

Synthesis of a Novel Gallosilicate with the Ferrierite Structure

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Aluminium-free (Si, Ga)-ferrierite with Si/Ga = 6.6 has been prepared by direct synthesis, and its orthorhombic unit cell parameters are $a = 19.01(1)$, $b = 14.15(1)$, and $c = 7.481(3)$ Å, the unit cell volume being 0.55% larger than for (Si, Al)-ferrierite; solid-state n.m.r. spectroscopy shows that pyrrolidine, the template molecule, is essentially intact in the channels of the new material.

Structural and chemical consequences of the isomorphous substitution of Si and Al in zeolite frameworks by elements such as B, P, Ge, and Ga are of considerable interest. Many such materials have been prepared. Two of the recently synthesised classes of molecular sieves can be considered as derived by a partial (SAPO) or total (ALPO) substitution of Si by P in aluminosilicate frameworks. (Si, Ga)-analogues of zeolites sodalite,^{1,2} faujasite,¹⁻⁴ thomsonite,⁵ offretite,⁶ mordenite,⁷ ZSM-5,^{8,9} theta-1,¹⁰ natrolite, analcite, Ω (synthetic mazzite),¹¹ F, Zh, L,^{12,13} and ABW¹⁴⁻¹⁶ have been made by direct synthesis. Gallium has also been inserted into silicalite-II, the pure silica form of zeolite ZSM-11, by post-synthesis treatment with a gallate solution.^{17,18} The preparation of (Si, Ga)-zeolites was stimulated by their usefulness in the Cyclar process.¹⁹ It has also been reported that methane can be converted into aromatics over (Si, Ga)-ZSM-5.²⁰

Ferrierite is a high-silica zeolite with a Si/Al ratio of $\geq ca. 6$, crystallising with orthorhombic symmetry and typical unit cell parameters $a = 18.97-19.22$, $b = 14.12-14.15$, and $c = 7.48-7.51$ Å.^{21,22} Aluminium-free ferrierite, synthesised in the presence of ethylenediamine and boric acid, has a smaller unit cell ($a = 18.557$, $b = 13.889$, and $c = 7.249$ Å).²³ The structure²⁴ is based on 5-membered rings. Four such rings are linked to give [5⁴] polyhedral units from which the three-dimensional framework can be constructed. In ferrierite there are two types of intersecting channels: the main channels run along the [001] crystallographic axis and are outlined by 10-membered rings (0.43×0.55 Å in diameter); the side channels are outlined by 8-membered rings (0.34×0.48 Å) and run along the [010] axis.

Other structurally related zeolites, such as ZSM-35^{25,26} and FU-9²⁷ have been prepared in the presence of organic templates. Although a relatively small-pore zeolite, ferrierite displays catalytic activity in reactions such as the cracking of n-hexane, methanol conversion, and the alkylation of toluene.^{28,29}

(Si, Ga)-ferrierite was synthesised as follows. Ga₂O₃ (1.87 g) and NaOH (1.05 g) were dissolved in H₂O (5 g). The resulting sodium gallate solution was added with vigorous

stirring into a mixture of pyrrolidine (4.13 g) and Ludox AS-40 (18.15 g). The homogeneous gel was then transferred into a Teflon-lined stainless-steel autoclave and heated to 200 °C for 15 days without stirring. The product was washed and dried, giving sample 1 with Si/Ga = 6.6 and Na/Ga = 0.81 as determined by atomic absorption. The unit cell content of sample 1 was Na_{3.8}Si_{31.3}Ga_{4.7}O₇₂. (Si, Al)-ferrierite was

