Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 28 (2008) 177–181

www.elsevier.com/locate/jeurceramsoc

Formation of inorganic polymers (geopolymers) from 2:1 layer lattice aluminosilicates

Kenneth J.D. MacKenzie*, Suwitcha Komphanchai, Ray Vagana

School of Chemical and Physical Sciences, Victoria University of Wellington,
P.O. Box 600, Wellington, New Zealand

Received 25 February 2007; received in revised form 4 June 2007; accepted 21 June 2007
Available online 6 August 2007

Abstract

Attempts to produce fully reacted aluminosilicate inorganic polymers (judged on the basis of their hardening at ambient temperatures, amorphous XRD patterns and their ^{27}Al and ^{29}Si NMR spectra) from the crystalline 2:1 layer lattice mineral pyrophyllite were unsuccessful. Although dehydroxylation of this pyrophyllite at 800 °C produces significant changes in the Al coordination, the dehydroxylate does not form a viable geopolymer, probably because of its retention of a crystalline 2:1 layer structure which encloses the Al–O sheet by Si–O sheets and prevents alkaline attack to form soluble aluminate species.

Disruption of the crystalline 2:1 layer lattice structure by severe mechanochemical processing (ball-milling for 60 h or vibro-milling for 15 min) leads to the formation of four-, five- and sixfold coordinated Al as in metakaolinite, and enables viable inorganic polymers to be formed at 60 °C which show the characteristic XRD, ^{27}Al and ^{29}Si MAS NMR spectra. These results illustrate the important role of the aluminate species in the formation of aluminosilicate inorganic polymers.

Keywords: Geopolymers; Pyrophyllite; Mechanochemical processing; Inorganic polymers

1. Introduction

Inorganic polymers (often termed geopolymers[1]) are typically formed by reaction between a solid aluminosilicate and sodium silicate solution under highly alkaline conditions.[1] The solid aluminosilicate is typically metakaolin (the dehydroxylated form of the 1:1 layer lattice aluminosilicate mineral kaolinite), and although alkali-activated materials from undehydroxylated kaolinite have been reported,[2] these materials do not cure and harden at ambient temperatures and conditions characteristic of geopolymerisation.[3] In addition to the attainment of final strength at ambient temperatures, the unique features of an aluminosilicate inorganic polymer are the presence of an X-ray amorphous network of aluminium and silicon atoms in solely tetrahedral coordination with oxygen, the charge compensation being provided by alkali metal cations.[4] Solid-state MAS NMR has proved to be the most useful tool for determining the degree of geopolymerisation in these X-ray amorphous systems.[4]

Although the 1:1 layer lattice aluminosilicates are typically used in the preparation of geopolymers, it is of interest to know whether the 2:1 minerals would react similarly. The 2:1 analogue of kaolinite is pyrophyllite, $Al_4Si_6O_{20}(OH)_4$, in which the octahedral Al–O sheet is enclosed above and below by two tetrahedral Si–O sheets to form the repeating unit.[5] The structural (hydroxyl) water associated with the octahedral sheet is removed by heating at 550–900 °C.[5]

Preliminary attempts to synthesise viable geopolymers from pyrophyllite, both unheated and dehydroxylated at 800 °C, failed to produce a product which hardened at ambient temperatures. The aim of the present work was to investigate the reasons for this difference in geopolymerisation behaviour of a well-characterised 2:1 layer lattice aluminosilicate (pyrophyllite) and to determine possible synthesis strategies using this starting material, by using mechanochemical treatment (high-energy grinding) to disrupt the crystalline silicate lattice. In this work,

---

* Corresponding author.
E-mail address: Kenneth.MacKenzie@vuw.ac.nz (K.J.D. MacKenzie).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.06.004

the criteria of geopolymerisation were taken as the hardening of the system at temperatures <60 °C and the development of the typical X-ray and NMR characteristics.[4]

2. Experimental

The pyroplyllite used in this work was a well-characterised crystalline mineral from Pukepaukina, New Zealand, described in detail elsewhere.[5] The main crystalline impurity in this mineral is quartz, with minor amounts of kaolinite and illite. Samples were dehydroxylated by heating at 800 °C for periods up to 24 h, while other samples were prepared by grinding both the unheated and heated mineral in a planetary ball mill (Frisch Pulverisette) at 400 rpm for periods up to 60 h. The milling pot and media (3 mm diameter balls) were of toughened zirconia and the weight ratio of sample:media was 1:50. Other milling experiments were carried out in a vibratory-type mill (Bleuler, Switzerland) for periods of up to 15 min.

