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Preparation of Si–C–N–Fe magnetic ceramics from iron-containing polysilazane

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A new type of hyperbranched polysilazane containing iron (PSZI) compound was synthesized by the polycondensation of silazane lithium salts with $FeCl_3$, and the structure of the PSZIs was investigated by IR, NMR and elemental analyses. The PSZIs were pyrolyzed under nitrogen, argon or NH_3, and magnetic ceramics could be obtained. The ceramic yields of the PSZIs were higher than those of their corresponding silazanes, and the PSZIs or silazanes with reactive groups containing Si—H, —CH=CH_2 or higher branched structures had higher yields. The magnetism of the ceramics could be controlled by a pyrolytic atmosphere and temperature: the saturation magnetization M_s ranged from 20 to 100 emu g^{-1} and coercivity H_c ranged from 463 to 50 Oe. The transformation of the magnetic loop of the PSZIs pyrolyzed at different temperatures under NH_3 was quite different from those under nitrogen. It was shown by X-ray diffraction measurements that the magnetic crystalline form could exist as Fe_4N, Fe(0) or Fe_3N depending on temperature under NH_3, but under a nitrogen atmosphere Fe(0) was nearly the only magnetic crystalline form from 600 to 1100 °C. By dipping or spin-coating of the PSZI solution, then through pyrolysis under nitrogen, argon or NH_3, thin uniform magnetic ceramic films could be fabricated on the substrates. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: polysilazane containing iron; ceramic composite; magnetic ceramics; precursor; pyrolysis; Si–C–N–Fe; iron nitride

INTRODUCTION

High-performance ceramics, especially SiC, Si_3N_4, or Si–C–N-based materials, are of considerable interest because of their high thermal and chemical stabilies, low density, and high mechanical strength and hardness. In the past two decades, intense research[1–12] has focused on fabrication of these materials by pyrolysis of organosilicon polymers or oligomers. This offers several advantages, including milder processing temperatures and improved control over composition, microstructures and final form of the materials. Although most of the work on polymer-derived ceramics has emphasized the mechanical strength and stability of materials, some researchers have paid more attention to the electronic and magnetic properties of the polymer-derived materials.[13–20] Pyrolysis of poly(ferrocenylsilanes) was used by Manners and coworkers to obtain magnetic Si–C–Fe ceramics.[13–15] Corriu and coworkers prepared Si–C–Fe(Co) or Si–C–Fe(Co)–O ceramics by pyrolysis of polycarbosilanes containing metal (iron or cobalt) carbonyl[16,17] groups.

Recently, we have synthesized a series of polysilazanes containing a transition metal as precursor of Si–C–N–M ceramics by the condensation reaction of silazane lithium or sodium salts with MCl_n (M = Fe, Ti, Zr; n = 2–4). Although as early 1963 Burger and Wannagat first reported on molecules containing Si—N—M bonds synthesized by this method,[21] and some other authors continually used this reaction to synthesize new compounds,[22–24] polymers containing Si—N—M bonds prepared by this method have not been reported. This paper describes both the synthesis of a new

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polysilazane containing iron (PSZI) using this method and the pyrolysis of PSZI to prepare magnetic ceramics.

EXPERIMENTAL

Materials

All chlorosilanes were purchased from the Kaihua Organosilicon Factory in China and purified by distillation. Tetrahydrofuran (THF), *n*-hexane and toluene were commercially available and dried by refluxing over sodium and distilled under nitrogen. *n*-Butylithium (*n*-BuLi; 1.6 M in hexane) was purchased from Aldrich.

Synthesis of cyclosilazane and silazane oligomers

Hexamethylcyclotrisilazane (SiN-1) prepared according to the literature[25] was the product of ammonolysis of Me_2SiCl_2. The silazane oligomers SiN-2, SiN-3 and SiN-4 were obtained from co-ammonolysis of $Me_2SiCl_2/MeSiCl_3$ = 1:1, $Me_2SiCl_2/ViSiCl_3$ = 1:1 and $MeHSiCl_2/Me_2SiCl_2/ViSiCl_3$ = 0.5:0.5:1 in molar ratio respectively. A typical procedure is described as follows. Into a 5000 ml three-necked flask containing a reflux condenser, a gas inlet tube and a mechanical stirrer under nitrogen were added 3000 ml of toluene, 2.1 mol (271 g) of Me_2SiCl_2 and 2.1 mol (314 g) of $MeSiCl_3$. Dry NH_3 was introduced into this system accompanied by high-speed stirring until no NH_3 was absorbed (about 24 h) at room temperature or cooled with water. The reaction mixture was filtered, then 1000 ml toluene was added to wash the slurry two or three times, and ammonium chloride was removed to obtain a transparent solution. The solution was concentrated and dried below 80 °C under vacuum to a constant weight. The product (SiN-2) was obtained as 253 g of viscous liquid in 87% yield. The same synthetic procedure was used for SiN-3 and SiN-4, except that the solution was concentrated and dried below 60 °C under vacuum, and viscous liquid products in 85% and 78% yields were obtained respectively.

