

Iron-doped zircon: the mechanism of formation

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Iron-doped zircon (zirconium silicate) has been prepared from silica, zirconia and iron(II) sulphate heptahydrate using a mixture of sodium halides and alkali metal nitrates as mineralisers to lower the temperature of reaction. The formation of a silicon- and fluorine-containing glassy phase in the reaction vessel, together with evidence for a SiF_3 breakdown product and the analysis of solid phases formed at intermediate temperatures, implicate the participation of a volatile silicon fluoride intermediate, probably SiF_4 , in the formation of the iron-doped zircon. © 1999 Kluwer Academic Publishers

1. Introduction

Zirconium silicate, ZrSiO_4 , commonly called zircon, adopts a garnet-related structure [1]. The compound can be made directly by the calcination of zirconia, ZrO_2 , and silica, SiO_2 , above 1500°C . However, the calcination of zirconia and silica in the presence of alkali metal halides and other sodium- and potassium-salts (known as mineralisers) significantly reduces the temperature of the formation of zircon to about 1000°C [2–4].

During the synthesis of zircon it is possible to incorporate other metal atoms into the structure to give coloured materials [2, 3] which are used commercially as pigments: vanadium imparts a strong blue coloration, praseodymium gives yellow materials and iron-doped zircon is coral coloured. The structures of the vanadium- and praseodymium-doped zircons are thought to be well understood [2, 3–6], whereas iron-doped zircon has received less attention. Our investigations of the structural properties of iron-doped zircon [7] have shown that iron-doped zirconium silicate containing low concentrations of iron (ca < 1.0 wt % Fe) formed by the reaction of zirconia, silica, ferrous sulphate and mineralizers at 1060°C and subsequently washed in 5 M HCl, contains Fe^{3+} in low symmetry rhombic sites together with inclusions of $\alpha\text{-Fe}_2\text{O}_3$. In materials with higher iron content (ca > 1.0 wt % Fe) the Fe^{3+} occupies higher symmetry sites and the amount of included $\alpha\text{-Fe}_2\text{O}_3$ increases. The colour of the materials is associated with the presence of both Fe^{3+} in low symmetry sites and with the presence of inclusions of $\alpha\text{-Fe}_2\text{O}_3$, although the latter dominates the colour properties at higher Fe concentrations. We describe here our studies of the processes which occur during the reaction to prepare iron-doped zircon, and the roles played by the different mineralisers.

2. Experimental

2.1. Preparation of iron-doped zircon

Iron-doped zircon with iron concentrations ranging from 0.19 to 1.82 wt % Fe, as determined by ICP-AES analysis [7], was prepared by mechanically mixing (5 min) monoclinic ZrO_2 (1 mol), SiO_2 (1 mol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.1–0.25 mol), NaCl (0.1–0.3 mol), NaF (0.25–0.67 mol), and MNO_3 (0.03–0.1 mol, $M = \text{alkali metal}$). Water (15 cm^3) was added and mixing continued (5 min). The reactant mixture was heated in a covered, unglazed ceramic crucible to 1060°C with a ramp rate of 100°C per hour, held at 1060°C (6 h) and cooled in the furnace. Preparations were also made at calcination temperatures of 500 and 700°C .

X-ray powder diffraction (XRD) patterns were recorded with a Siemens D5000 X-ray diffractometer using CuK_α radiation.

Energy dispersive X-ray (EDX) analysis was performed on a JEOL FX2000 microscope under an accelerating voltage of 200 kV using a beam of diameter 14 nm.

Simultaneous thermal analysis (STA) was performed with a Stanton Redcroft STA1500 instrument on ca 5 mg of sample and a similar amount of γ -alumina reference in a platinum crucible. Air was passed ($50 \text{ cm}^3/\text{min}$) through the furnace, which was heated at $15^\circ\text{C}/\text{min}$ from 25– 1060°C .

Thermal mass spectrometry measurements were performed with a Stanton Redcroft STA 700 connected to a VG Analytical TS 250 magnetic sector mass spectrometer. The reaction mixture was heated at a rate of $100^\circ\text{C}/\text{min}$, to 1000°C .

3. Results and discussion

When zirconia and silica were calcined at 1060°C the X-ray powder diffraction pattern showed no evidence of

