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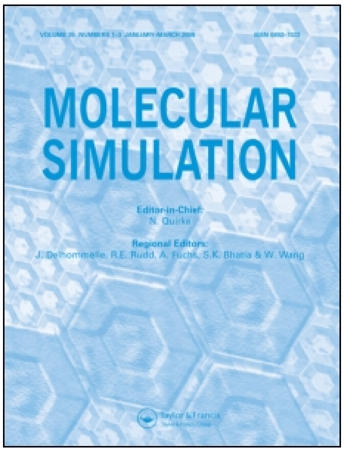

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Computational Study of Germanate Frameworks

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This paper tackles the structures and energetics of various simulated GeO_2 open-frameworks. The viability of as-synthesized germanates upon template extraction, i.e. calcination treatment, and of germanates as zeotypes is discussed.

Keywords: Open-framework germanates; Microporous materials; Simulation; Polymorphism

INTRODUCTION

The synthesis of zeolites and related solids has a long standing history due to their use in industry as catalysts, sorbents, or ions exchangers. Many of these new materials were aluminosilicates or porous materials including phosphates, borates, nitrides and sulfides with the possible incorporation of metals in the framework [1]. The required properties of this class of solids should be thermal stability, ease of separation from the liquid or gaseous products and shape selectivity. Recently, several new open-frameworks have been synthesized from GeO_2. In 1991, Xu [2,3] reported the possibility of making open-framework germanates with an organic template. Germanium is the neighbor of silicon in the column IV. By contrast with Si, Ge may adopt three different coordinations (IV, V, and VI) due to its larger atomic radius than that of silicon. The metal–oxygen bond is about 1.76 Å for Ge–O and about 1.61 Å for Si–O. Also, Ge–O–Ge angles [120–135°] are smaller than those observed in porous silicates [140–145°], which may typically allow the formation of 3-rings [4] in germanates, and favor low network density. A regain of the research efforts on open-framework germanates started at the end of the last decade. Some of them possess very large pores such as FDU-4 [5], the structure of which contains 24-membered-rings, or networks constructed from D4Rs (double-four-ring) units such as ASU-14 [6] and ASU-7 [7].

Simulation tools are important in materials science. Particularly in the area of zeolites, simulations are useful to predict the behavior of materials and facilitate their characterization. In the present work, our goal is to tackle the structure and energetics of open-framework germanates. We want to study zeotype architectures with the GeO_2 composition using lattice energy minimizations, both starting from existing as-synthesized germanates or silicogermanates, and hypothetical zeotype models [8]. These calculations originally aim at finding criteria of stability of germanates when compared to other families such as silicates, for example.

The development of forcefields has gradually covered an increasing number of elements of the periodic table, ranging from silicates [9–11], AlPOs [12], GaPOs [13–15], with the recent extension to silico-germanates by Sastre and Gale [16]. The forcefield used was derived for Ge and Si atoms in microporous frameworks, by empirically fitting parameters against the structure and physical properties of GeO_2–quartz and GeO_2–rutile. Using their forcefield, we minimize 11 microporous GeOs structures all with the GeO_2 composition. They include hypothetical germanates analogues of zeolites and silico-germanates (see Table I).

In the present work, the structures and energetics of the various simulated GeO_2 openframeworks are discussed. Since all minimized structures have identical GeO_2 chemical composition, lattice energies relative to the GeO_2–quartz structure, the highest-density germanates polymorph, are discussed and compared to one another. On the basis of structures

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TABLE I Energy minimized GeO_2 models derived from as-synthesized germanates and exisitng zeotypes