Synthesis of silazane lithium salts and PSZIs

Silazane lithium salts were prepared according to the method of Fink,[26–28] and then $FeCl_3$ was added to react with them directly.

Into a 250 ml three-necked flask equipped with a dropping funnel and a gas inlet tube, 60 ml of freshly distilled *n*-hexane and 15.8 g (0.072 mol) SiN-1 were added, and 128 ml 1.6 M *n*-BuLi was charged into the dropping funnel by syringe after air was replaced by dry nitrogen. *n*-BuLi was added in a dropwise manner while stirring, and a white precipitate formed. The reaction mixture was stirred for 8 h at room temperature, and then the solvent was removed by filtration under nitrogen. Under the protection of nitrogen, 160 ml toluene, 2 ml triethylamine and 11.09 g (0.068 mol) $FeCl_3$ was added into the flask while stirring, then the flask was heated to 80 °C and kept at that temperature while continuously stirring for 24 h. After standing overnight, the upper black solution was filtered out, and 80 ml toluene was added into the flask to wash the slurry. The procedure of washing and filtration was repeated twice more. The incorporated solution was concentrated to 100 ml by distillation under vacuum below 80 °C, and 100 ml hexane was added into it while stirring. After standing for more than 24 h, the solution was filtered, and the solvent was distilled under vacuum to give 16.6 g of black solid, denoted as PSZI-1.

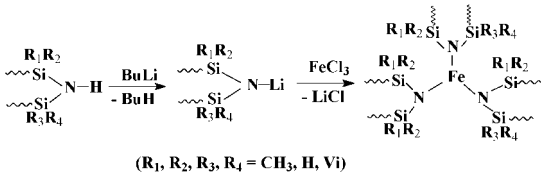
Into a 1000 ml three-necked flask equipped with a dropping funnel and a gas inlet tube, 265 ml *n*-hexane and 32.55 g SiN-2 were added, and 195 ml 1.6 M *n*-BuLi was charged into the dropping funnel by syringe under the protection of dry nitrogen. The *n*-BuLi was added in a dropwise manner while stirring. The reaction mixture was stirred for 24 h at room temperature. After standing for several hours, the 100 ml upper clear solvent was removed by filtration, then 150 ml THF, 5 ml triethylamine was added into the flask while stirring, 17.0 g $FeCl_3$ dissolved in 200 ml THF was discharged into the dropping funnel, and then the flask was heated to reflux for 24 h. After standing overnight, the upper black solution was filtered out; the slurry was washed with 80 ml toluene three times. Then the incorporated solution was distilled under vacuum below 50 °C to remove THF, and 300 ml toluene and 150 ml hexane was added into it to dissolve the residual product with stirring. After standing for over 24 h, the solution was filtered to remove the insoluble residue, and the solvent was distilled under vacuum to give 35.8 g of black solid, denoted as PSZI-2. The preparation procedure used for PSZI-2 was also used to prepare PSZI-3 from SiN-3 and PSZI-4 from SiN-4.

Pyrolysis

Pyrolysis was performed using an SK-1-10 tube furnace equipped with an Intelligent Universes PID controller and quartz tube. Al_2O_3 ceramics boats were used to contain the precursors in the quartz tube. After the samples (1–3 g) were introduced in the tube, it was evacuated and purged with nitrogen, argon or NH_3 three times before heating. Then the gas flow was controlled at 40 ml min^{-1}. The temperature program used was as follows: ambient temperature to 150 °C at 2.5 °C min^{-1}, then 0.75 °C min^{-1} to 350 °C, hold 0.5 h at 350 °C, then 1 °C min^{-1} to a given temperature, hold at this temperature for 1 h, then cool to ambient temperature. As a control, a heating rate of 5.0 or 1.0 °C min^{-1} was also applied.