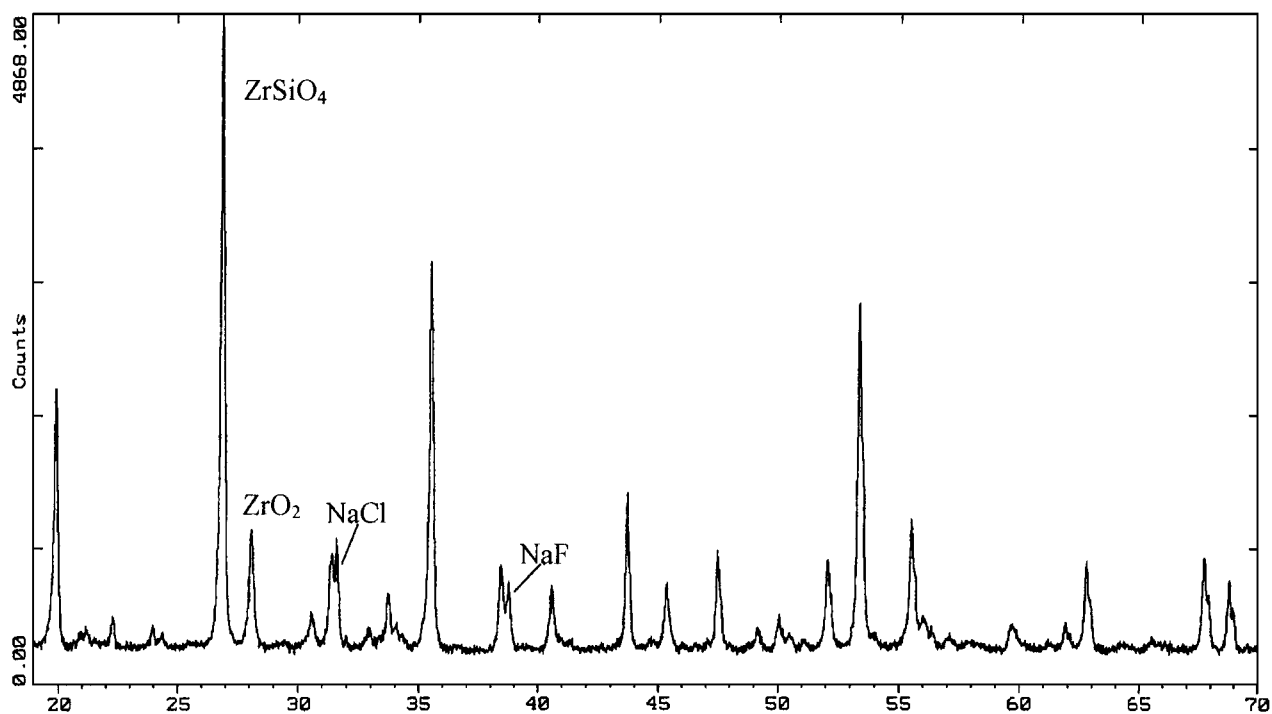


Figure 1 XRD pattern for the calcination product of zirconia, silica and mineralisers at 1060 °C.

TABLE I Phases detected by XRD in products formed by the reaction of zirconia and silica in the presence of mineralisers

Calcination temp. (°C)	Phases present					
	ZrO ₂	SiO ₂	ZrSiO ₄	NaF	NaCl	MNO ₃
Starting mixture	✓	✓	×	✓	✓	×
500	✓	✓	×	✓	×	×
700	✓	✓	×	✓	×	×
1060	✓	×	✓	✓	✓	×

KEY: ✓ phase detected, × phase not detected.

zircon formation. However, the addition of mineralisers to the reaction mixture gave a multiphasic zircon-containing product at 1060 °C (Fig. 1, the most intense peak due to each species is marked). The crystalline phases detectable by XRD are summarised in Table I (note that the nitrate species was below the limits of detectability by XRD before calcination).

The results show the formation of zircon at 1060 °C together with some unreacted zirconia, sodium fluoride and sodium chloride. Given the use of stoichiometric quantities of zirconia and silica in the reaction mixture, the absence of unreacted silica is indicative of the possible loss of some silica during the reaction, a proposition which is confirmed by other evidence (see below). The XRD patterns of the products formed at 500, 700, and 1060 °C showed a decrease in the NaF content with increasing calcination temperature indicating that NaF is consumed during the reaction to form zircon. The peaks corresponding to NaCl in the XRD pattern disappeared when the mixture was calcined at 500 and 700 °C but were present in the product formed by calcination at 1060 °C: similar behaviour has been reported for the preparation of *M'*-RTaO₄ phosphors using various flux materials (Li₂SO₄, LiCl, Na₂SO₄) and such fluxes have been termed *reactive fluxes* [8]. Earlier studies [9] of the

TABLE II Phases detected in the preparation of 1.55 wt % Fe iron-doped zircon in the absence of mineralisers

Calcination temp. (°C)	Phases present				
	ZrO ₂	SiO ₂	ZrSiO ₄	FeSO ₄ ·7H ₂ O	α-Fe ₂ O ₃
Starting mixture	✓	✓	×	✓	×
500	✓	✓	×	×	✓
700	✓	✓	×	×	✓
1060	✓	✓	✓	×	✓

KEY: ✓ phase detected, × phase not detected.

reaction between zirconia and silica, when separated by a platinum wire and sodium fluoride, concluded that silica migrates to the zirconia, not vice versa.

An iron-containing zircon-related phase (denoted Fe/ZrSiO₄), the characterization of which was reported earlier [7], was formed from the reaction of ZrO₂, SiO₂ and FeSO₄·7H₂O in the absence of mineralisers at 1060 °C (Fig. 2). The crystalline products of this reaction, formed at different calcination temperatures, are shown in Table II. The small amount of iron-doped zircon detected in the product formed at 1060 °C, together with unreacted ZrO₂ and SiO₂, indicate that FeSO₄·7H₂O and/or its decomposition products also act as weak mineralisers (the α-Fe₂O₃ arises from the heating of FeSO₄·7H₂O in air [10]).

Iron-doped zircon was also prepared from ZrO₂, SiO₂, FeSO₄·7H₂O and all three mineralisers (Fig. 3). The products of the reaction at three different calcination temperatures and for three different concentrations of Fe, are shown in Table III. The formation of Fe/ZrSiO₄ was first observed in products formed by calcination at 700 °C. Following calcination at 1060 °C, Fe/ZrSiO₄ was the major phase formed together with a small quantity of unreacted ZrO₂. Once again, NaCl was not present in the 500 and 700 °C products, but