All the solid starting materials were subjected to a standardised geopolymer synthesis as follows.

1.5 g of the solid aluminosilicate was blended with 0.5 g NaOH dissolved in 2 g water and 0.5 g sodium silicate solution (FERNZ, NZ, Type "O", concentration 668 g/l, $Na_2O/SiO_2 = 0.3$). The oxide ratios of the reaction mixture (calculated on the basis of the raw pyrophyllite) were: $SiO_2/Al_2O_3 = 4.6$, $Na_2O/SiO_2 = 0.37$, $H_2O/Na_2O = 18.8$, $H_2O/SiO_2 = 6.9$.

The blended mixture was placed in a plastic mould, sealed with plastic film and allowed to cure for 24 h at 60 °C before removal of the film and drying at 60 °C.

Both the raw materials and the corresponding geopolymers were characterised by X-ray powder diffraction (Philips PW 1700 computer-controlled goniometer with Co Kα radiation and a graphite monochromator) and by ^{27}Al and ^{29}Si MAS NMR at 11.7 T (Varian Unity 500 spectrometer with a 4 mm Doty MAS probe spun at 10–12 kHz for Al and 6 kHz for Si). The NMR conditions were:

- ^{27}Al: spectrometer frequency 130.224 MHz with a 1 μs ($\pi/10$ pulse for solution) and a 1 s delay, the spectra referred to $Al(H_2O)_6^{2+}$,
- ^{29}Si: spectrometer frequency 99.926 MHz with a 6 μs ($\pi/10$) pulse and 100 s delay, the spectra referenced to tetramethylsilane (TMS).

3. Results and discussion

The XRD trace of the raw material (Fig. 1a) is consistent with well-crystallised pyrophyllite (ICDD file no. 24–11) together with a significant quartz impurity (ICDD file no. 33–1161) and a trace of kaolinite (ICDD file no. 14–164) and illite (ICDD file no. 25–001). The ^{27}Al MAS NMR spectrum (Fig. 2a) shows it to contain predominantly octahedral Al ($\delta = 4$ ppm), with a small amount of tetrahedral Al ($\delta = 70$ ppm), located in the illite impurity phase. The ^{29}Si MAS NMR spectrum (Fig. 3a) shows two major tetrahedral resonances, that at −95 ppm corresponding to Q^3 silicate units and that at −86 ppm arising from a Si site more saturated in Al. The small shoulder at about −107 ppm corresponds to the quartz impurity.

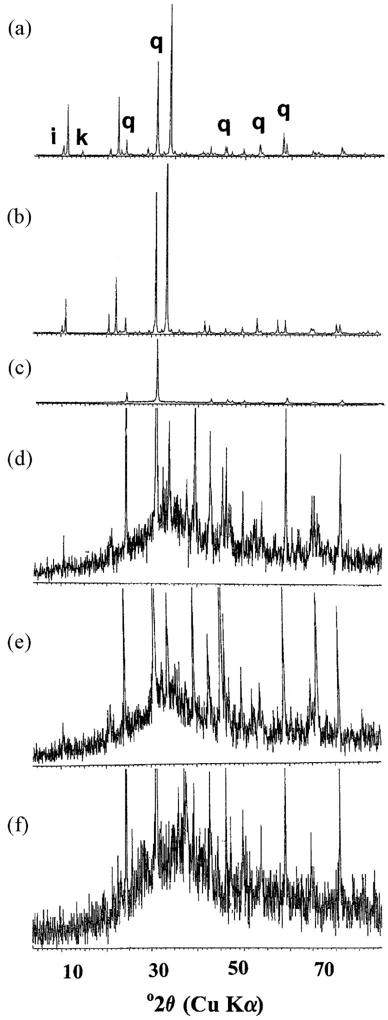

Fig. 1. X-ray diffraction patterns of pyrophyllite treated in various ways and the products of geopolymer synthesis. (a) Unheated pyrophyllite. (b) Pyrophyllite dehydroxylate formed at 800 °C. (c) Unheated pyrophyllite ball-milled for 20 h. (d) Geopolymer formed from (c). (e) Geopolymer formed from unheated pyrophyllite ball-milled for 60 h. (f) Geopolymer formed from unheated pyrophyllite vibro-milled for 15 min. Key: q = quartz, k = kaolinite, i = illite. Unmarked peaks are from pyrophyllite.

