

Received November 3, 2014; reviewed; accepted March 2, 2015

HYDROTHERMAL SYNTHESIS OF LITHIUM SILICATE FROM WASTE GLASS. A PRELIMINARY STUDY

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Abstract: Current environmental directives to conserve resources and to divert waste streams have generated significant interest in mineral recycling. In this respect, this preliminary study has demonstrated that lithium metasilicate can be prepared by hydrothermal reaction between waste container glass and lithium hydroxide solutions at 100 °C. Minor proportions of calcium hydroxide, calcite, lithium carbonate and tobermorite were also produced during the reaction. Percentage crystallinity and proportion of lithium metasilicate in the reaction product were found to increase as functions of lithium hydroxide concentration (between 1 and 4 M). This research has also shown that the lithium metasilicate phase can take up 6.4 mmol/g of Zn²⁺ ions after 24 h during batch sorption. Further work to optimise the yield and to appraise the antimicrobial properties of Zn²⁺-bearing lithium metasilicate is now warranted.

Keywords: *hydrothermal synthesis, glass, cullet, recycling, lithium metasilicate, zinc*

Introduction

During the past decade, a number of research projects has been carried out to "up-cycle" surplus soda-lime-silica glass from the municipal waste-stream. Potential value-added applications for waste glass include the production of ion-exchange and water filtration media, lightweight aggregates and ceramics (Ayadi et al., 2011; Coleman et al., 2014; Korkosz et al., 2012; Matteucci et al., 2002; Velis et al., 2014).

Lithium metasilicate, Li₂SiO₃, is a synthetic alkaline inosilicate comprising Q² silicate chains and charge-balancing lithium ions which crystallises in the orthorhombic system (Pfeifer et al., 1998). The current technological significance of lithium metasilicate arises from its potential applications as a breeder material for tritium, ionic conductor, gas-sensor and CO₂-sorbent (Ortiz-Landeros et al., 2011). This material can be obtained *via* a range of synthetic routes including: solid state reaction (Ortiz-Landeros et al., 2011; Pfeifer et al., 1998); modified combustion (Cruz and Bulbulian, 2003); sol-gel synthesis (Pfeifer et al., 1998; Zhang et al., 2008);

hydrothermal processing (Ortiz-Landeros et al., 2011) and mechanical milling (Yang et al., 2012). To date, the reported preparations of lithium metasilicate have been carried out using refined silicate reagents such as colloidal silica, tetraethoxysilane, amorphous silica gel and silicic acid.

This preliminary study explores the possibility of using waste container glass as a reactive silicate source for the hydrothermal synthesis of lithium metasilicate at 100 °C in the presence of 1 M, 2 M and 4 M lithium hydroxide solutions. The reaction products were characterised by powder X-ray diffraction analysis (XRD) and the sample prepared with 4 M lithium hydroxide solution was also analysed by ²⁹Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) and Fourier transform infrared spectroscopy (FTIR). The potential of this material to be used as a carrier for antimicrobial zinc ions was also considered.

Materials and methods

Materials, synthesis and characterisation

Lithium hydroxide, LiOH·H₂O, was obtained from Sigma-Aldrich UK and used as-received. Colourless soda-lime-silica glass containers were collected from the municipal waste stream in Rochester, Kent, UK, and ground to pass 125 μm. An oxide analysis of the glass, obtained by X-ray fluorescence spectroscopy at the Materials Research Institute, Sheffield Hallam University, Sheffield, UK, is given in Table 1.

Table 1. Composition of waste glass

Oxide Component	Mass %
SiO ₂	72.1
Na ₂ O	13.4
CaO	11.3
MgO	1.30
Al ₂ O ₃	1.14
K ₂ O	0.39
SO ₃	0.21
Fe ₂ O ₃	0.08
TiO ₂	0.05
Mn ₃ O ₄	0.03
Loss on ignition	Nil

The syntheses of lithium metasilicate were attempted by heating of 3.0 g of waste glass and 60 cm³ of either 1 M, 2 M or 4 M LiOH_(aq) at 100 °C in hermetically sealed

PTFE reaction vessels for 5 days. The syntheses were carried out in triplicate and the reaction products were washed with deionised water to pH ~ 7 and dried to constant mass in air at 40 °C. Specimens produced in 1 M, 2 M and 4 M LiOH_(aq) were labelled LS-1, LS-2 and LS-4, respectively.