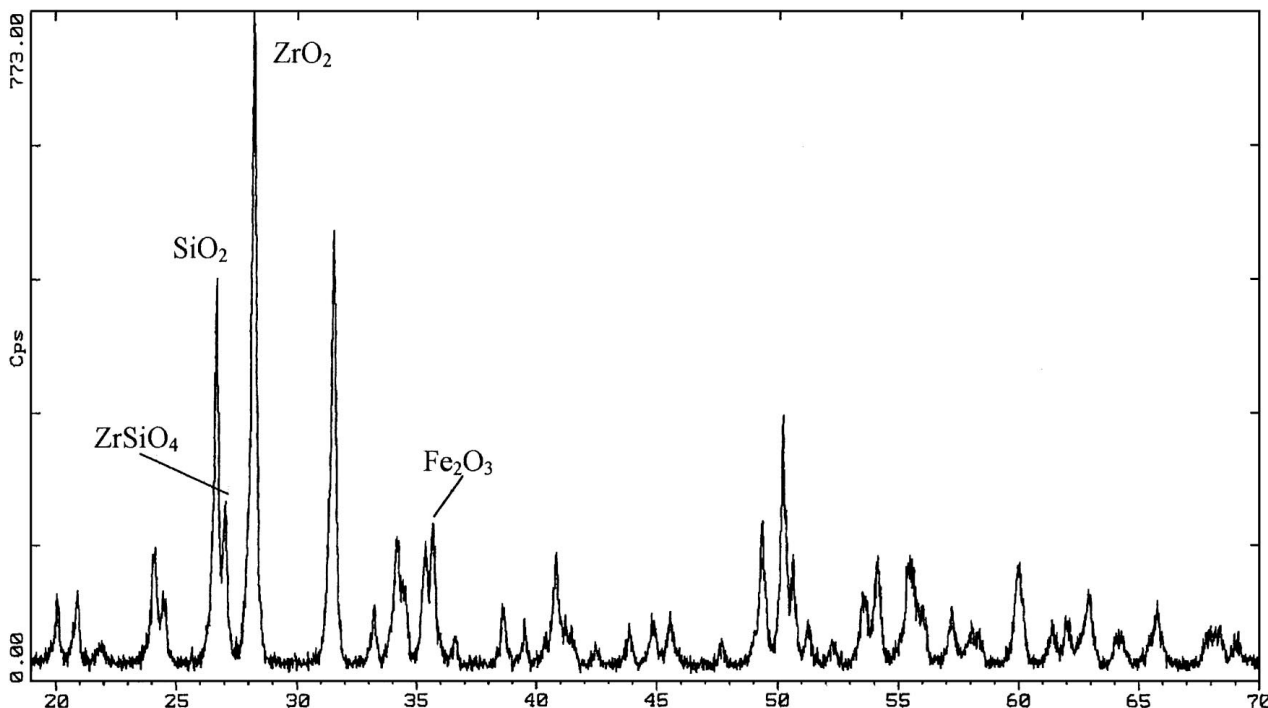


Figure 2 XRD pattern for the calcination product of zirconia, silica and ferrous sulphate.

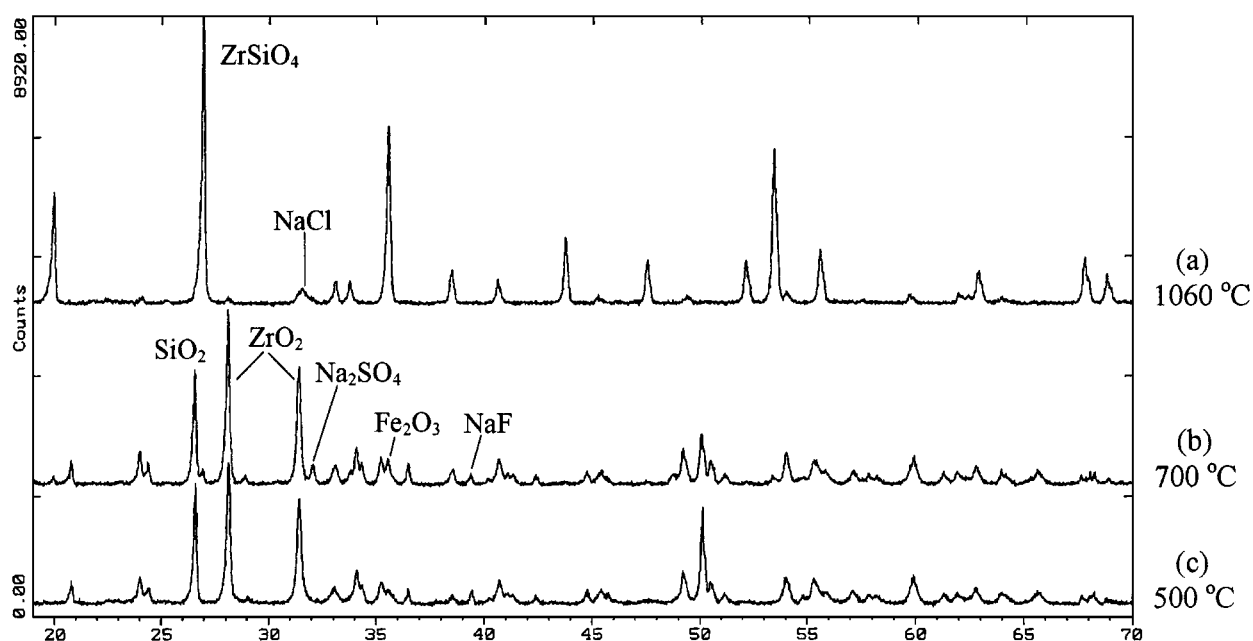


Figure 3 XRD patterns for the calcination products of zirconia, silica, ferrous sulphate and mineralisers (1.55 wt % Fe) at 500, 700 and 1060 °C.

reappeared after calcination at 1060 °C, suggesting a catalytic involvement in the reaction process. The appearance of sodium sulphate in the product formed at 700 °C, implies the reaction of ferrous sulphate with one of the sodium salts present. NaCl disappears not only in both these reactions but also during the reaction to form undoped zircon, and so may not be implicated in the formation of sodium sulphate. However, the amount of NaF in the product decreased both with calcination temperature and with increasing amounts of iron(II) sulphate in the reaction mixture, so it seems likely that the sodium fluoride reacts with the ferrous sulphate on calcination at 700 °C to give sodium sulphate which

decomposes at elevated temperatures. No unreacted silica or NaF was observed by XRD after calcination at 1060 °C.