Composition			*Coordination of Ge*	*S.G.*	*a*	*b*	*c*	α	β	γ
Models derived from existing germanates										
Quartz	GeO_2	Calc.	IV	$P3_22_1$	4.99	4.99	5.66	90	90	120
	GeO_2	Exp.		$P3_22_1$	4.99	4.99	5.65	90	90	120
ASU-7(ASV)	GeO_2	Calc.	IV	*P*ccm	9.00	9.06	14.51	90	90	90
	$(GeO_2)_{10}[(CH_3)_2NH]H_2O$	Exp.		*P*4/mcc	8.78	8.78	14.47	90	90	90
ASU-9(AST)	GeO_2	Calc.	IV	*C*2/m	13.03	14.51	9.15	90	134.8	90
	$GeO_2(N_2C_6H_{12})H_2O$	Exp.		*I*4/m	9.23	9.23	14.10	90	90	90
ICMM3	GeO_2	Calc.	IV	$P2_1$	7.78	19.57	7.71	90	120.8	90
	$Ge_8O_{16}(OH)^-(MeNH_3)^+(MeNH_2)$	Exp.		$P2_1$	7.49	19.15	7.49	90	120	90
FOS-5(BEC)	GeO_2	Calc.	IV	*I*mma	26.48	26.54	27.32	90	90	90
	$(Me_3N)_6Ge_{32}O_{64}(H_2O)_{4.5}$	Exp.		$I4_1$/amd	25.99	25.99	27.27	90	90	90
ASU-20	GeO_2	Calc.	IV, V	*C*2/c	15.66	16.99	20.65	90	131.7	90
	$Ge_7O_{14}F_4[H_2DACH]_{1.5}(H_2O)_2$	Exp.	IV, V, VI	*C*2/c	15.95	17.55	19.00	90	109	90
ITQ-7(ISV)	GeO_2	Calc.	IV	*P*1	13.40	13.41	26.63	89.8	90.6	90.1
	SiO_2	Exp.		$P4_2$/mmc	12.88	12.88	25.21	90	90	90
ITQ-21	GeO_2	Calc.	IV	*P*1	20.58	20.53	26.62	87.0	89.9	90.1
	$Si_{0.66}Ge_{0.34}O_2$	Exp.		*F*m-3c	19.59	19.59	27.69	90	90	90
Models derived from hypothetical frameworks										
ACO	GeO_2	Calc.	IV	$C222_1$	13.73	10.37	14.09	90	90	90
	SiO_2	Calc.		*I*m-3m	9.80	9.80	9.80	90	90	90
ACOt	GeO_2	Calc.	IV	$P2_1$/c	9.68	9.21	13.32	90	131.3	90
	SiO_2	Calc.		*P*4/mnc	9.30	9.30	9.84	90	90	90
AFY	GeO_2	Calc.	IV	P-3_1m	12.97	12.97	9.29	90	90	120
	SiO_2	Calc.		P-3_1m	12.34	12.34	8.60	90	90	120
LTA	GeO_2	Calc.	IV	*R*-3m	17.60	17.60	21.70	90	90	120
	SiO_2	Calc.		*P*m-3m	11.83	11.83	11.83	90	90	90

(Due to the statistical distribution of oxygen atoms in the as-synthesized structures ASU-7 and ASU-9, they were, respectively minimized in space groups *P*ccm and *C*2/m as calcined). Cell parameters in Å, angles in °.

TABLE II Selected structural features and lattice energies of model GeO_2 frameworks

Composition				*Ge–O*	*O–Ge–O*	*Ge–O–Ge*	*Energy kJ/mol/ atom Ge*	*Energy relative to quartz*	*Density atoms/ 1000 A^3*
Models derived from existing germanates									
Quartz	GeO_2	Calc.	min	1.716	105.8	132.7	− 11,752.8	0.00	24.64
			max	1.732	111.5	132.7			
ASU-7(ASV)	GeO_2	Calc.	min	1.663	104.6	133.8	− 11,734.4	18.46	16.92
			max	1.777	113.9	141.5			
ASU-9(AST)	GeO_2	Calc.	min	1.707	107.7	136.4	− 11,734.6	18.20	16.30
			max	1.730	111.8	142.6			
ICMM3	GeO_2	Calc.	min	1.700	104.8	128.7	− 11,730.9	21.94	15.88
			max	1.745	114.2	148.5			
FOS-5(BEC)	GeO_2	Calc.	min	1.699	104.2	133.7	− 11,734.4	18.14	13.33
			max	1.739	115.0	156.3			
ASU-20	GeO_2	Calc.	min	1.690	83.2	115.0	− 11,716.4	36.43	21.99
			max	2.115	166.8	155.4			
ITQ-7(ISV)	GeO_2	Calc.	min	1.699	99.8	130.5	− 11,734.3	18.51	13.38
			max	1.751	117.8	154.1			
ITQ-21	GeO_2	Calc.	min	1.693	98.8	127.8	− 11,732.5	19.84	12.81
			max	1.743	118.6	173.3			
Models derived from hypothetical frameworks									
ACO	GeO_2	Calc.	min	1.684	100.1	120.2	− 11,733.5	19.32	15.95
			max	1.731	114.7	173.7			
ACOt	GeO_2	Calc.	min	1.706	106.0	130.6	− 11,733.8	19.02	17.94
			max	1.733	112.2	144.5			
AFY	GeO_2	Calc.	min	1.697	103.0	124.2	− 11,729.0	23.88	11.82
			max	1.726	113.2	180.0			
LTA	GeO_2	Calc.	min	1.704	108.2	136.2	− 11,730.2	22.68	12.37
			max	1.724	111.5	150.5			