Heating the material to the dehydroxylation temperature (800 °C) reduces the intensity of all the pyrophyllite XRD peaks with a slight shift in the 0 0 1 reflections as reported by Wardle and Brindley[6] corresponding to the formation of pyrophyllite dehydroxylate (Fig. 1b). As expected, the intensity of the quartz peaks remains unchanged by this thermal treatment. However, heating produces large changes in the ^{27}Al MAS NMR spectrum (Fig. 2b), converting most of the octahedral Al to tetrahedral, and shifting the major peaks of the ^{29}Si MAS NMR spectrum (Fig. 3c) to −91 and −101.5 ppm, respectively, but retaining the relative intensities of the two Si sites. A similar shift in the position of the −95 ppm Si resonance has previously been reported by Sanchez-Soto et al.[7]

However, as found in previous unpublished experiments, neither pyrophyllite or its dehydroxylate produced a geopolymer

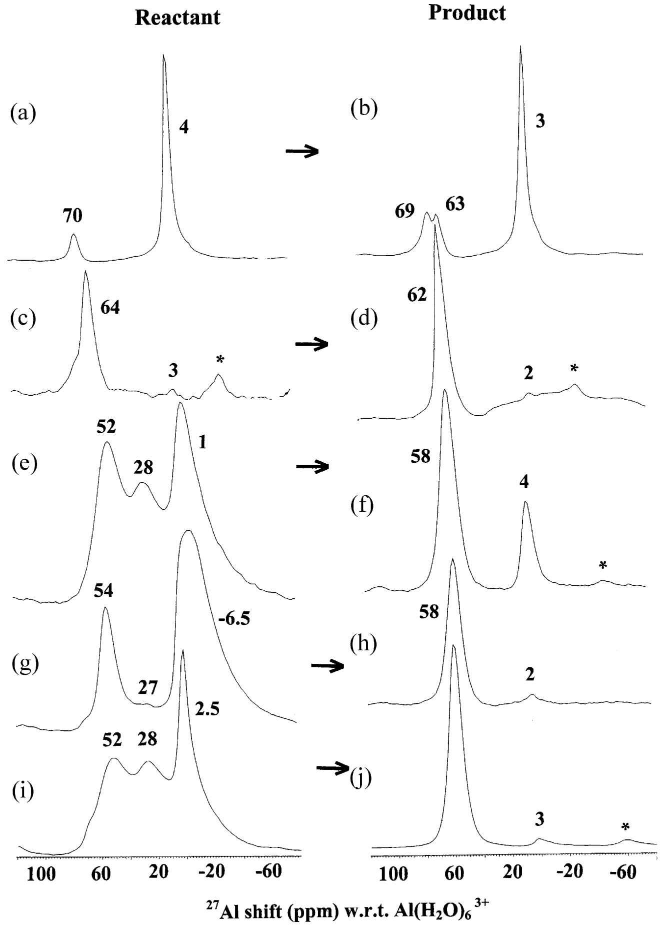

Fig. 2. 11.7 T ^{27}Al MAS NMR spectra of pyrophyllite pre-treated in various ways (a,c,e,g,i) and the corresponding geopolymers formed from these materials (b,d,f,h,j). (a,b) Unheated pyrophyllite. (c,d) Pyrophyllite dehydroxylate formed at 800 °C. (e,f) Unheated pyrophyllite ball-milled for 20 h. (g,h) Unheated pyrophyllite ball-milled for 60 h. (i,j) Unheated pyrophyllite vibro-milled for 15 min.