During the preparation of both zircon and the iron-doped zircon using mineralisers, it was observed that a glassy phase, shown by XRD to be amorphous, formed on the upper sides and lid of the crucible. EDX analysis (Fig. 4) showed that the glass contained Al, Si, Mg, K, Ca, Fe and F. All of these elements, except F, were also identified in the crucible material. (The measurement of the concentration of F using EDX, is not quantitative, due to absorption of some of the characteristic X-rays by the Be window.) In addition, the Si

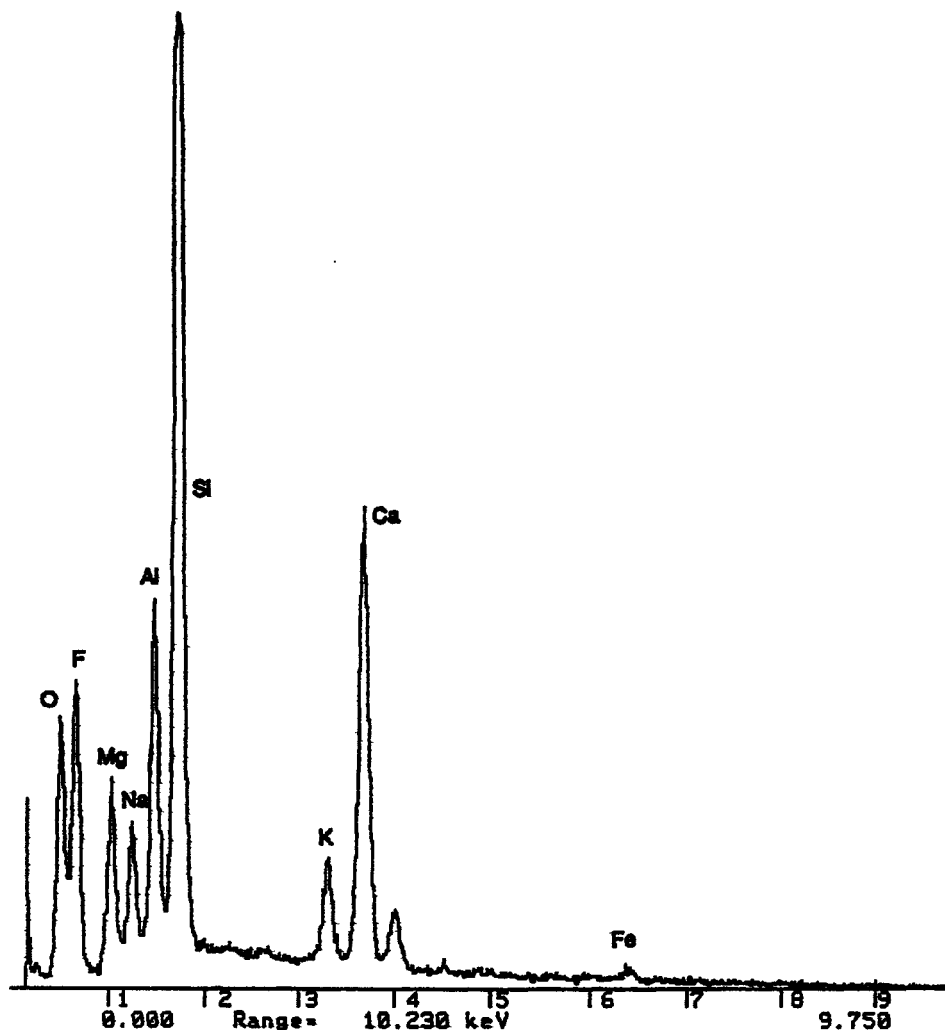


Figure 4 EDX analysis of the glassy phase.

TABLE III Phases detected in the preparation of iron-doped zircon in the presence of mineralisers, calcined at 500, 700 and 1060 °C

Conc. iron/ wt % Fe	Phases present						
	ZrO ₂	SiO ₂	Fe/ZrSiO ₄	α-Fe ₂ O ₃	NaF	NaCl	Na ₂ SO ₄
500 °C							
0.19	✓	✓	×	×	✓	×	×
0.22	✓	✓	×	✓	✓	×	×
1.55	✓	✓	×	✓	✓	×	×
700 °C							
0.19	✓	✓	×	×	✓	×	×
0.22	✓	✓	×	✓	✓	×	✓
1.55	✓	✓	✓	✓	✓	×	✓
1060 °C							
0.19	✓	×	✓	×	✓	✓	×
0.22	✓	×	✓	✓	✓	✓	×
1.55	✓	×	✓	✓	×	✓	×