Bond in A, angles in °.

and energies, the viability of germanates upon template extraction, i.e. calcination treatment, and as zeotypes is discussed.

SIMULATION METHOD

Interatomic Potential

The potential model used here is based on a formal-charge shell model. The interatomic potential describing the interaction between two ions, i and j, is the sum of three terms: (i) a short-range term evaluated by a Buckingham potential, with a cutoff of 12 Å, (ii) a coulombic term calculated using an Ewald summation, and (iii) a core-shell term, i.e. a core and a shell coupled by a harmonic spring [17], used to represent ionic polarization of oxygen atoms. The total energy of the system is given by the equation:

$$E_{\text{total}} = A_{ij}\exp(-r_{ij}/\rho_{ij}) - C_{ij}r_{ij}^{-6} + q_i q_j/r_{ij} + \frac{1}{2}k_0(r_{\text{core-shell}})^2$$

where A_{ij}, ρ_{ij}, and C_{ij} are short-range parameters, q_i and q_j are the charges of the ions i and j, and k_0 is the core-shell spring constant. Three-body terms are not taken into account to allow the simulation of Ge atoms in various coordinations. All calculations were done using the program GULP [18].

Germanate Structural Models

They were derived from existing crystal structures following three different strategies. (i) Germanate frameworks were derived directly from existing as-synthesized germanates. Six zeotype models with GeO_2 composition were derived from Ge–quartz, ASU-7[ISV] [7], ASU-9[AST] [7], ICMM-3 [4], FOS-5[BEC] [19] and ASU-20DACH [20] (the zeotype is indicated in brackets). All these frameworks were considered in their template-free forms. To create template-free GeO_2 structures, all structural or adsorbed water molecules, hydroxy groups and template molecules were eliminated prior the simulations. However, the as-synthesized germanates modified by removal of oxygen atoms or hydroxy groups around Ge atoms lead to initial GeO_2 structural models (before lattice energy minimizations) where Ge atoms have very distorted environments. Such distortions are shown in Fig. 1 where the removal of F atom from as-synthesized ASU-20 structure generates neutral distorted tetrahedral configurations around Ge atoms. (ii) Silicogermanates open-frameworks such as ITQ-7 [21] and ITQ-21 [22] that have chemical compositions close to pure GeO were used to build two distinct GeO_2 models, allowing us to study their viability as pure germanates. (iii) Finally, germanates analogues of existing zeotypes, such as AlPOs and aluminosilicates, were built by simply substituting Al, S, Co and Si atoms and other ions by Ge atoms when needed. Four GeO_2 zeotype models were derived from template-free zeotype structures [8], ACO, ACOt, AFY, LTA.

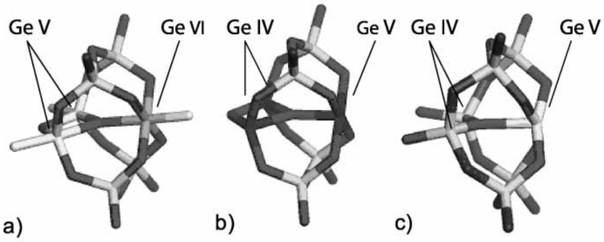

FIGURE 1 (a) Framework fragment extracted from the as-synthesized ASU20-DACH structure. (b) After removal of F atoms and before energy minimizations, Ge atoms are in distorted tetrahedral or square pyramid environments. (c) After energy minimizations, tetrahedral Ge become regular and Ge-square pyramid remains distorted.