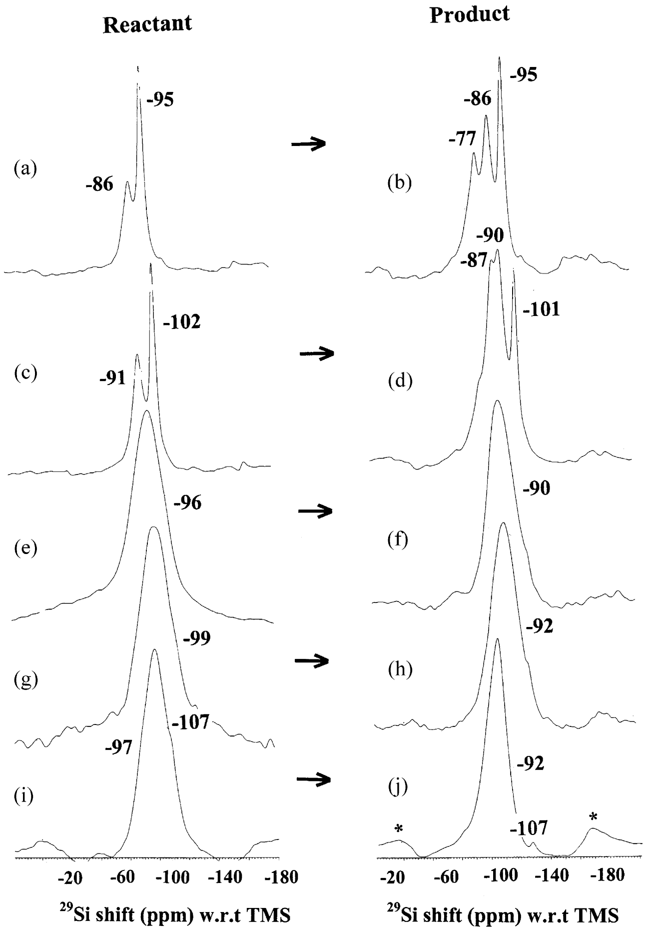

Fig. 3. 11.7 T ^{29}Si MAS NMR spectra of pyrophyllite pre-treated in various ways (a,c,e,g,i) and the corresponding geopolymers formed from these materials (b,d,f,h,j). (a,b) Unheated pyrophyllite. (c,d) Pyrophyllite dehydroxylate formed at 800 °C. (e,f) Unheated pyrophyllite ball-milled for 20 h. (g,h) Unheated pyrophyllite ball-milled for 60 h. (i,j) Unheated pyrophyllite vibro-milled for 15 min.

which cured to a hard, strong body under the present standard conditions. The reacted material derived from the unheated mineral showed a ^{27}Al MAS NMR (Fig. 2b) similar to the unheated material, but containing an additional small tetrahedral resonance at 63.4 ppm. The ^{29}Si MAS NMR spectrum of the same sample (Fig. 3b) is also similar to that of the raw material, but contains an additional resonance at −77 ppm. Neither of these spectra is consistent with the broad ^{29}Si resonance of a well-cured geopolymer, centred at about −90 ppm.[8] Similarly, subjecting the pyrophyllite dehydroxylate formed at 800 °C to the geopolymer synthesis reaction produces only small changes in the ^{27}Al and ^{29}Si NMR spectra; the ^{27}Al spectrum (Fig. 2d) is essentially unchanged, while the ^{29}Si spectrum (Fig. 3d) shows a broadening and splitting of the resonance at −91 ppm and the development of a shoulder at −78 ppm corresponding to the much sharper peak at −77 ppm in the geopolymerised samples derived from the unheated material (Fig. 3b).

This inability to form a viable hard, strong inorganic polymer from dehydroxylated pyrophyllite is in direct contrast to the behaviour of the 1:1 aluminosilicates kaolinite and halloysite. Dehydroxylation of the 1:1 minerals brings about major changes, especially in the octahedral Al–O layers which are most closely associated with the structural hydroxyl groups.[9] This is graphically illustrated by the change in the ^{27}Al MAS NMR spectrum from a sharp octahedral Al–O resonance in kaolinite to a broadened spectrum containing both octahedral and tetrahedral resonances, and a third resonance at about 30 ppm, usually attributed to fivefold coordinated Al–O.[10] Such disruption of the aluminate structure to form an X-ray amorphous phase (metakaolinite) renders the mineral reactive both to selective acid-leaching of the Al–O sheet,[11] as well as to the influence of the alkaline reaction conditions of geopolymerisation.