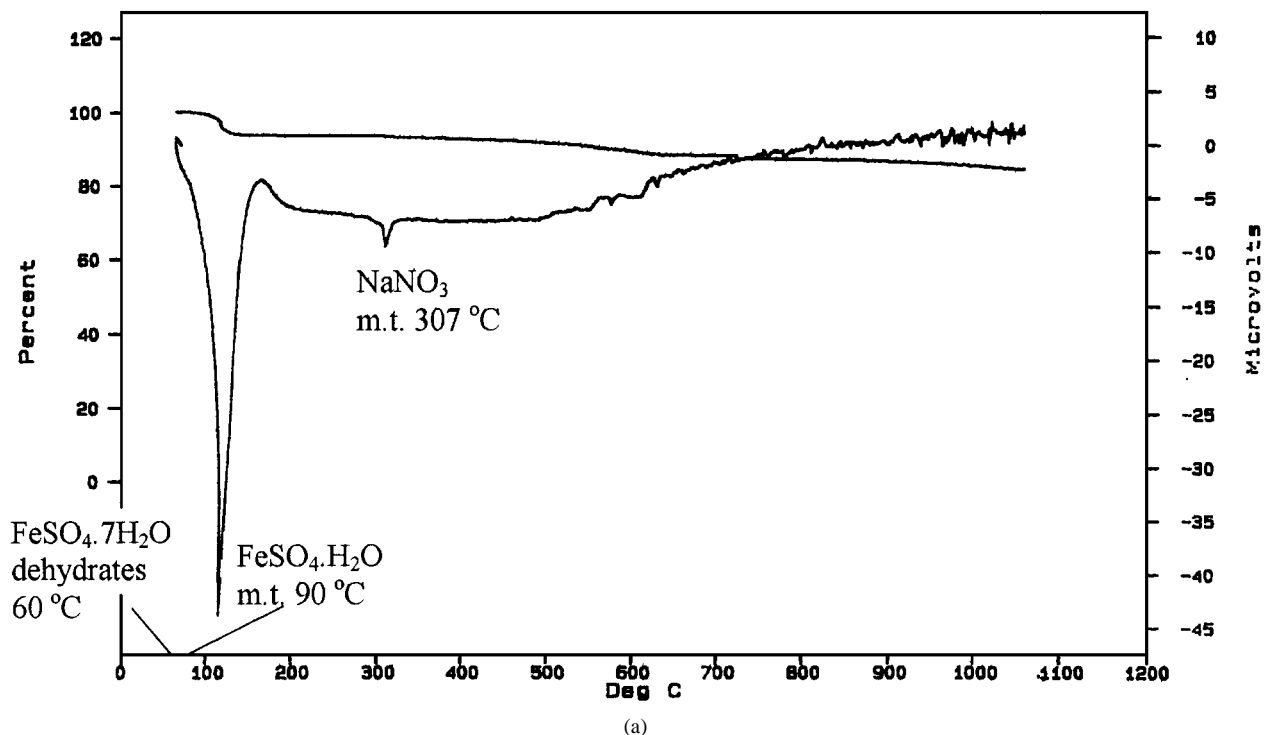
KEY: ✓ phase detected, × phase not detected.

peak in the EDX data recorded from the glaze was much bigger than that corresponding to the Si content of the crucible material. The results are indicative of a significant silicon concentration in the glaze which is formed during the reaction process. The observations suggest that the volatile species condensing to form the glaze contain silicon-fluorine species. This is consistent with

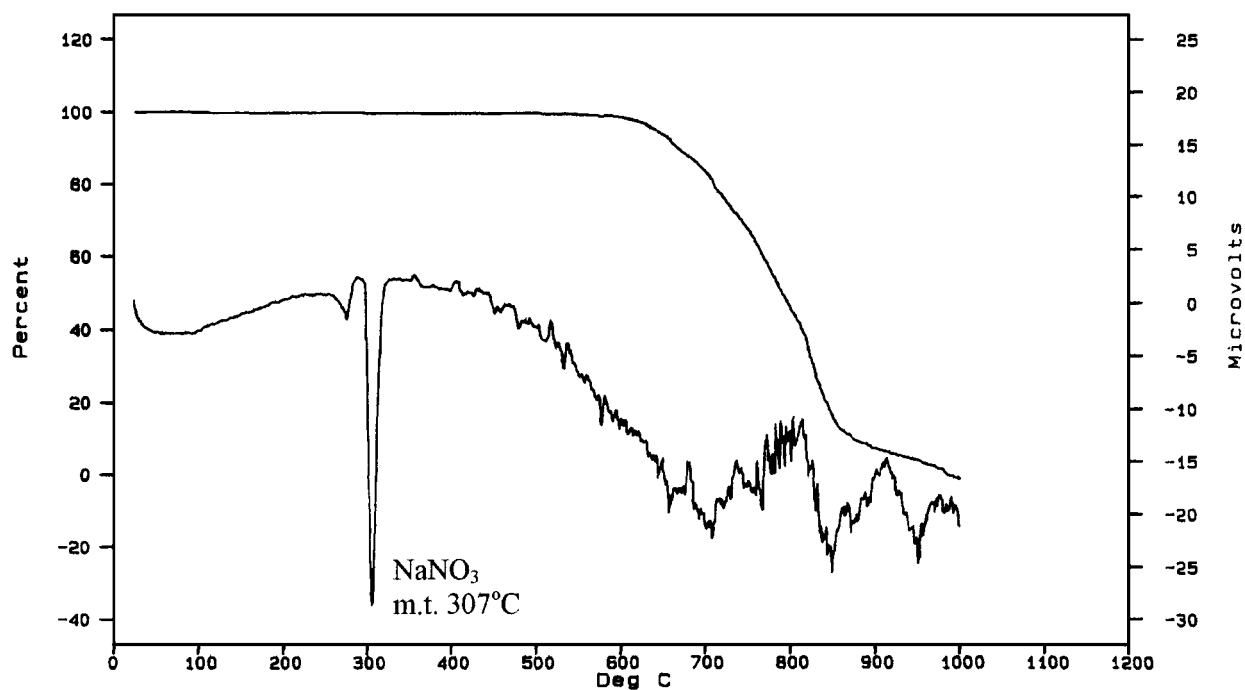
the XRD evidence for the loss of silica and the decrease in sodium fluoride in the products formed at 1060 °C.

The mechanism of the reaction was examined by STA and thermal mass spectrometry. The STA profile for the reaction mixture is compared with the profiles for FeSO₄·7H₂O and NaNO₃ in Fig. 5. The initial weight loss in the reaction mixture, up to 100 °C, corresponds to the loss of six of the water molecules from FeSO₄·7H₂O at 60 °C (Fig. 5c) (the final water molecule is lost at 300 °C when FeSO₄ boils) [10]. The endotherm at low temperature corresponds to the melting of ferrous sulphate [10] (Fig. 5c) and the endotherm at about 300 °C to the melting of the alkali metal nitrate (Fig. 5b) [10].

