Novel Routes for the Preparation of a Range of Germanium Containing Zeolites

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Since their first use as catalysts in the petroleum industry in the 1960s, aluminosilicate zeolites have become one of the most important families of inorganic materials due to their acidity, selectivity, and ion exchange capacity.[1] Diversification can be achieved by framework substitution to yield “zeotypes” such as the AlPOs, SAPOs, and MeAPOs.[2−4] Gallium and germanium are obvious contenders for framework sites, and although gallium-containing zeolites are becoming increasingly well-known,[5−7] the replacement of silicon by germanium still remains a rather neglected field.[8−13] Barrer reported several germanium-containing zeolites,[14] but these were prepared in glass vessels, resulting in silicon leaching. To achieve full Ge substitution for a range of zeolite types, we therefore embarked on an investigation of aluminogermanate materials.

Our initial studies in the Al−Ge−O system were directed toward four topologies: FAU (faujasite), RHO (rho) , NAT (natrolite), and GIS (gismondine).[15] Zeolite rho demonstrates exceptional framework flexibility,[16,17] with potential for a high degree of catalytic selectivity; in a similar manner, natrolite, with a small kinetic diameter of 2.6 Å, permitting adsorption of molecules smaller than ammonia, displays significant framework distortions.[18] Zeolite X, a synthetic faujasite with Si/Al ≤ 1.5,[19] has applications in gas separation and selectively binds certain chlorofluorocarbon(CFC)/hydrofluorocarbon(HFC) isomers,[20] a property of increasing interest due to environmental concerns regarding ozone depletion. Finally, the ion exchange capacity of gismondine has potential application as a water softener in laundry detergent.[21] For each of these topologies our goal was the synthesis, structure solution, and determination of properties such as ion exchange, catalytic activity, and selectivity. This paper reports the realization of the first of these objectives.

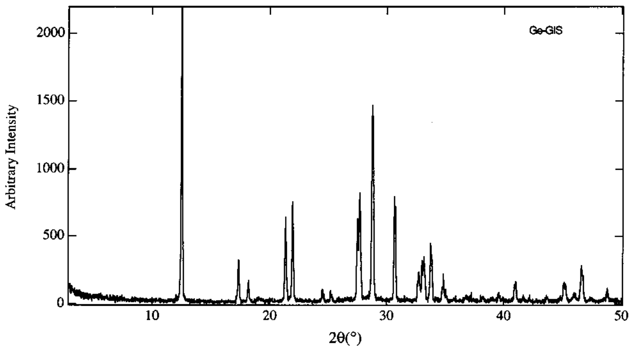

Figure 1. Powder X-ray diffraction pattern of Ge-GIS.

All syntheses were conducted in Teflon or polymethylpentene vessels to avoid silicon contamination. Alkali−metal germanate precursors were used as the preferred Ge source. Sodium metagermanate was presynthesized at 800 °C by heating a stoichiometric amount of germanium(IV) oxide and sodium carbonate for 24 h. Cesium and potassium germanates were similarly made at 600 °C for 16 h. Tetramethylammonium (TMA) cations were used in natrolite synthesis, for which germanium(IV) oxide was reacted with a 25% w/w aqueous solution of TMAOH, and the remainder of the reagents were then added (see Table 1). The aluminum source was either $NaAlO_2$ or hydrated alumina, and metal hydroxides were used as appropriate to achieve the desired composition. Germanium analogues of FAU, GIS, NAT, and RHO[15] have been synthesized as described in Table 1. Starting mixtures were initially agitated vigorously for 5 min, after which the reactions were static, except for the room-temperature preparation of RHO, for which stirring was continuous.