Lattice Energy Minimizations

For each model, both cell parameters and atomic positions were relaxed during lattice energy minimizations at constant pressure. Each GeO_2 model was minimized in the space group of its original crystal structure. For all minimized models, the phonon spectra at the Γ point were calculated to check by the absence of imaginary modes that the space group used was valid. When imaginary modes were found, the model was minimized in $P1$ instead, with no imaginary frequencies. In this work, GeO_2–α–quartz is considered as the reference structure, as the simplest and highest density germanate. All the results presented here are computed relatively to the quartz structure. Lattice energies and selected structural features are given in Table II.

RESULTS AND DISCUSSION

Models Derived from Existing Germanates

After template elimination and lattice energy minimization, the four structures ASU-7, ASU-9, FOS-5, and ICMM-3 are found to be viable in their calcined forms, i.e. all metal Ge atoms display a regular tetrahedral environment typical of zeotype structures. Table II shows selected structural and energetic features. The O–Ge–O angles describe a restricted range [104.2–115.0°], with average O–Ge–O angles of 109.5°, with Ge–O bond lengths [1.663–1.777 Å] consistent with those found in GeO_2–quartz. The Ge–O–Ge angles belong to a restricted range [128.7–156.3°], with average Ge–O–Ge angles of 140°. The simulations show that these virtually calcined structures are indeed regularized upon lattice energy minimization.

Our simulation findings are in partial agreement with the experimental ones regarding the stability of these as-synthesized germanates upon calcination. Indeed, ASU-7 and FOS-5 are known to be stable in their calcined forms up to 540°C [7] and 500°C [19], respectively, the structures of which are well captured by our simulations. However, in contrast with what our simulations anticipate, the template extraction from ASU-9 is reported to be unsuccessful [7], since the template molecules cannot be removed from the cages without the destruction of the structure. Regarding ICMM-3, the experimental study shows a loss of template upon heating to 375°C and the structure is maintained to finally collapse after 4 h [4]. It is noteworthy that the simulation ICMM-3 calcined structure leads to the highest energy relative to quartz among these four as-synthesized frameworks.

In contrast with the above simulated calcined structures, the simulated calcined ASU-20 shows unrealistic structural features because of important framework distortions upon lattice energy minimizations. Irregular GeO_4 tetrahedra are found together with very distorted GeO_5 trigonal pyramids, where one oxygen atom is shared with three Ge atoms ($O-\mu_3$). The Ge–O distances range from 1.690 to 2.215 Å, while O–Ge–O angles vary from 83.2 to 166.8°, both describing unrealistic ranges. Accordingly, experimental data report that ASU-20 is not stable upon template extraction.

Models Derived from Silicogermanates

The pure germanate forms of two silico-germanates, ITQ-7 [21] and ITQ-21 [22], were simulated (see Table II). Experimentally, the incorporation of germanium is known to facilitate their synthesis and stabilize their structures. The simulation of their related pure GeO_2 forms is therefore of special interest.

In GeO_2–ITQ-7 (simulated in *P*1 to avoid negative phonon modes), the O–Ge–O angles describe the range [99.8–117.8°], and the Ge–O–Ge angles belong to the range [130.5–154.1°], to be compared to the ranges [100.5–119.5°] and [134.8–166.1°], respectively, in the experimental ITQ-7. The Ge–O bond lengths cover an acceptable range [1.699–1.751 Å].

ITQ-21 has got a ratio of Si/Ge $= 1.91$ in the space group *F*m-3c (226). In order to avoid the disorder of Ge atoms that would derive from the experimental space group, the pure GeO_2 form of ITQ-21 was constructed and minimized in *P*1. After minimization, O–Ge–O angles describe a range [98.8–118.6°] and Ge–O–Ge angles belong to a large range [127.8–173.7°], in comparison with [97.37–133.57°] and [129.7–166.7°], respectively, in the ITQ-21 experimental structure. Ge–O bond lengths cover a realistic range of [1.693–1.743 Å] interval, while angles involving oxygen increase from 166.1 to 173.7° upon simulation, with an error of less than 4.2%. While GeO_2–ITQ-7 shows viable structural features, the GeO_2–ITQ-21 structure might be unviable.