The STA profiles of pairs of mineralisers are shown in Fig. 6. A 1 : 1 mixture of NaF and NaCl (Fig. 6a) showed one sharp endotherm at ~680 °C, which is a lower temperature than that recorded for either of the individual compounds (993 and 801 °C respectively) indicating reaction between the two sodium halides which we associate with the formation of a low temperature flux thus facilitating reactant diffusion. This temperature coincides with the temperature at which Fe/ZrSiO₄ formation is first observed (Table III). The results recorded from a 1 : 1 mixture of NaF and MnO₃ (Fig. 6b) appear to be a superposition of the individual profiles of each salt, and indicate that no reaction has taken place



(a)



(b)

Figure 5 STA profiles for (a) the reaction mixture: ZrO_2 , SiO_2 , $FeSO_4 \cdot 7H_2O$, NaF , $NaCl$ and MnO_3 , (b) $NaNO_3$ and (c) $FeSO_4 \cdot 7H_2O$. (Continued)

at temperatures up to $1100^\circ C$. The STA profiles from a 1 : 1 mixture of $NaCl$ and $NaNO_3$ (Fig. 6c) showed several endotherms; the one at $\sim 300^\circ C$ is consistent with the melting of $NaNO_3$, but the two small peaks at $260\text{--}290^\circ C$ do not correspond to the melting temperatures of either $NaNO_3$ ($307^\circ C$) or $NaCl$ ($801^\circ C$) and so are indicative of an interaction between the two salts. We associate this with the provision of oxidising conditions in the reaction between the alkali metal salts and the ferrous sulphate (see below).

Thermal mass spectrometry was used to detect the volatile species emitted during the reaction. Water was evolved at $\sim 100^\circ C$ and at $190\text{--}250^\circ C$ corresponding

to the loss of added water and to the dehydration of ferrous sulphate. NO from the decomposition of MnO_3 [11] was detected at 220 and $380^\circ C$. These temperatures are lower than expected for the decomposition of pure nitrate because of the interaction with $NaCl$. (NO_2 was not detected because the oxidation of NO to NO_2 is third order and only very small quantities would be expected.) SiF_3 was detected between 600 and $800^\circ C$ in small quantities, probably as a breakdown product of SiF_4 . SiF_4 , with a mass of 104 amu, was outside the detection limits of the spectrometer.

Experiments using individual salts as the mineraliser for the formation of iron-doped zircon showed the alkali

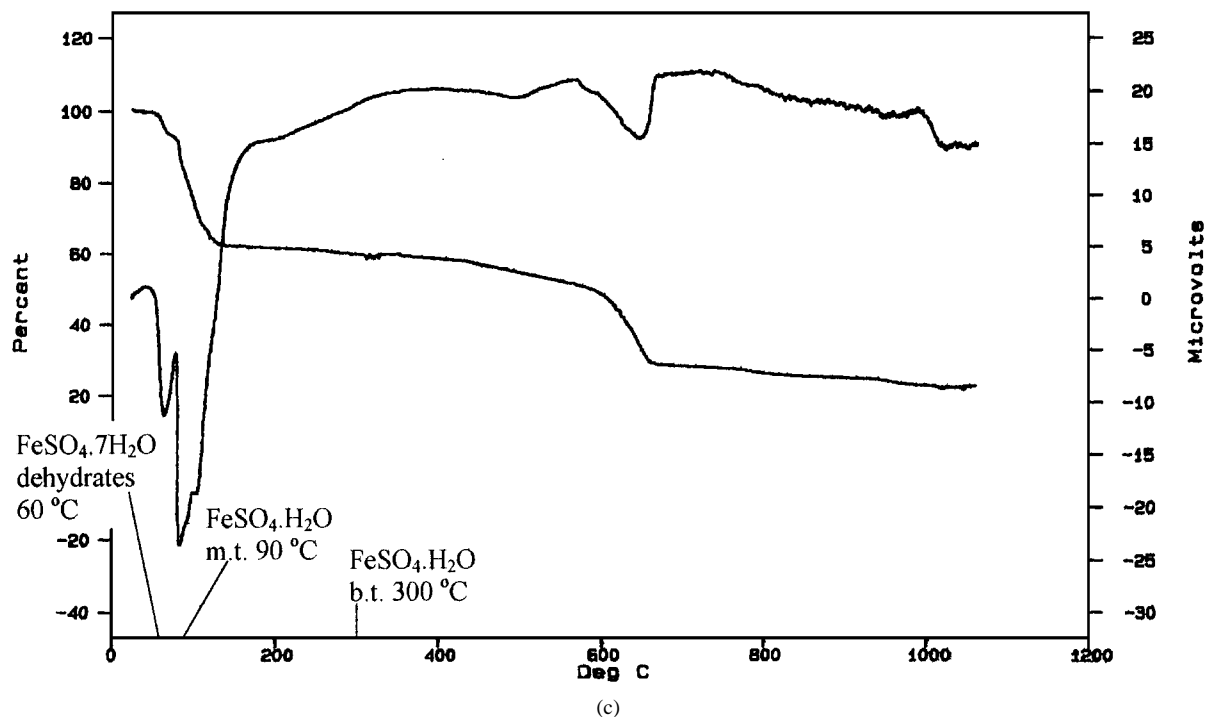


Figure 5 (Continued).