The reaction products were analysed by powder XRD using a Bruker D8 diffractometer with Cu K α = 0.15406 nm, a step size of 0.019 ° in the 2 θ range from 5 to 60 ° and a measuring time of 1 s *per* step. X-ray diffraction data were compared with JCPDS files using DIFFRAC.EVA software (supplied by Bruker, Germany). Quantitative XRD analysis and crystallite size calculations were carried out by Rietveld refinement using a fundamental parameters approach with full axial model (Cheary and Coelho, 1992) on TOPAS version 4.2 structure analysis software (Bruker, Germany). The lithium metasilicate structure used for the quantitative analysis was described by Tang et al. (2012) and all other structures were selected from the TOPAS structure database.

Secondary electron images of the LS-4 products were obtained from uncoated samples attached to carbon tabs on an Hitachi SU8030 scanning electron microscope with an accelerating voltage of 1 kV. The ²⁹Si MAS NMR spectrum of the LS-4 reaction products was recorded on a JEOL JNM-ECX 300 MHz spectrometer using a pulse delay of 60 s, an acquisition time of 0.02048 s and 20000 scans. ²⁹Si chemical shifts were referenced to tetramethylsilane (TMS). The FTIR spectrum was obtained using a Perkin Elmer Paragon spectrometer in transmission mode on a pressed KBr disc between 500 and 4000 cm⁻¹ wavenumbers.

Zn²⁺-uptake

The uptake of Zn²⁺ ions by the LS-4 reaction products was determined by batch sorption at 25 °C by contacting 50 mg of material with 200 cm³ of 0.5 mM zinc nitrate solution in a screw-capped polypropylene bottle for up to 24 h. At various intervals the supernatant liquors were recovered and analysed for zinc by inductively coupled plasma spectroscopy (using a Perkin-Elmer Optima 4300DV spectrometer). Each batch sorption experiment was carried out in triplicate.

Results and discussion

Characterisation

The powder XRD patterns of the hydrothermal reaction products of waste container glass and 1 M, 2 M or 4 M aqueous lithium hydroxide solutions are shown in Fig. 1. These data confirm that the principal reaction product in each case is orthorhombic lithium metasilicate (which matches JCPDS file 29-0828), and that minor quantities of calcium hydroxide, calcite, lithium carbonate and tobermorite are also present in varying proportions.

An example of the experimental and calculated XRD patterns for LS-4 and the residual difference between the two sets of data are shown in Fig. 2. The small residual difference indicates that the fitting is satisfactory.

The relative proportions of the components (by mass) of each of the samples and the calculated lattice parameters for the lithium metasilicate phase are listed in Table 2. In each case, weighted profile R-factors (R_{wp}) below 10% demonstrate that the fittings are satisfactory. These data indicate that percentage crystallinity and proportion of lithium metasilicate present in the product increase with increasing concentration of lithium hydroxide in the reaction mixture. The proportions of calcite, lithium carbonate and calcium hydroxide in the product also increase as functions of lithium hydroxide concentration. Additionally, the poorly crystalline calcium silicate hydrate mineral, tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), is found to be present in specimens LS-1 and LS-2 at 5.6% and 3.8%, respectively; although, this phase is absent in sample LS-4.