Measurements

The ^1H and ^{29}Si NMR spectra were recorded on a Unity 200 or Bruker WM 300 spectrometer using $CDCl_3$ for ^1H and $THF/CDCl_3$ = 1/1 for ^{29}Si as solvent. IR spectra were measured on a PE 2000 IR spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 TGA, at a heating rate of 10 °C min^{-1} under nitrogen. X-ray diffraction (XRD) diagrams were recorded on a powder



Scheme 1.

diffractometer (Rigaku D/M4X 2500) using Cu Kα radiation. The morphology of the pyrolysis products was investigated on an S-530 scanning electron microscope (SEM). Magnetization measurements were carried out using a vibrating sample magnetometer (LDJ 9600) at a temperature of 300 K.

RESULTS AND DISCUSSION

Synthesis and characterization of the PSZIs

PSZIs were prepared from the reaction of silazane lithium salts with $FeCl_3$, and silazane lithium salts were synthesized from the reaction of silazane with *n*-BuLi as shown in Scheme 1. Because of multifunctional condensation, too high a lithiation degree (Li/NH molar ratio) will make the reaction of silazane lithium salts with $FeCl_3$ difficult, and the isolation of products also becomes troublesome. In our experiments, with a lithiation degree of 1/2–2/3, the polycondensation reaction can take place smoothly in THF, or a mixture of THF with toluene or hexane at above 60 °C. For SiN-1, using a lithiation degree up to 0.95 and toluene as solvent can also make the reaction and isolation proceed without difficulty.

Although the products were complex because of the complication of 3–2 or 3–3 polycondensation between silazane lithium salts and $FeCl_3$, the PSZIs were characterized by NMR, FTIR spectra, and elemental analyses. The IR absorptions (Fig. 1) of SiN-*x* and PSZIs are at 2954–2960, 2897–2960 and 1403–1408 cm^{-1} (C—H), 1253–1260, 790, 839 cm^{-1} (Si—CH_3), 3390 and 1170–1180 cm^{-1} (N—H), and

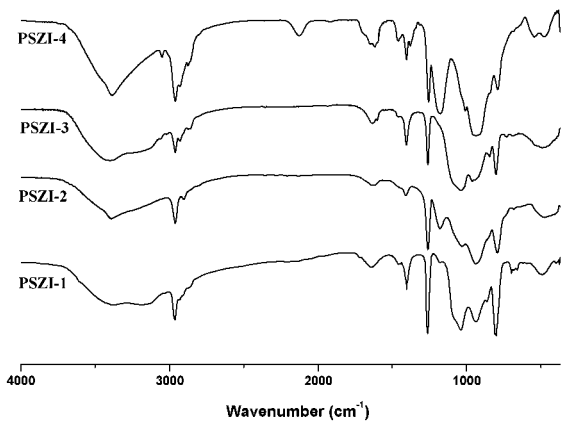


Figure 1. The FTIR spectra of PSZIs.

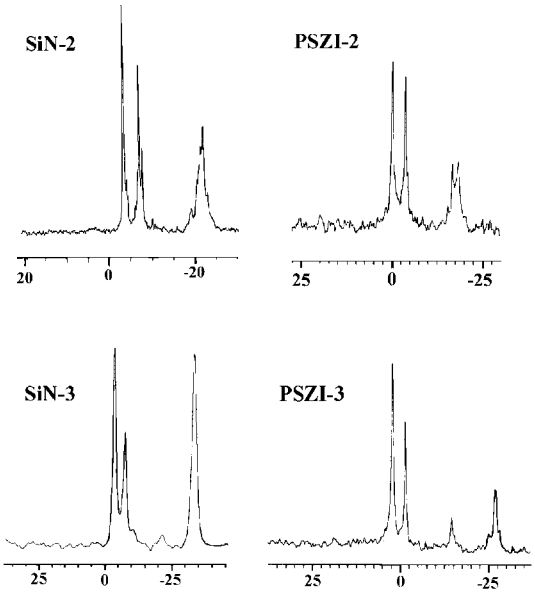
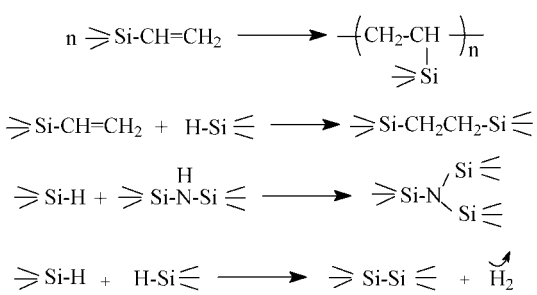