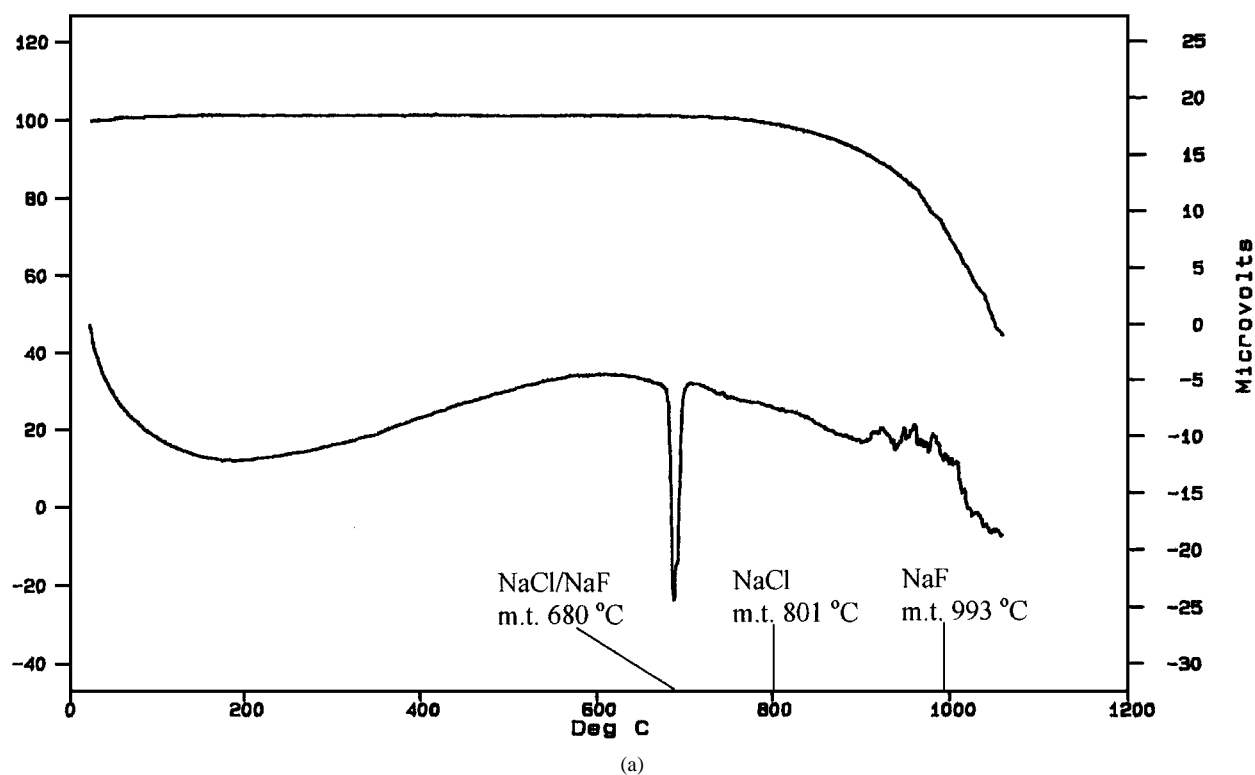


Figure 6 STA profiles for (a) a mixture of NaCl and NaF, (b) a mixture of NaF and NaNO₃ and (c) a mixture of NaCl and NaNO₃. (Continued)

metal fluorides to be more effective than the chlorides. Sodium- and potassium-nitrates and sodium sulphate proved to be only very weak mineralisers when used alone. It was also noted that only a small amount of the silicon-containing glaze formed when using chloride as a mineraliser, and none from the use of the nitrates and sulphates. It has not been possible to completely rule out the formation of a silicon-containing glass in the reaction product, which is not detectable. However,

such a glass might be expected to form in the presence of individual sodium salts, and so these observations furnish further evidence that, even if present, such glass formation is not important in the reaction mechanism, but that a volatile silicon fluoride species is involved in the formation of a zircon-related phase.

When ferric sulphate, α -Fe₂O₃ or Fe₃O₄ were used as the source of iron, in the absence of other mineralisers, no Fe/ZrSiO₄ formation was detected. It would