The powder X-ray diffraction patterns (Figures 1, 3, 5, and 6) were compared with the JCPDS[22] database,

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Table 1. Summary of Synthetic Parameters for Ge Zeolites

reagent composition	aging	crystallization	product
(2.0−2.3):(0.7−0.9):(2−2.5):1:(70−75) Na_2O:Cs_2O:GeO_2:Al_2O_3:H_2O	25 °C, 6d	60 °C, 6 h	Ge-RHO
2.3:0.7:2:1:70 Na_2O:Cs_2O:GeO_2:Al_2O_3:H_2O	no	60 °C, 20 h	Ge-RHO
2.3:0.7:2:1:70 Na_2O:Cs_2O:GeO_2:Al_2O_3:H_2O	no	25 °C, 168 h	Ge-RHO[b]
2:(2−2.7):1:(50−75) Na_2O:GeO_2:Al_2O_3:H_2O	no	95 °C, 4 h	Ge-X
2:2:1:50 Na_2O:GeO_2:Al_2O_3:H_2O	no	850 W, 10 s[a]	Ge-X
2:(2−3):1:(50−70) K_2O:GeO_2:Al_2O_3:H_2O	no	95 °C, 16 h	Ge-GIS
(1−1.5):(8−10):(4−4.5):(300−320) Na_2O:Al_2O_3:GeO_2:$(TMA)_2O$:H_2O	no	95 °C, 24 h	Ge-NAT

[a] Microwave synthesis, 2.45 GHz, operating at full power [b] Majority phase, with a low-level, unknown impurity.

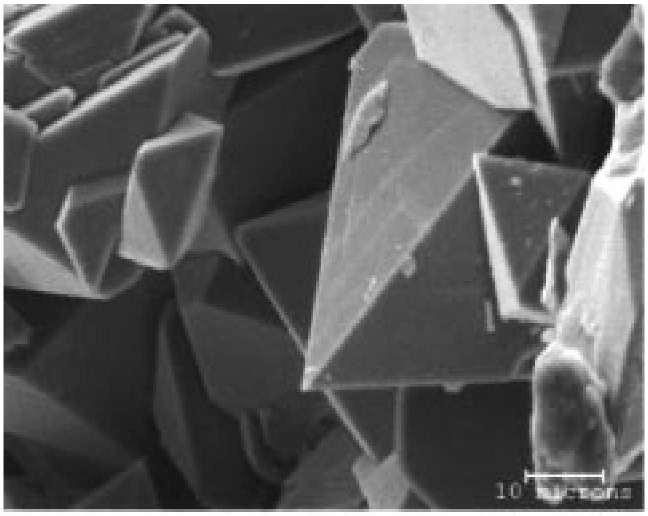

Figure 2. Electron micrograph of Ge-GIS.

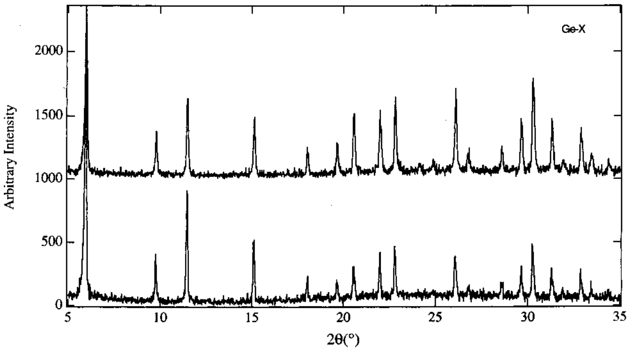

Figure 3. Powder X-ray diffraction pattern of NaGeX prepared via the standard solution route, upper, and microwave heating, lower.

which showed them to be analogues of aluminosilicate zeolites. The data set requiring most clarification is that of gismondine: although the similarities with gobbinsite and garronite are apparent, the precise structure type needs to be resolved. An electron micrograph picture (Figure 2) illustrates the highly crystalline nature of this material, and it is our intention to use these small crystals to determine exact structural details. Preliminary analysis indicates an orthorhombic unit cell with $a = 10.29(6)$ Å, $b = 9.86(2)$ Å, and $c = 10.53(3)$ Å, $\beta = 93.6°$, although more detailed characterization is required. ICP chemical analysis revealed $K_{6.1}Ge_{7.7}Al_{8.3}$ in the unit cell; charge balance requires equal potassium and aluminum contents, which when combined with Loewenstein's rule, suggests a unit cell composition of $K_8Al_8Ge_8O_{32}$, in line with aluminosilicate gismondines.