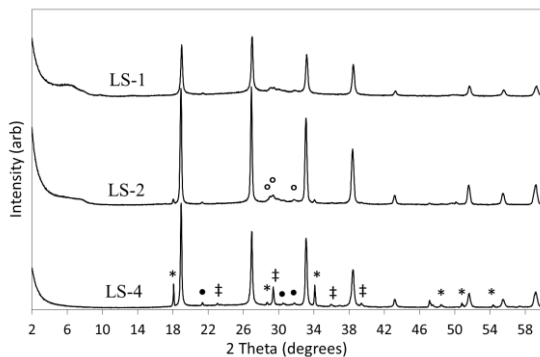


Fig. 1. Powder XRD data for the hydrothermal reaction products of waste glass and aqueous lithium hydroxide (key: Li_2SiO_3 – unmarked; $\text{Ca}(\text{OH})_2$ – *; CaCO_3 – †; Li_2CO_3 – •; $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ – °)

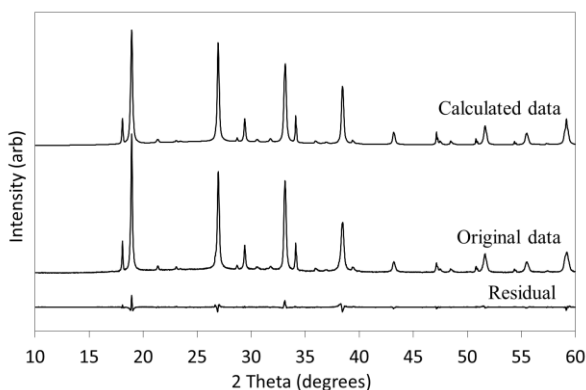


Fig. 2. Experimental and calculated powder XRD patterns for LS-4 and the residual difference between the two data sets

These findings indicate that high concentrations of lithium hydroxide facilitate the breakdown of the silicate network of the glass and promote the crystallisation of the lithium metasilicate product. High concentrations of lithium hydroxide also suppress the solubility of calcium ions leached from the glass network which precipitate out as calcium hydroxide and calcite (*via* atmospheric carbonation). The solubility of calcium ions increases as the concentration of lithium hydroxide is reduced, thus enabling the through-solution formation of the by-product calcium silicate hydrate phase, tobermorite in samples LS-1 and LS-2.

Mean crystallite sizes of the lithium metasilicate phases in each of the products are given in Table 2. These data show that the crystallite sizes are in the region of 40 to 60 nm and that the lithium hydroxide concentration of the reaction mixture has no specific impact on the size of the crystals produced.

Table 2. Composition, Li_2SiO_3 lattice parameters and crystal size of hydrothermal reaction products

Property	LS-1	LS-2	LS-4
Li_2SiO_3 (wt%)	47.3	58.2	67.9
Amorphous phase (wt%)	45.3	33.0	20.0
$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (wt%)	5.6	3.8	0
CaCO_3 (wt%)	1.1	1.9	3.8
Li_2CO_3 (wt%)	0.7	2.6	4.9
$\text{Ca}(\text{OH})_2$ (wt%)	0	0.5	3.4
Weighted profile R-factor (R_{wp})	6.1	9.5	8.9
Lattice parameters (Å)	$a = 9.386$	$a = 9.393$	$a = 9.392$
	$b = 5.401$	$b = 5.401$	$b = 5.404$
	$c = 4.688$	$c = 4.688$	$c = 4.684$
Crystal size (nm)	40 ± 6	60 ± 15	55 ± 7

The most highly crystalline specimen (80% crystallinity) comprising the highest proportion of lithium metasilicate (68% Li_2SiO_3), LS-4, was selected for further analysis by SEM, NMR and FTIR. Scanning electron micrographs of LS-4 are presented in Fig. 3 and indicate that the material is principally composed of granules in the size range 50 to 100 μm comprising ~ 400 nm blocky interlocking particles.

The ^{29}Si MAS NMR spectrum of LS-4 is given in Fig. 4 and comprises a single Q^2 resonance at -75.5 ppm and a low-intensity Q^1 signal at -72 ppm in the ratio 65:1. A very broad weak signal also appears in the spectrum at approximately -110 ppm. The Q^2 mid-chain silicate resonance is consistent with those reported in the literature for phase-pure lithium metasilicate (Pfeifer et al., 1983; Zhang et al., 2008). However, the NMR data presented by Zhang et al. (2008) consists of an asymmetrical Q^2 signal with additional downfield intensity in the Q^1 region which may arise from chain-end silicate species. It is on this basis that the discrete Q^1 resonance observed in this study is tentatively assigned to the terminal groups of the silicate chains; although, the

possible presence of a minor sorosilicate phase cannot be dismissed. The very broad signal centred around -110 ppm arises from Q^4 amorphous silica.