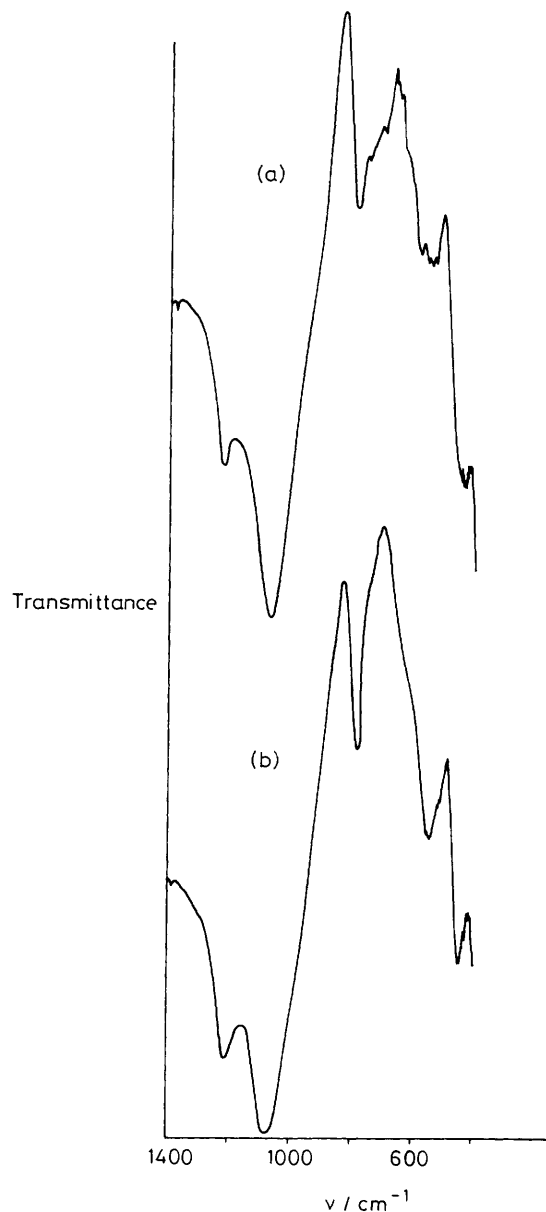


Figure 1. I.r. spectra in the framework vibration region. (a) (Si, Al)-ferrierite (sample 2); (b) (Si, Ga)-ferrierite (sample 1).

Table 1. Interplanar spacings, $d/\text{Å}$, and relative X-ray diffraction pattern peak intensities in Ga-ferrierite (sample 1).

$d/\text{Å}$	I/I_0	$d/\text{Å}$	I/I_0	$d/\text{Å}$	I/I_0
11.248	26	3.863	97	2.892	11
9.499	74	3.781	100	2.861	11
7.064	20	3.751	76	2.714	6
6.965	31	3.676	58	2.647	8
6.617	29	3.541	92	2.481	11
5.768	15	3.480	96	2.150	7
5.669	12	3.391	22	1.999	15
4.961	11	3.316	24	1.951	8
4.057	53	3.226	8	1.870	12
3.988	78	3.056	20	1.787	10
3.946	67				

prepared for comparison starting from a reaction mixture containing NaAlO₂ instead of NaGaO₂.²⁶ The product (sample 2, Si/Al = 6.1) was filtered off, washed, and dried. The unit cell content of sample 2 was Na_{4.4}Si_{30.9}Al_{5.1}O₇₂.

Powder X-ray diffraction (XRD) patterns were obtained on a Philips PW1710 vertical goniometer. The XRD pattern of (Si, Ga)-ferrierite is similar to that of its aluminosilicate counterpart except that the relative peak intensities are somewhat different and shifted towards lower 2θ, which indicates an expansion of the unit cell in comparison with (Si, Al)-ferrierite. Interplanar spacings and peak intensities of sample 1 are listed in Table 1. The XRD pattern of the highly crystalline sample was indexed on the basis of the ferrierite structure.³⁰ Silicon powder was used as internal standard and lattice constants were calculated by means of a refinement program. The unit cell parameters of the orthorhombic (Si, Al)-ferrierite were *a* = 19.01(1), *b* = 14.11(1), and *c* = 7.461(4) Å, while for the (Si, Ga) counterpart we obtained *a* = 19.01(1), *b* = 14.15(1), and *c* = 7.481(3) Å. The Ga–O bond is longer than the Al–O bond (the ionic radii for Al³⁺ and Ga³⁺ are 0.57 and 0.62 Å, respectively), and consequently the corresponding unit cell constants for Ga-ferrierite are slightly larger than those found for its aluminosilicate analogue. The expansion takes place along the *b* and *c* axes while parameter '*a*' remains essentially constant. The expansion of the unit cell upon the introduction of gallium is similar to that found in other zeolitic structures.^{1–3}

The i.r. spectra of (Si, Al)- and (Si, Ga)-ferrierites are compared in Figure 1. The absorption bands for (Si, Ga)-ferrierite are at 1210, 1074, 787, 619 (shoulder), 544, and 447 cm⁻¹, and for (Si, Al)-ferrierite at 1225, 1068, 792, 698 (broad), 544, and 447 cm⁻¹, respectively. The Si–O–Al symmetric stretch vibration at 698 cm⁻¹ is poorly resolved from the Si–O–Si vibration at 792 cm⁻¹ in sample 2. In (Si, Ga)-ferrierite the Si–O–T vibration³¹ is shifted towards lower frequencies and is seen as a shoulder at 619 cm⁻¹.

The ¹³C magic-angle-spinning (m.a.s.) n.m.r. spectrum of Ga-ferrierite (not shown) reveals that pyrrolidine is essentially intact in the channels of sample 1. The chemical shifts of the α- and β-carbons are at 63.7 and 24.7 p.p.m. from tetramethylsilane, respectively, as compared with 47.1 and 25.7 p.p.m. in liquid pyrrolidine.³² This shift of ¹³C resonances to higher frequencies is a result of the interaction of the intracrystalline environment with the guest molecule.^{33,34}

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