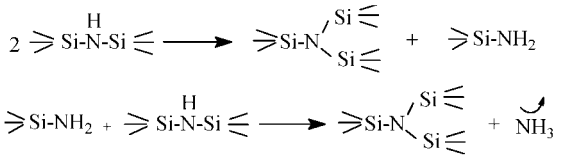
Figure 2. The ^{29}Si NMR of PSZI-2 and PSZI-3 and their corresponding silazanes (relative to tetramethylsilane: $\delta = 0$).

940 cm^{-1} (Si—N—Si). In the IR spectra of SiN-3, SiN-4, PSZI-3 and PSZI-4, absorptions at 3048, 3007, 1594 (—CH=CH_2) are observed; absorption at 2130 cm^{-1} (Si—H) is also observed in SiN-4 and PSZI-4. For PSZIs, three new absorption at 1630–1639, 1035 and 474–494 cm^{-1} appear, which may result from the formation of Si—N—Fe bonds. For the ^{29}Si NMR of SiN-2 (Fig. 2), signals in the range $\delta - 3.8$ to -8.1 are assigned to HN—*Si*Me_2—NH, and $\delta - 21$ to -22.4 are assigned to $(HN)_3$—*Si*Me; for the ^{29}Si NMR of SiN-3 (Fig. 2), signals in the range $\delta - 3$ to -7 are assigned to HN—*Si*Me_2—NH, and $\delta - 33$ is assigned to $(HN)_3$—*Si*Vi. It is observed that the signals of their counterpart PSZIs shift 4–8 ppm to lower magnetic field. From the ^{29}Si and ^{1}H NMR of the PSZI-3 and PSZI-4, the Vi and Si—H contents decrease considerably, which might result from the reactions shown in Scheme 2 (*n*-BuLi and $FeCl_3$ might promote these reactions).

The SiN-1, SiN-2, SiN-3, and SiN-4 samples are transparent liquids and can be easily dissolved in common



Scheme 2.



Scheme 3.

solvents, such as toluene, THF and hexane. The PSZIs are soluble in acetone and THF, soluble or partly soluble in toluene, and insoluble in hexane; the solubility degree is PSZI-1 > PSZI-2 > PSZI-3 > PSZI-4. After the solvent was extracted, especially for PSZI-4, their resolubility decreased, due to the hyperbranched structure and the gelling or crosslinking reactions at elevated temperature, as shown in Schemes 2 and 3. The iron contents of PSZI-1, PSZI-2, PSZI-3 and PSZI-4 are 16.1%, 12.4%, 12.7% and 11.0% respectively; this is lower than the theoretical content. The nitrogen content of the PSZIs is also somewhat lower than the theoretical content. The chlorine and lithium residue contents are about 0.1–1.0% and 0.1–0.5% respectively (variable from batch to batch).

Theoretical elemental content is on the basis that all Si—NH is completely changed to Si—NLi and then totally converted to Si—N—Fe(1/3). This is not achieved because of side reactions and the complex 2–3 and 3–3 multifunctional condensations. The lithiation degree of SiN-1 is 0.95 and the lithiation degree of SiN-2, SiN-3 and SiN-4 is 0.53, and we can calculate that the theoretical iron and nitrogen contents respectively of PSZIs are as follows: PSZ-1 19.7% and 15.6%; PSZI-2, 15.2 and 21.6; PSZI-3, 14.2 and 20.1; PSZI-4, 14.8 and 21.0. The actual results for these complexes are (in the same order), 16.1 and 13.8; 12.4 and 18.8; 12.7 and 17.2; and 11.0 and 16.9 respectively. The experimental iron content is lower by about 4% than the theoretical and the nitrogen content lower by 2–4%. These results are reasonable in view of the complex oligomeric and polymeric nature of such complexes. Besides the side reactions, the more hyperbranched polysilazanes (containing higher iron and nitrogen) have lower solubility, or gel, and could not be extracted, and this also leads to lower iron and nitrogen contents. Besides the side reaction in Scheme 3, the PSZIs are sensitive to water in air; and hydrolysis of the Si—N bonds during the grinding process and measurements also decrease nitrogen content.