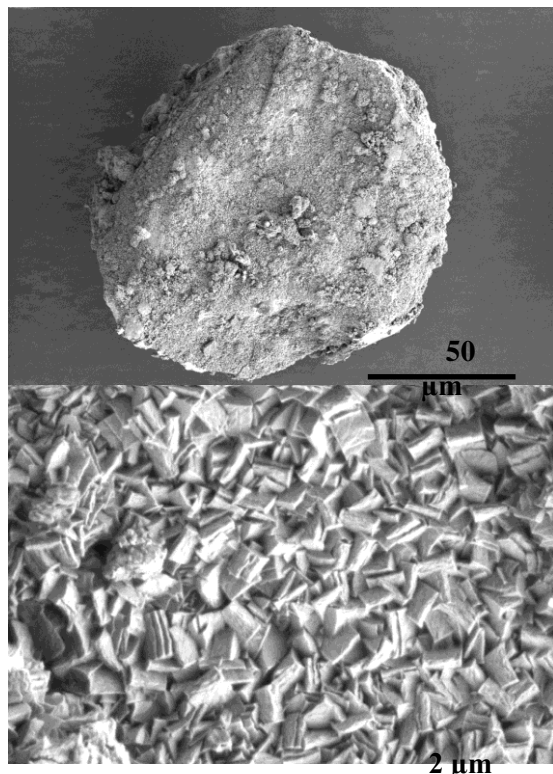


Fig. 3. SEM micrographs of sample LS-4

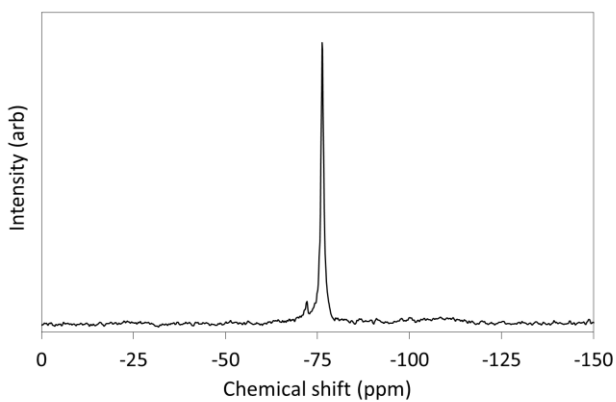


Fig. 4. ^{29}Si MAS NMR spectrum of the hydrothermal reaction products of waste glass and aqueous lithium hydroxide

The FTIR spectrum of LS-4 is presented in Fig. 5 and closely resembles those of lithium metasilicate reported in the literature (Yang et al., 2012; Zhang et al., 2008). Bands at 1043, 983, 736 and 619 cm^{-1} arise from Si-O-Si vibrations. The signal at 523 cm^{-1} is assigned to Si-O-Li deformations and O-Si-O vibrations give rise to the bands at 945 and 863 cm^{-1} . Stretching vibrations of adsorbed water and hydroxide groups appear at 3440 cm^{-1} and the bands at 1500 and 1440 cm^{-1} are attributed to carbonate stretching modes of calcite and lithium carbonate.

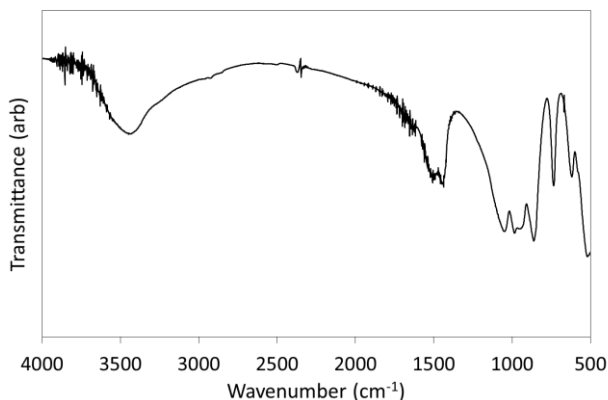


Fig. 5. FTIR spectrum of the hydrothermal reaction products of waste glass and aqueous lithium hydroxide