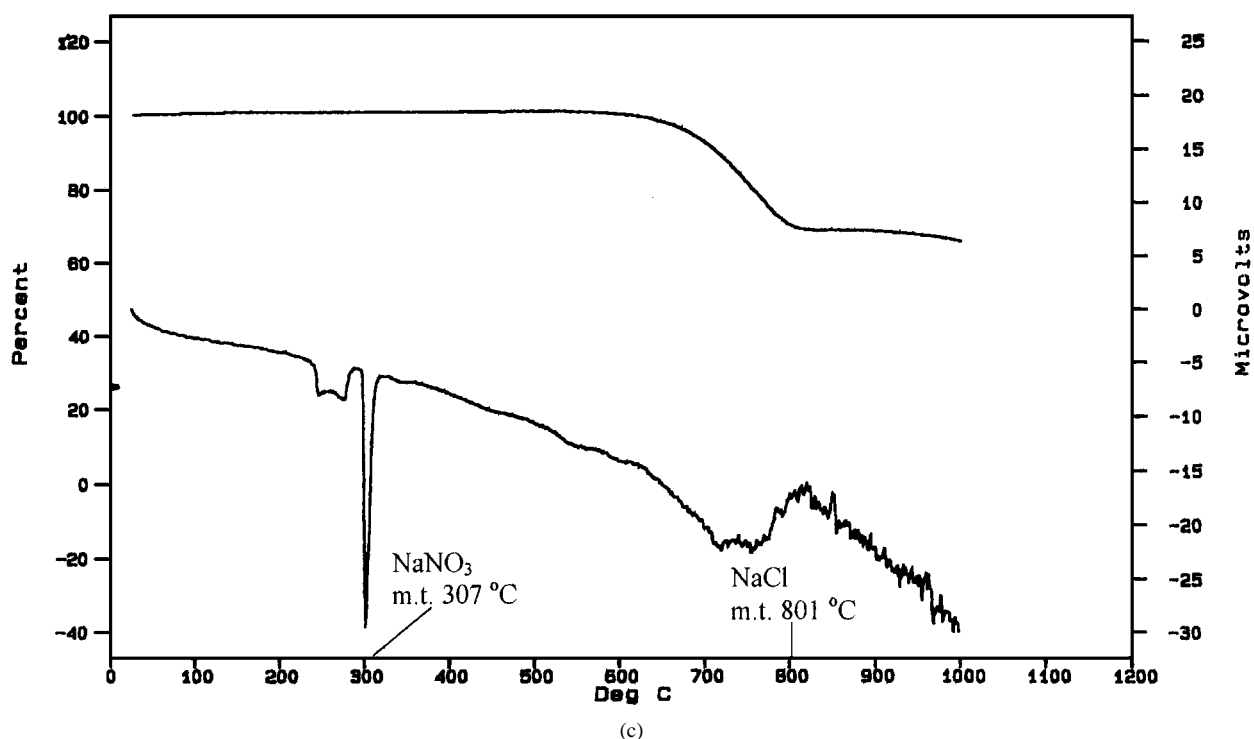
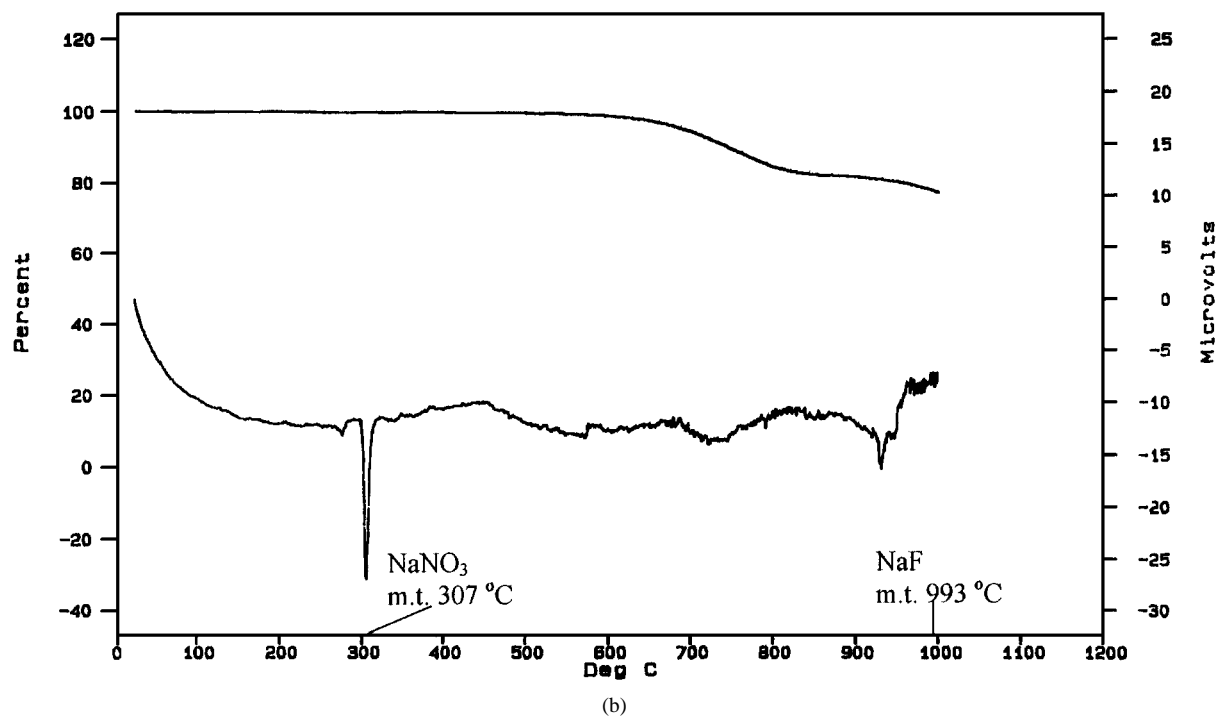
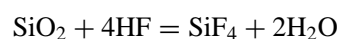
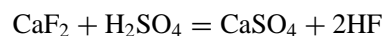


Figure 6 (Continued).

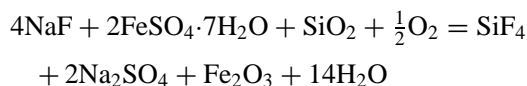
seem therefore, that an initial reaction between the alkali metal salts and ferrous sulphate followed by oxidation to α - Fe_2O_3 , is implicated in the mechanism of zircon formation. Presumably the reaction detected by STA between NaNO_3 and NaCl provides the necessary oxidising conditions and together with the formation of the NaF/NaCl flux, accounts for the disappearance of NaCl in the products isolated at 500 and 700 °C (Table I).

Taken together, the formation of a silicon-fluorine containing glassy phase, as identified by EDX, together with the evidence from mass spectrometry for a SiF_3 breakdown product, and the XRD evidence for the loss of SiO_2 and NaF , all point towards the formation of

a silicon fluoride intermediate in the formation of the iron-doped zircon when using NaF , NaCl and MnO_3 as mineralisers. Silicon tetrafluoride, which is volatile under the conditions of the reaction to form iron-doped zircon, is known to be formed from the reaction of silica, calcium fluoride and sulphuric acid [12]:



We suggest that a similar reaction takes place between silica, sodium fluoride and ferrous sulphate under the oxidising conditions used in this work:



The formation of SiF_4 accounts for the absence of silica and the consumption of sodium fluoride as evidenced by XRD, and results in the formation of the silicon-fluorine containing glaze on the lid and sides of the crucible. This is also consistent with the earlier studies [9] that showed migration of the silica to the zirconia during reaction and not vice versa.

4. Conclusion

In summary, our studies suggest that the oxidising conditions of this reaction enable the formation of a volatile silicon fluoride species, such as silicon tetrafluoride, and that this species transports the silicon to the zirconia interface where the reaction to form iron-doped zircon takes place. The diffusion process is facilitated by the formation of a low-temperature flux from NaF and NaCl at 680 °C.

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