In summary, the PSZIs can be synthesized by this method, but the structure is complicated and detailed structure characterization and investigation is under progress in our laboratory.

Pyrolysis behavior and ceramic yields of PSZIs

To evaluate PSZIs as ceramic precursors, we performed a series of bulk pyrolysis and TGA experiments on these samples and their corresponding silazanes. The TGA curves of silazanes and PSZIs are shown in Fig. 3, and the bulk

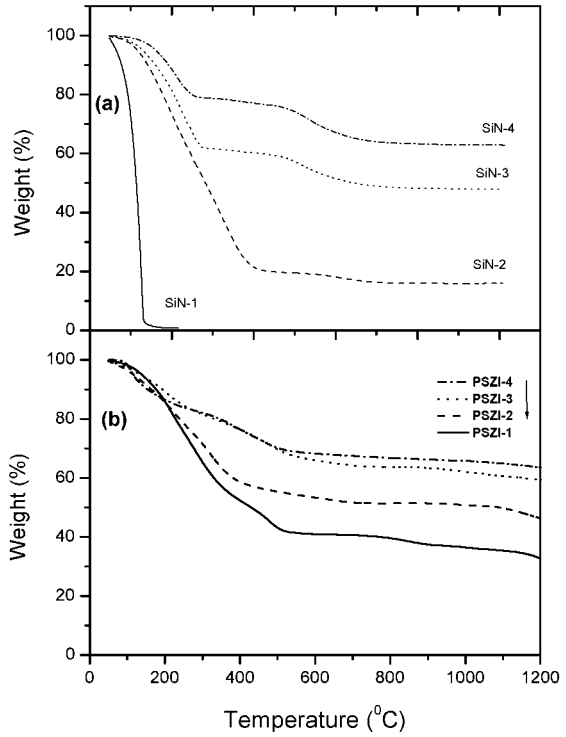
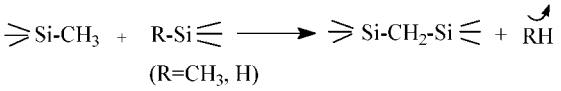


Figure 3. TGA curves of silazane oligomers (a) and PSZIs (b).

pyrolysis results are shown in Table 1. The pyrolytic behavior and yields of the preceramic polymers are affected by their structure. SiN-1 has no branched structure and reactive group; SiN-2, SiN-3, and SiN-4 have similar branched structures containing about 50% ═SiNH and 50% —$Si(NH)_{1.5}$, but different substituents are attached on the silicon atoms: SiN-3 contains the reactive group —CH═CH_2, and SiN-4 contains —CH═CH_2 and Si—H, so the ceramic yield order is SiN-4 > SiN-3 > SiN-2 > SiN-1. For the same reasons, the order of yields for the PSZI is PSZI-4 > PSZI-3 > PSZI-2 > PSZI-1. This agrees with the literature,[1] that the presence of a crosslinked structure or the capability of a

Table 1. Bulk pyrolytic yields of PSZIs and silazane oligomers at 900 °C

	Yield (%)	
Sample	N_2	NH_3
SiN-1	0.2	
SiN-2	16	
SiN-3	47	
SiN-4	65	
PSZI-1	28	25
PSZI-2	58	44
PSZI-3	68	58
PSZI-4	72	63



Scheme 4.

polymer to crosslink further at low temperature thwarts the thermolytic retroversion reaction, frequently encountered in organosilicon chemistry. The heating rate also affects the pyrolytic yield considerably. Under nitrogen or argon the pyrolytic yield of PSZI-1 and PSZI-4 at a heating rate of 5 °C min^{-1} is almost equal to that at 1 °C min^{-1}; however, for PSZI-2 and PSZI-3, the yields at a heating rate of 5 °C min^{-1} are about 48% and 64% respectively, but are respectively 10% and 4% lower than that at 1 °C min^{-1} (58% for PSZI-2, 68% for PSZI-3). When the silazane ceramics precursor is pyrolyzed under an inert atmosphere, the thermolytic retroversion reaction and crosslinking reaction as shown in Schemes 2–4 take place simultaneously. For PSZI-2 and PSZI-3, a lower heating rate is more favorable for the crosslinking reactions. For PSZI-1, the overall effect of the crosslinking and retroversion reaction means that the heating rate hardly affects the yield. For PSZI-4, the high reactive Si—H and Si—Vi bonds make a heating rate of 5 °C min^{-1} sufficient to crosslink, so no evident yield difference exists between heating rates of 5 and 1 °C min^{-1} either. From Table 1, we can observe that the pyrolysis atmosphere also plays a crucial role in the ceramic yield. Under NH_3, the pyrolytic yield is lower than that for dinitrogen and argon. In fact, the pyrolytic yields of PSZIs and silazane oligomers at 600 °C are almost the same as those at 900 °C, and the yields at 300 °C under NH_3 are almost the same as under dinitrogen, so incorporation of nitrogen with associated loss of carbon occurs at 300–600 °C.