Models Derived from Zeotypes

Figure 2 shows the four zeotypes, ACO, ACO_{tilted}, LTA and AFY, both in their SiO_2 and GeO_2 forms, together with the corresponding X-ray diffraction patterns of the germanate forms. Indeed, the simulations lead to a systematic increase of the cell sizes upon the Si → Ge substitution, consistently with the larger Ge–O bond length (1.76 Å) in respect to that of Si–O (1.61 Å) (see Table I). However, the two Ge–ACO and Ge–AFY zeotypes germanates are found to be unviable, showing unrealistic structural features such as Ge–O–Ge angles at 180°, in a similar fashion to the simulated SiO_2–ACO and SiO_2–AFY pure silicates [15]. More interestingly, the two zeotypes Ge–ACO_{tilted} and Ge–LTA are found to be viable. In contradiction with previous studies [23], Ge–ACO_{tilted} and Ge–LTA appear indeed to be energetically and structurally viable. Typically in Ge–LTA, the Ge–O distances range from 1.704 to 1.724 Å, while Ge–O–Ge angles cover a realistic range [135.2–150.5°] (see Table II). This range is consistent with that observed for tetrahedral germanium in existing and well-characterized germanates, such as FOS-5 possessing Ge–O–Ge angles around 145° [19], or ICMM2 possessing Ge–O–Ge angle up to 157° [24].

Energetic Viability

The minimized lattice energy for each structure (derived from existing germanates or hypothetical ones) was normalized relative to the number of Ge atoms in the structure and compared to the normalized energy of the existing dense polymorph GeO_2–α–quartz, which is considered as the reference structure. Figure 3 plots the calculated lattice energies as a function of density (number of Ge atoms per volume units). Leaving apart the GeO_2 models considered as structurally unviable (i.e. ASU-20, ITQ-21, ACO and AFY) the energies of the structurally viable models are in the range [17.77–22.68 kJ mol^{-1}/T sites]. Strikingly, this range computed here from both experimental and hypothetical germanates is indeed consistent with the experimental range of [14.8–21.1 kJ mol^{-1}/T site] reported by Navrostky *et al.*, for the enthalpies of formation of silicogermanate zeolites [25] relative