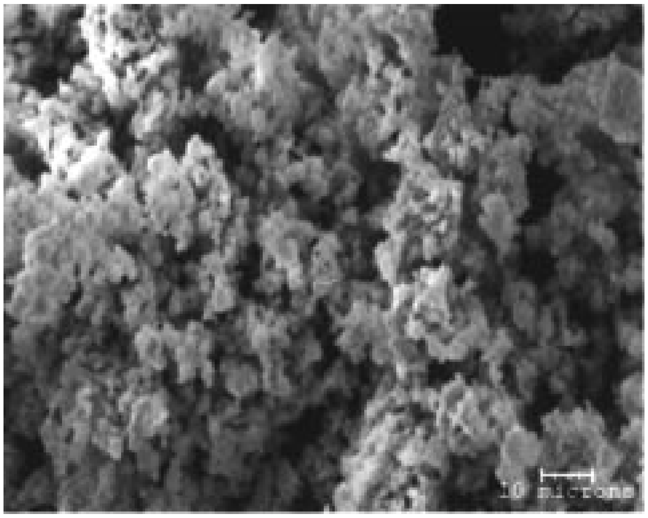

Figure 4. Electron micrograph of Ge-X.

Monophasic sodium germanium X (NaGeX) has been prepared in a domestic microwave oven (see Figure 3) at 850 W for 10 s using a Parr microwave digestion bomb. While accurate determination of temperature and pressure is difficult, this demonstrates how easily these phases can be prepared without specialized apparatus. Although NaGeX has been previously prepared,[12] to our knowledge this is the first synthesis using microwave radiation. For comparison, we repeated this procedure for Low Silica X (LSX), using the composition of Kühl.[23] No crystalline phase formed, indicating that NaGeX can be more readily synthesized under these conditions than LSX. This is significant, since industrially feasibility relies on a facile synthetic route. It appears that crystallization of NaGeX may be incomplete: comparative sorption capacities of NaGeX and LSX will be performed as part of our property determination. The electron micrograph of NaGeX is shown in Figure 4. The influence of reaction time on the conventional solution preparation of NaGeX was subsequently examined, with rapid NaGeX formation again observed − a reaction time of only 15 min at 90 °C yielded a product comparable in crystallinity with that after 4 h. This implies a particularly facile route for NaGeX synthesis. Structural and chemical analyses reveal a cubic unit cell of $Na_{96}Al_{96}Ge_{96}O_{384}\cdot wH_2O$ with $a = 25.589(1)$ Å.[24]

A detailed structural investigation of Ge-rho[25] indicates a composition of $Na_{16}Cs_8Al_{24}Ge_{24}O_{96}\cdot wH_2O$, with cell parameters of 14.6738(2) and 15.05(4) Å for dehydrated and hydrated forms, respectively. We have subsequently successfully synthesized Ge-rho by simply stirring a suitable reaction mixture at ambient temperature for several days. Although the resultant material

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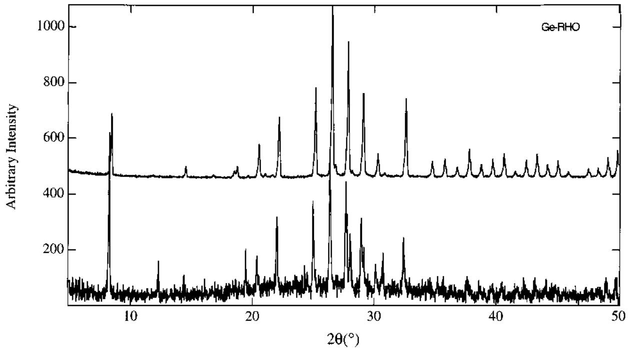

Figure 5. Powder X-ray diffraction pattern of Ge−RHO prepared at 60 °C, upper, and at room temperature, lower.