Magnetism of pyrolytic residue of the PSZI

All the pyrolytic products of PSZIs at above 500 °C can be readily attracted to a bar magnet at room temperature. We thus used the vibration sample magnetometer to investigate their magnetization behavior in magnetic fields.

The magnetic loop of PSZI-1 pyrolyzed at different temperatures under nitrogen and NH_3 is shown in Fig. 4. Under nitrogen, M_s increases with the pyrolytic temperature, and increases to 85.2 emu g^{-1} at 900 °C; on the other hand, magnetic remanence M_r and H_c increase to a maximum at 600 °C, and then decrease with temperature. But under NH_3, M_s increases to a maximum at 700 °C, and then decreases with temperature; the M_r and H_c change little with temperature, as shown in Fig. 4b and Table 2. The M_s of PSZI-2, PSZI-3 and PSZI-4 pyrolyzed at 900 °C under nitrogen or at 700 °C under NH_3 is about 20–40 emu g^{-1}. The transformation of the magnetic loop of PSZI-1 pyrolyzed at different temperatures and with different atmospheres can be explained by a change of the major magnetic

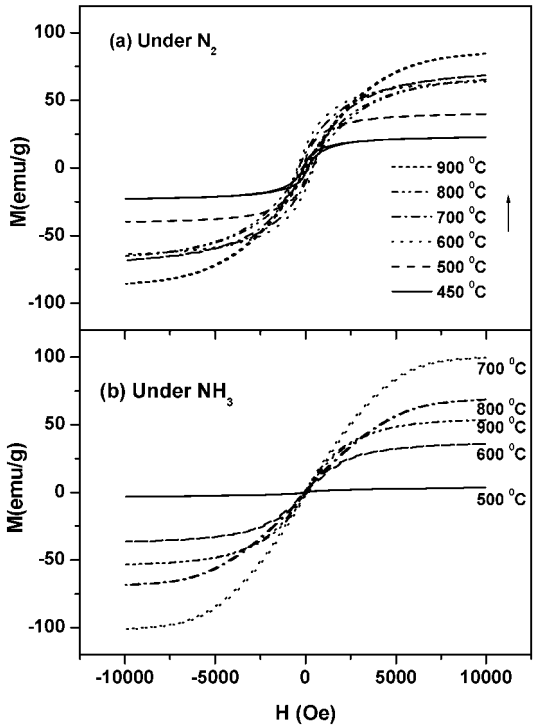


Figure 4. Hysteresis loops for PSZI-1 pyrolyzed at different temperatures.

crystallite. The XRD patterns of these samples are shown in Figs 5 and 6. These reveal that iron is the magnetic component of the PSZI pyrolyzed under nitrogen or argon from 600 to 1100 °C; however, under NH_3, the crystallite is Fe_3N at 500 and 600 °C, Fe_4N and iron at 700 °C, iron at 800 °C and Fe_4N and Fe_3N at 900 °C. It is reported[29,30] that Fe_4N and Fe_3N have bulk M_s values of 208 emu g^{-1} and 123 emu g^{-1} respectively. So, when PSZI-1 is pyrolyzed under NH_3 at 800 °C or higher temperatures, the M_s of the as-prepared ceramics decreases. When pyrolyzed under air, because only weakly magnetic α-Fe_2O_3 is formed, the M_s of the ceramics is only 10–20% of that under nitrogen and argon, and the product is brown.