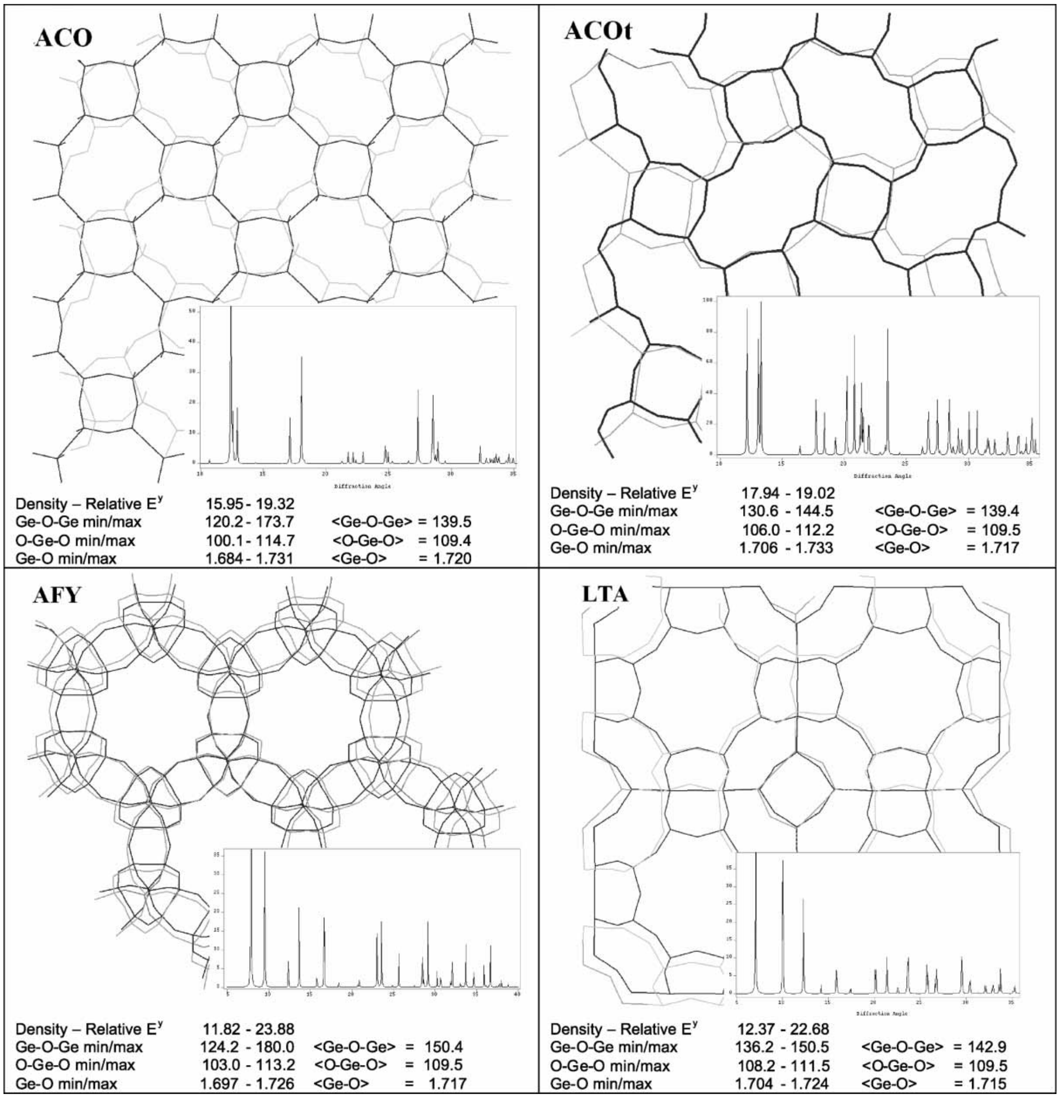

FIGURE 2 Comparison between energy minimized Ge–zeolites (light) and Si–zeolites (dark).

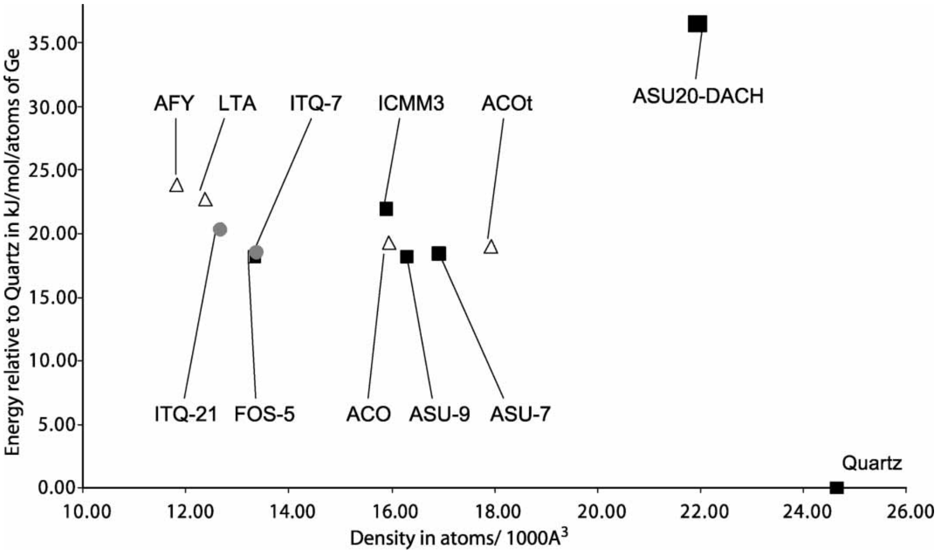

FIGURE 3 Plot of calculated lattice energies as a function of the framework density for germanates. (■): GeO_2 frameworks built from as-synthesized germanates. (△):The hypothetical GeO_2 frameworks derived from zeotypes are shown with triangles. (●): Simulated GeO_2 from silicogermanates.

to a mixture of GeO_2 and SiO_2 quartz polymorphs. This range is larger than that reported for zeotype silicates [6.8–14.4 kJ mol^{-1}/T sites] [25] and reflects that the framework germanates are relatively more metastable structures in comparison with framework silicates.

To conclude, our results suggest (i) that simulations may be used to possibly anticipate the structure and energetics of as-synthesized germanates upon template extraction, by predicting the related calcined form, and (ii) that novel germanates with interesting open-framework might be accessible by synthesis.

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