By contrast, the structure of the 2:1 aluminosilicate pyrophyllite leads to a dehydroxylated phase of which the crystallinity is not greatly different from that of the parent mineral, but the Al is in predominantly fivefold coordination.[6] The structure of the dehydroxylated phase retains the 2:1 stacking sequence, and the Al–O sheet remains enclosed by the upper and lower silica sheets. The fivefold Al coordination of this structure has been confirmed by NMR experiments at 14.1 T and fast spinning speeds, under which conditions the Al resonance is clearly resolved as a quadrupolar lineshape with a simulated isotropic chemical shift of 29 ppm and a nuclear quadrupole coupling constant of 10.5 MHz.[12] Fitzgerald et al. report that this quadrupolar lineshape is only resolved at high fields, and their results indicate that the field strength at which the present experiments were carried out the lineshape of the five-coordinate species would not be observed.[12]

Comparison of the structures of the dehydroxylated phases of kaolinite and pyrophyllite suggests two possible reasons for the reluctance of the latter to undergo geopolymerisation, namely its crystallinity and inaccessibility of the Al–O sheet to the alkaline reaction solution. This in turn underscores the importance of the formation of sodium aluminate as a determining factor in the geopolymerisation reactions, confirmed by the successful synthesis of viable geopolymers from sodium aluminate and sodium silicate solutions without the need for solid aluminosilicate sources.[13] In the present case, only slight changes are engendered in the Al environment by the alkaline conditions of the geopolymer synthesis, but slightly greater changes occur in the silicate structure. It appears that not even the conversion of the predominantly octahedral Al in the raw materials to lower coordination upon heating sufficiently exposes the aluminium structure to the alkaline solution to permit the condensation reaction to proceed.

Following this reasoning, it may be possible to induce geopolymerisation in the present pyrophyllite or its dehydroxylate if their crystalline lattices are sufficiently disrupted. One possible approach is mechanochemical activation (high-energy grinding) which has previously been shown by ^{27}Al NMR to induce changes in the Al coordination number of kaolinite similar to those produced by thermal dehydroxylation.[10] Mechanochemical treatment of pyrophyllite has been reported to partially destroy the crystalline structure and convert some of the six-coordinate Al to four and five-coordinate.[14] Furthermore, such mechanochemical treatment has been found to facilitate geopolymerisation in an undehydroxylated 1:1 aluminosilicate mineral (halloysite).[3]. Mechanochemical processing of 1:1 aluminosilicate geopolymer precursors using a planetary ball mill has previously proved to be less effective than grinding in a vibratory mill,[3] but both means of pre-treatment were investigated here.

Ball-milling for 20 h of both the unheated pyrophyllite and pyrophyllite dehydroxylate prepared at 800 °C have a similar effect on the XRD pattern (Fig. 1c), completely removing the pyrophyllite-related reflections and reducing the intensity of the quartz reflections by >50%. However, the sample which was dehydroxylated prior to grinding shows X-ray evidence of the formation of amorphous material in the form of a slightly bulging baseline which is totally absent in pyrophyllite ground under the same conditions. Grinding for longer periods, up to 60 h produces only a slight further decrease in the intensity of the quartz reflections. The corresponding ^{27}Al MAS NMR spectra of the heated and unheated sample ball-milled for 20 h (Fig. 2e) are identical, containing broad resonances at about 50, 28, and 1 ppm corresponding to four-, five- and six-coordinated Al, respectively. These spectra strongly resemble that of a typical metakaolinite.[10] The ^{29}Si MAS NMR spectra (Fig. 3e) are also similar, containing a single broad resonance at −95 ppm. Ball-milling for 60 h produces a large change in the ^{27}Al spectrum (Fig. 2g) in which the five-coordinated Al feature is reduced to an inflexion at 27 ppm, but little difference is seen in the ^{29}Si spectrum (Fig. 3g). These results are consistent with those of Sanchez-Soto et al.[14] who reported that prolonged grinding of pyrophyllite broadens the ^{29}Si NMR spectrum and produces a progressive increase in the amount of Al of lower CN.[14]

