$CsFeSiO_4$: a maximum iron content zeotype

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The alkali-metal iron silicate, $CsFeSiO_4$, has been synthesised, using a gel decomposition method followed by high temperature annealing, and shown to adopt the zeolite ABW structure constructed from alternating FeO_4 and SiO_4 tetrahedra surrounding caesium.

Substitution of iron into zeolitic frameworks using hydrothermal methods has been investigated by several groups[1–5] but with limited success due to the difficulty of attaining purely tetrahedral Fe(III) in an aqueous environment. Levels of tetrahedral iron that can be incorporated into the framework, replacing aluminium, are generally restricted to a few percent and octahedral iron species often block the zeolite pores. The main motivation behind substitution of transition metal centres (particularly Fe, Co, Mn and Cr) into frameworks lies in the attempt to build selective redox catalysts by utilising the channels inherent within zeolite structures. A secondary idea is the possibility of producing new pigments by incorporating coloured species into frameworks rather than intercalating coloured species into the channels within frameworks.[6–9]

Some complex tetrahedra based iron silcate materials have been previously reported in the literature: $KFeSiO_4$ exists in three forms,[10] α-$KFeSiO_4$ is orthorhombic but of unknown structure, β-$KFeSiO_4$ adopts the stuffed tridymite structure and γ-$KFeSiO_4$ has the kaliophilite structure. Studies into the K_2O-Fe_2O_3-SiO_2 phase field[11,12] have also shown the existence of iron leucite, $KFeSi_2O_6$, and iron feldspar, $KFeSi_3O_8$, which show analogous polymorphism with their corresponding aluminium compounds.

A polycrystalline sample of $CsFeSiO_4$ was prepared as follows. Stoichiometric quantities of LUDOX (40% by weight SiO_2 in water, Aldrich) and $Fe(NO_3)_3·9H_2O$ (99.9%, Aldrich) were dissolved in 50 ml of 2M HNO_3. A 1.5-fold excess of $CsCO_3$ (99.9%, BDH) was then added to the solution; excess was added to compensate for the high volatility of caesium salts at the intermediate temperatures used in the experimental procedure. 100 ml ethanol was added under constant stirring followed by 10 ml of .880 ammonia solution, added dropwise. A brown spongy material was seen to precipitate from the solution as the ammonia was added, which partially redissolved on addition of further ammonia solution. The mixture was heated to dryness over a period of 12 h. The resultant solid was then partially decomposed in an alumina crucible at a temperature of 250 °C for a further 12 h. The brown powder obtained was thoroughly ground and heated for a further 16 h at 600 °C, then 850 °C and finally 1000 °C. After each heat treatment a powder X-ray diffraction (PXD) pattern was collected, using a D5000 Siemens diffractometer (Cu-Kα_1 radiation) operating in reflection geometry. The annealing at 1000 °C was repeated until there was no observable change in the powder diffraction pattern. The final product was found to be mustard yellow in colour. Data, for Rietveld analysis using the GSAS suite of programs,[13] were obtained over 16 h for the 2θ range 10–110° using a step size of 0.02°.

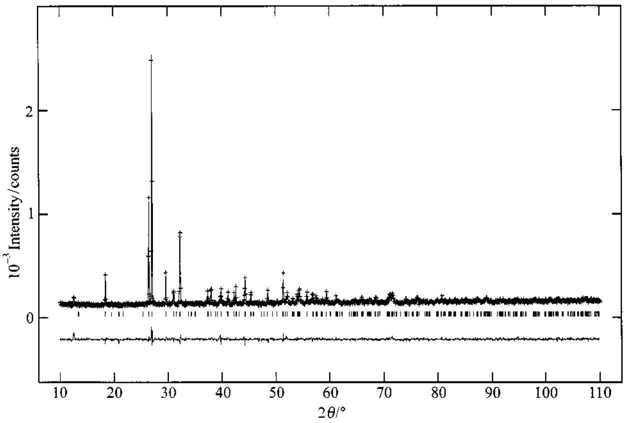

Fig. 1 Final Rietveld refinement profile of $CsFeSiO_4$. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections and the lower line is the difference plot; R_{wp} = 6.85%, R_p = 5.24%, R_e = 5.63% and R_{F**2} = 13.52% for 355 observations.

The initial PXD pattern collected from $CsFeSiO_4$ after annealing at 600 °C was found to contain no discernible Bragg reflections. The PXD pattern collected after annealing at 850 °C showed a new phase to be present, although the diffraction pattern was very weak. Repeated annealing at 1000 °C gave a crystalline material with sharp Bragg reflections, which were indexed on an orthorhombic unit cell using the PC program TREOR90.[14] Comparison of the PXD pattern with that simulated for a material adopting the zeolite ABW structure with the calculated lattice parameters gave very good agreement. No evidence of leucite or feldspar type impurities were found in the pattern.