Table 2. The magnetism of pyrolytic product of PSZI-1 at different temperature under nitrogen and NH_3

Temperature (°C)	N_2		NH_3	
	H_c (Oe)	M_s (emu g^{-1})	H_c (Oe)	M_s (emu g^{-1})
450	101.0	22.7		
500	143.3	39.9	62.9	3.43
600	462.6	63.9	70.8	35.9
700	380.2	68.4	69.6	100.5
800	190.0	65.4	43.4	68.7
900	50.0	85.2	57.4	53.6

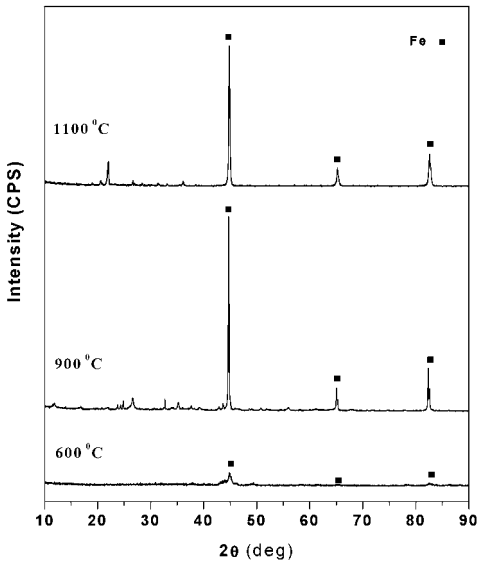


Figure 5. XRD of PSZI-1 pyrolyzed at different temperatures under nitrogen.

Toluene or THF solutions of PSZI-4 will gel after about 1 or 2 months sealed storage at room temperature, but solutions of PSZI-1, PSZI-2 and PSZI-3 can be kept stable for a long time, and can be fabricated into uniform thin films by dipping or spin-coating, as shown from the SEM morphology in Fig. 7. This offers a simple and valid way to fabricate magnetic thin films, which is attractive for industrial applications.

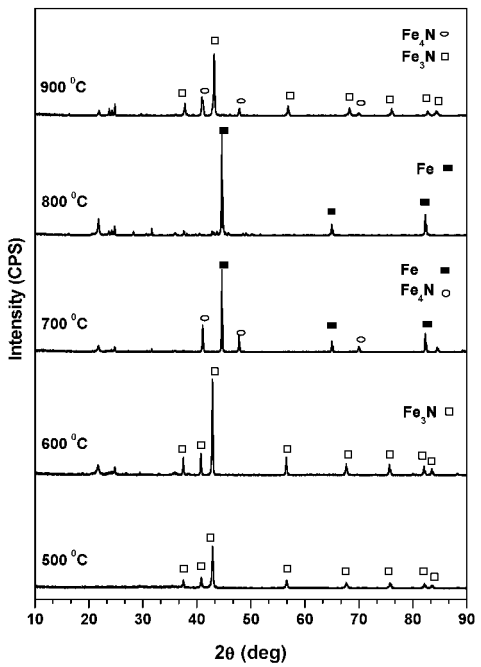


Figure 6. XRD of PSZI-1 pyrolyzed at different temperatures under NH_3.

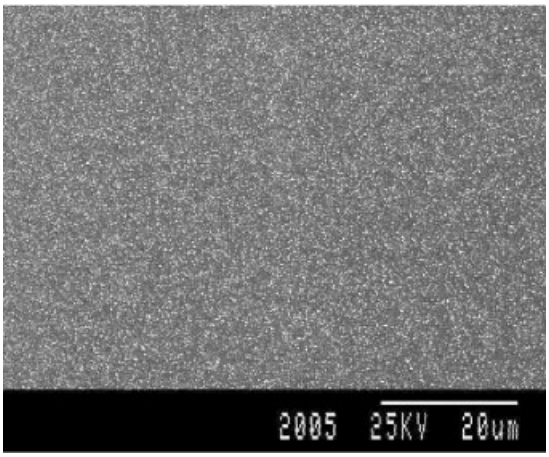


Figure 7. SEM image. Film of PSZI-2 on silicon wafer pyrolyzed at 700 °C under NH_3.

CONCLUSIONS

Iron can be incorporated into the main chain of polysilazanes by polycondensation of silazane lithium salts with $FeCl_3$. The condensation reaction can take place in warm THF, toluene, or a mixture of THF with hexane. This new PSZI can be transformed into Si–C–N–Fe ceramic materials, whose electrical and magnetic properties can be controlled by designing the structure and pyrolysis conditions of PSZI. The PSZIs with reactive groups like Si—H and —CH=CH_2, or higher branched structures, have higher ceramic yields. By dipping or spin-coating of PSZI solutions, then through pyrolysis under nitrogen, argon or NH_3, thin uniform magnetic films can be fabricated on the substrates.

Acknowledgements

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