Neither the unheated or dehydroxylated samples ball-milled for 20 h produce particularly strong, well-hardened geopolymers under the present reaction conditions. The XRD traces of both reacted compounds are similar (Fig. 1d), showing the sharp peaks of the quartz impurity superimposed on a small amount of amorphous material (partly formed geopolymer) and several other small peaks corresponding to a hydrated sodium aluminosilicate with its major peak in the area of faujasite (ICDD file no. 38–238) or sodalite (ICDD file no. 43–140). The degree of geopolymerisation in the unheated ball-milled reactant is seen from the ^{27}Al MAS NMR spectrum (Fig. 2f) to be incomplete, retaining a significant amount of six-coordinated Al, although the centre-point of the broad ^{29}Si NMR spectrum (Fig. 3f) is close to that of a well-formed geopolymer. The ^{27}Al MAS NMR spectrum of the product from pyrophyllite dehydroxylate ball-milled for 20 h shows less unconverted Al(VI), indicating a greater degree of reaction in this material.

The geopolymer derived from undehydroxylated pyrophyllite ball-milled for 60 h sets well, achieving acceptable strength and hardness under the present reaction conditions. Its XRD powder pattern (Fig. 1e) displays similar features to that of the sample milled for 20 h but with a greater amorphous content and almost complete conversion of Al(VI) to Al(IV) (Fig. 2h) and a ^{29}Si NMR spectrum (Fig. 3h) consistent with that of a viable geopolymer.

To reduce the time and energy involved in ball-milling for 60 h, a more vigorous vibratory mill was used, for grinding periods up to 15 min. Milling in this way for 15 min has a similar effect on the XRD pattern as ball-milling for 60 h, while the ^{27}Al NMR spectrum (Fig. 2i) shows the characteristic three resonances of four-, five- and sixfold coordinated Al associated with a labile aluminosilicate system and the ^{29}Si NMR spectrum (Fig. 3i) is similar to that of the sample ball-milled for 60 h. The geopolymer produced from pyrophyllite vibro-milled for 15 min cures and hardens well under the present reaction conditions and shows an XRD pattern (Fig. 1f) with features similar to that observed for the geopolymer derived from the sample ball-milled for 60 min. The ^{27}Al and ^{29}Si NMR spectra (Figs. 2j and 3j, respectively) are also consistent with a well-formed geopolymer.

This severe mechanochemical treatment (ball-milling for 60 h or vibro-milling for 15 min) is necessary to disrupt the 2:1 layer lattice structure sufficiently for the geopolymerisation reaction to proceed. Even under these severe pre-treatment conditions, a fully X-ray amorphous product is not obtained; in addition to the crystalline quartz impurity which survives geopolymerisation, small quantities of other poorly crystalline phases of a zeolitic nature are formed. The formation of similar phases has been reported in high-alumina geopolymerised systems[15] and is also known to occur at much higher curing temperatures (90–100 °C) which approximate to hydrothermal conditions in these solid systems. Since neither of these explanations is clearly applicable to the present experiments, the formation of zeolites may simply be reflecting the behaviour of the original material under highly alkaline conditions.

4. Conclusions

Based on the criteria of their ability to cure and harden under ambient conditions, their amorphous XRD patterns and their ^{27}Al and ^{29}Si NMR spectra, attempts to produce viable, fully reacted aluminosilicate geopolymers from the crystalline 2:1 layer lattice mineral pyrophyllite were unsuccessful. Dehydroxylation of this pyrophyllite at 800 °C produces significant changes in the Al coordination, but the dehydroxylate does not form a viable geopolymer, probably because dehydroxylation does not form an X-ray amorphous phase, by contrast with the 1:1 mineral kaolinite. It is suggested that this inability to form viable geopolymers may be due to the retention of the crystalline 2:1 layer structure in pyrophyllite and its dehydroxylated phase, enclosing the Al–O sheet by the upper and lower Si–O sheets and protecting it from alkaline attack to form soluble aluminate species.

