFT method. In this way, the hypothetical energy barrier between the initial model and the regular zeotype structure has already been overcome. Strikingly, both minimizations rapidly converged toward the distorted structures of ULM-4. This unambiguously shows that the above zeotype form of ULM-4, as given by the force field of Murashov, is unlikely to be a true local minimum. Our force field successfully captures this feature, which further establishes its validity for the simulation of GaPOs.

The major difference between our force field and that of Murashov's is an additional polarization term in our potential, encapsulated in the core−shell model. However, force field models derived from ab initio calculations take indirectly into account the polarizability of the atoms through the values given for $A$, $\rho$, $C$, and the partial charges $q$. Therefore, it is not required to use only the shell model for polarization. Murashov's force field may lead to nonexisting local potential simply because the parameters used in the calculation of the energy are wrong, that is to say they are drawn from cluster simulations and not from the calculation of an extended solid.

To check the role of the polarization term in our force field, we minimized the initial model for calcined ULM-4 without taking into account the polarization term. This time, the resulting structure has a regular environment around all metal atoms. The addition of the polarization term in the force field has a huge influence on the lattice energy of the predicted calcined ULM-4 structure. The energy drops from $-12\,235.4$ kJ mol$^{-1}$ per T site before the calculation to $-12\,709.1$ kJ mol$^{-1}$ per T site without the polarization term, instead of $-12\,914.3$ kJ mol$^{-1}$ per T site when the polarization term was included, yielding a contribution of the polarization energy of 205.23 kJ mol$^{-1}$ per T site. While the present estimate is an upper bound to the true polarization energy and a crude estimate because of the simplicity of the shell model, these calculations show that the core−shell model stabilizes the distortions away from the regular structure.

Hence, the inclusion of polarizability is crucial for yielding results compatible with those obtained by first principles methods. For example, the inclusion of oxygen polarizability in force field calculations has also been shown to be essential for the correct simulation of Al−O−P angles in $AlPO_4$-5[63] and monoclinic distortions in silicalite.[64] In addition, the weight assigned to the polarizability in our force field is reasonably good since the results are in agreement with those obtained at a higher level.

## Conclusions

A series of 40 gallophosphate structures has been studied in their $GaPO_4$ forms using energy minimization; trial structures were derived from either their zeolitic $AlPO_4$ or their $MeGaPO_4$ analogues or obtained through virtual calcination of their experimental as-synthesized GaPOs (removal of template, water molecules, etc.).

Most of the minimized structures have zeolitic frameworks, that is, made of alternating $GaO_4$ and $PO_4$ tetrahedra. A direct correlation is observed between the lattice energies of the structures relative to the reference $GaPO_4$-quartz and the framework density, in a fashion similar to that known for other families of compounds, such as silicates and aluminophosphates. Among these structures, $GaPO_4$-tricl.CHA is known to be experimentally stable upon calcination (template and fluorine extraction) and to adopt the corresponding $GaPO_4$ form. Interestingly, this suggests that at least the zeotype $GaPO_4$ structures showing intermediate lattice energies between those of $GaPO_4$-quartz and $GaPO_4$-CHA should be viable.

However, 10 $GaPO_4$ structures (including four ULM-*n*, MIL-31, TREN-GaPO, etc.) show unrealistic structural features, including important framework distortions such as close O−O distances. Also, they do not follow the linear energy/density dependence and show systematically high, that is, unfavorable, energies. These results suggest that their original as-synthesized forms might be highly unstable upon calcination.

Despite the lack of experimental occurrence of $GaPO_4$ structures, this computational work shows that gallium atoms inserted in zeotype frameworks can lead to structurally and energetically viable structures. Also, this energy minimization method is thus a rapid technique, which enables the evaluation

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(64) Bell, R. G.; Jackson, R. A.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1990**, 782−783.

of the structure and lattice energies of the calcined form of a gallophosphate using the knowledge of its as-synthesized structure only. Our results underline the usefulness of careful experimental characterizations when performing calcination treatments. On the other hand, the thermodynamic instability of a few structures corroborated by their experimental collapse upon template extraction suggests that the host−guest interactions are important in the corresponding as-synthesized structures.

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