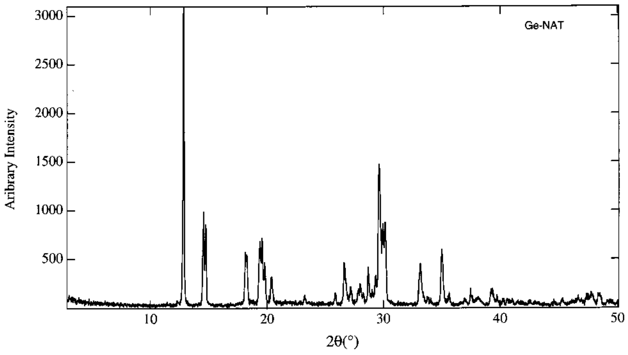

Figure 6. Powder X-ray diffraction pattern of Ge−NAT.

is not monophasic (Figure 5), it is evident that Ge-rho is the dominant phase. Despite extensive experimental and characterization efforts, the impurity was not identified, and since Ge zeolite analogues have not been widely studied, it is possible that this is an unknown phase. This work demonstrates that Ge zeolites can be synthesized under relatively mild reaction conditions, provided a suitable starting stoichiometry is chosen.

The importance of an appropriate stoichiometry is exemplified by Ge-natrolite, which has only been obtained using a mixture of TMA^+ and Na^+ cations. Excluding TMA^+ yields zeolite X. Similarly, if TMA^+ is replaced by Na^+ or K^+, NAT is not observed. This is interesting since the aluminosilicate usually crystallizes from gels rich in sodium, with no added organic structure reagent.[19] It is noteworthy that rubidium gallogermanate natrolite has been prepared under high temperature and pressure,[26] in contrast with the relatively mild conditions used here. Our material shows a strong resemblance to aluminosilicate paranatrolite,[27] and based on its orthorhombic indexing, we obtain unit cell parameters $a = 19.15(6)$ Å, $b = 19.64(5)$ Å, and $c = 6.81(4)$ Å. We have now prepared single crystals, analysis of which should permit structural similarities/differences from aluminosilicate paranatrolite to be resolved. ICP analysis (Galbraith) shows a weight percentage compositon of 9.55% Na, 11.07% Al, 46.98% Ge, and 1.34% N; using paranatrolite as a basis, this gives the formula $TMA_{0.45}Na_{1.96}Al_{1.94}Ge_{3.06}O_{10.0}$, where Ge/Al = 1.58. The Na level is virtually identical to the Al content and hence provides all the necessary charge balance, implying that any occluded TMAOH acts only as a structure-directing agent to promote the NAT topology. The electron micrograph is shown in Figure 7.

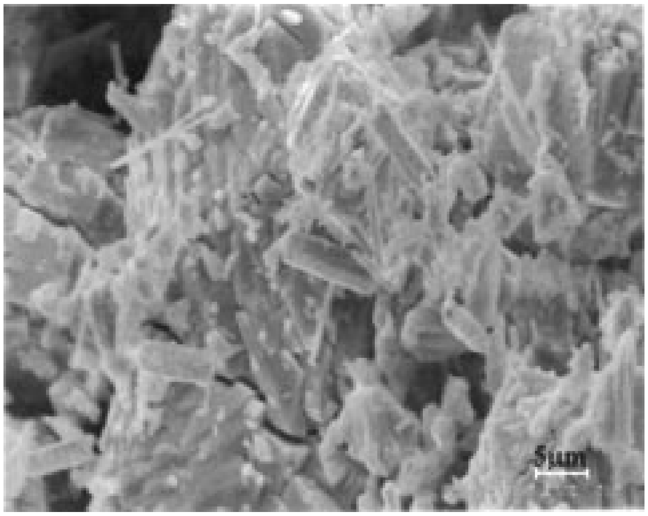

Figure 7. Electron micrograph of Ge−NAT.

In addition to our ongoing structural characterization, we are currently performing physical property measurements which will permit the influence of Ge incorporation to be resolved. Such structure/property relationships are crucial to the understanding and subsequent development of novel materials for industrial application.

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