Disruption of the crystalline 2:1 layer lattice structure by severe mechanochemical processing (ball-milling for 60 h or vibro-milling for 15 min) enables geopolymeric materials to be formed which attain reasonable hardness and strength at 60 °C and show ^{27}Al and ^{29}Si MAS NMR spectra consistent with well-formed geopolymers. However, these materials are not fully X-ray amorphous, their X-ray powder patterns showing traces of zeolitic phases.

References

1. Davidovits, J. and Davidovits, J., Geopolymers: inorganic polymeric new materials. *J. Therm. Anal.*, 1991, **37**, 1633–1656.
2. Berg, L. G., Demidenko, B. A., Remiznikova, V. A. and Nizamov, M. S., Unfired finishing building materials based on kaolinite. *Stroit. Mater.*, 1970, **10**, 22.
3. MacKenzie, K. J. D., Brew, D. R. M., Fletcher, R. A. and Vagana, R., Formation of aluminosilicate geopolymers from 1:1 layer-lattice minerals pre-treated by various methods: a comparative study. *J. Mater. Sci.*, 2007, **42**, 4667–4674.
4. MacKenzie, K.J.D., What are these things called geopolymers? A physicochemical perspective. Advances in ceramic matrix composites IX. In *Ceramic Transactions*, *vol. 153*, ed. N.P. Bansal, J.P. Singh, W.M. Kriven, H. Schneider, 2003, pp. 175–186.
5. MacKenzie, K. J. D., Meinhold, R. H., Brown, I. W. M. and Bowden, M. E., Thermal reactions of pyrophyllite studied by high-resolution solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy. *J. Am. Ceram. Soc.*, 1985, **68**, 266–272.
6. Wardle, R. and Brindley, G. W., The crystal structure of pyrophyllite 1Tc and of its dehydroxylate. *Am. Miner.*, 1972, **57**, 732–750.
7. Sanchez-Soto, P. J., Sobrados, I., Sanz, J. and Pĕrez-Rodrĭguez, J. L., 29-Si and 27-Al magic-angle spinning nuclear magnetic resonance study of the thermal transformations of pyrophyllite. *J. Am. Ceram. Soc.*, 1993, **76**, 3024–3028.
8. Barbosa, V. F. F., MacKenzie, K. J. D. and Thaumaturgo, C., Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers. *Int. J. Inorg. Mater.*, 2000, **2**, 309–317.
9. MacKenzie, K. J. D., Brown, I. W. M., Meinhold, R. H. and Bowden, M. E., Outstanding problems in the kaolinite-mullite reaction sequence investigated by ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance. I. Metakaolinite. *J. Am. Ceram. Soc.*, 1985, **68**, 293–297.
10. MacKenzie, K. J. D. and Smith, M. E., *Multinuclear Solid State NMR of Inorganic Materials, Pergamon Materials Series*, *vol. 6*. Pergamon/Elsevier, Oxford, 2002.
11. Okada, K. and MacKenzie, K. J. D., Nanoporous materials from mineral and organic templates. In *Nano Materials: From Research To Applications*, ed. H. Hosono, Y. Mishima, H. Takezoe and K. J. D. MacKenzie. Elsevier, Oxford, 2006, pp. 349–382.
12. Fitzgerald, J. J., Dec, S. F. and Hamza, A. I., Observation of five-coordinated Al in pyrophyllite dehydroxylate by solid state ^{27}Al NMR spectroscopy at 14 T. *Am. Miner.*, 1989, **74**, 1405–1408.
13. Brew, D. R. M. and MacKenzie, K. J. D., Geopolymer synthesis using silica fume and sodium aluminate. *J. Mater. Sci.*, 2007, **42**, 3990–3993.
14. Sanchez-Soto, P. J., Perez-Rodriguez, J. L., Sobrados, I. and Sanz, J., Influence of grinding in pyrophyllite-mullite thermal transformation assessed by ^{29}Si and ^{27}Al MAS NMR spectroscopies. *Chem. Mater.*, 1997, **9**, 677–684.
15. Fletcher, R. A., MacKenzie, K. J. D., Nicholson, C. L. and Shimada, S., The composition range of aluminosilicate geopolymers. *J. Eur. Ceram. Soc.*, 2005, **25**, 1471–1477.