Full Rietveld analysis was then performed using the structure of the known ABW material $LiAlSiO_4$[15] as the starting model but with iron on the aluminium position and caesium replacing lithium. In this model the silicon and aluminium positions are distinct, *i.e.* the framework is ordered with alternating tetrahedral ions in accordance with Loewenstein's rule.[16] The framework was refined, subject to some hard and soft constraints; these constraints are necessary due to the in-

Table 1 Atomic coordinates for $CsFeSiO_4$

Atom	Site	x	y	z	Occupancy	U_i/U_e ×100
Cs	4*a*	0.2021(4)	0.495(5)	0.5009(9)	1.013(10)	3.44(14)
Si	4*a*	0.082(5)	−0.018(19)	0.193(3)	1.0	2.30(28)
Fe	4*a*	0.417(3)	−0.021(13)	0.314(2)	1.0	2.30(28)
O1	4*a*	0.092(3)	0.007(13)	0.014(2)	1.0	4.8(6)
O2	4*a*	−0.007(10)	−0.246(9)	0.261(10)	1.0	4.8(6)
O3	4*a*	0.019(9)	0.232(10)	0.262(10)	1.0	4.8(6)
O4	4*a*	0.229(3)	−0.077(8)	0.276(6)	1.0	4.8(6)

Table 2 Cell and space group information

	$CsFeSiO_4$
Space group	$Pc2_1n$
a/Å	9.5858(4)
b/Å	5.5538(3)
c/Å	9.0476(4)
V/Å³	481.67(4)
Z	4

sensitivity of the technique for a caesium containing material. The thermal factors of the oxygen sites were constrained to be identical, as were those of the silicon and iron sites. The Si–O and Fe–O bond lengths were refined with a soft constraint (standard deviation of 0.005 Å) at 1.625 and 1.825 Å respectively. The refinement converged smoothly to give the excellent final profile fit illustrated in Fig. 1. Atomic data and cell data are given in Tables 1 and 2. Refinement was also attempted using the disordered framework ABW model of $CsAlTiO_4$[17] in the space group *Imma* but this gave much poorer profile fit parameters and was discarded. The refined structure is constructed of alternating SiO_4 and FeO_4 vertex linked tetrahedra with the alkali-metal cation occupying the large 8-ring cavities parallel to the crystallographic *b*-axis. Channels also exist along the *a*-direction (4-rings) and *c*-direction (6-rings) as illustrated in Fig. 2.

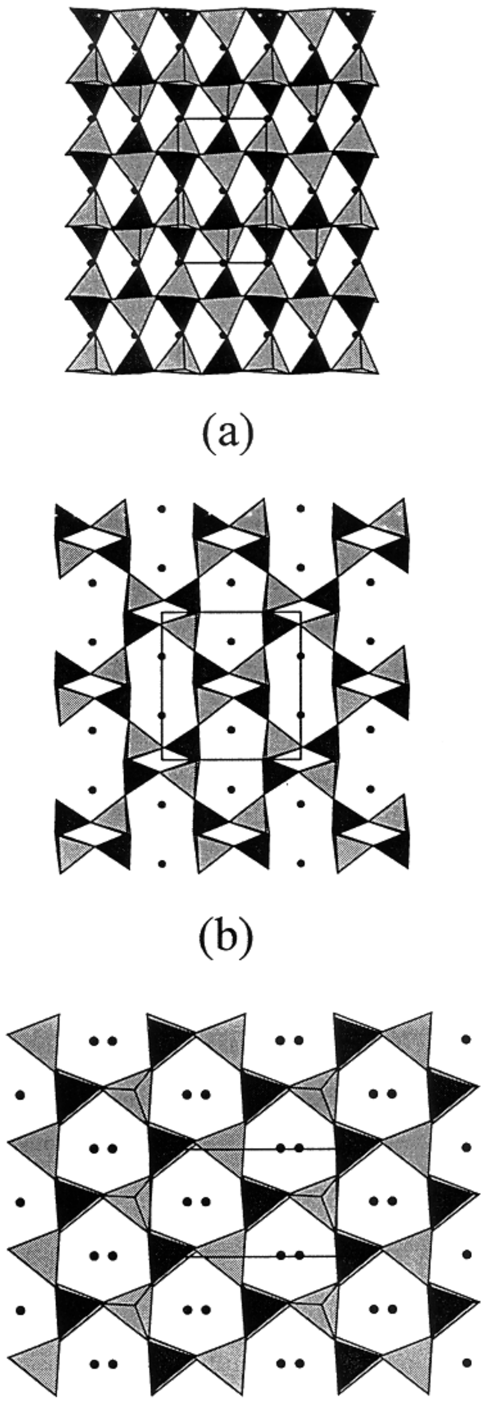

Fig. 2 Representations of the structure of $CsFeSiO_4$ along (a) [100], (b) [010] and (c) [001] illustrating the channels. Dark tetrahedra represent SiO_4, light tetrahedra represent FeO_4 and the black spheres are caesium.

The stability of the product material to moisture was studied by stirring in deionised water for 3 days at 45 °C. Residual water content was measured by thermogravimetric analysis (TGA) using an STA1500 TGA/DSC. Elemental analysis was carried out using a JEOL JSM-6400 SEM equipped with a TRACOR series II energy dispersive X-ray analysis system. TGA showed the as-made material to contain no residual water. Attempts were made to hydrate the material by exposure to water vapour for 3 days but subsequent TGA measurements showed no weight loss up to 1000 °C indicating no water uptake. The material was also found to be air and moisture stable. EDAX on $CsFeSiO_4$ showed the ratio of Cs : Fe : Si to be approximately 1 : 1 : 1 in accordance with that expected for an ABW product stoichiometry.

Further, $AFeTiO_4$ (A = Cs, Rb) have been synthesised using the same experimental technique as dark brown powders. Rietveld analysis on $CsFeTiO_4$ using powder X-ray data show this material also adopts the zeolite ABW structure and TGA reveals no residual water within the structure. Attempts to synthesise the germanium analogues have met with limited success. Further structural characterisation of materials using powder neutron diffraction data is planned to investigate the framework ordering in detail.

$CsSiFeO_4$, with a structure based on alternating FeO_4^{5-} and SiO_4^{4-} tetrahedra, is the first framework material having the maximum level of iron in a zeotype. The ability to incorporate such high levels of iron is a result of templating at high temperatures using caesium rather than in aqueous solution where six coordinate iron is unavoidable and influences the nature of the zeolite product.

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