Zn²⁺-uptake

Zinc is an essential antioxidant and anti-inflammatory agent in the human body, which also possesses antimicrobial properties by inhibiting nutrient uptake and interfering with proton transfer processes in bacteria. The sorption characteristics of numerous Zn²⁺-bearing zeolites, clays and synthetic silicates have been investigated with a view to these materials being incorporated into polymer blends, food packaging, pharmaceutical formulations and biomedical devices (Coleman, 2009; Coleman et al., 2010; El-Kamash et al., 2005; Purna Chandra Rao et al., 2006; Qui and Zheng, 2009).

The uptake of zinc ions by sample LS-4 as a function of time is plotted in Fig. 6. Within 24 h, the uptake of zinc ions is 6.4 mmol/g. The extent of zinc-loading far exceeds those of other synthetic silicates such as tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, (1.6 mmol/g) and umbite, $\text{K}_2\text{ZrSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$, (0.6 mmol/g) whose zinc-bearing phases have been shown to possess antimicrobial action against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Escherichia coli* (Coleman et al. 2009, Coleman, 2010).

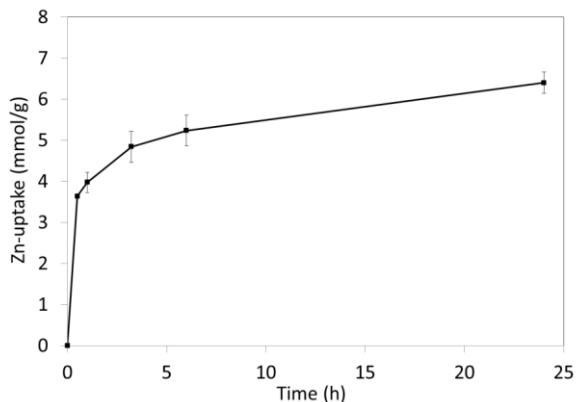


Fig. 6. Uptake of zinc ions by LS-4

The powder XRD pattern of the LS-4 sample after Zn^{2+} batch sorption is shown in Fig. 7. The small quantity of sample present after ion exchange (~ 100 mg recovered) compromises the signal-to-background ratio of these data; nonetheless, it is evident that a proportion of the lithium metasilicate has become amorphised during the Zn^{2+} -uptake process and that the relative intensities of the reflections of lithium metasilicate have altered. This indicates that, despite the similar size of the lithium Li^+ and zinc Zn^{2+} cations, 90 and 88 pm, respectively, significant structural disruption occurs during the Zn^{2+} -uptake process. This may arise from the more specific co-ordination requirements of zinc compared with those of lithium, although further work would be required to confirm the specific mechanism of interaction between the Zn^{2+} ions and the lithium metasilicate phase.

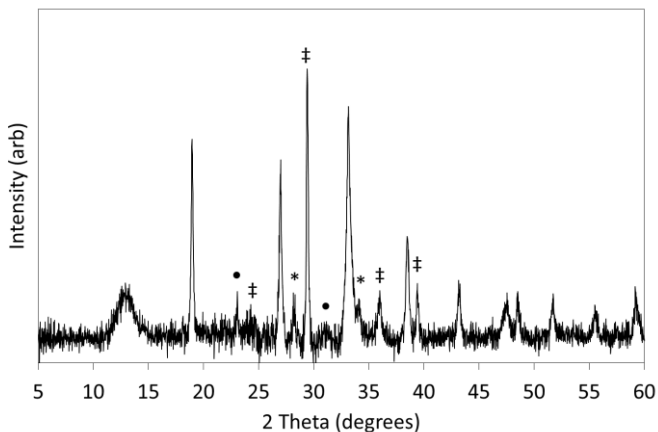


Fig. 7. Powder XRD pattern of zinc-exchanged LS-4
(key: Li_2SiO_3 – unmarked; $\text{Ca}(\text{OH})_2$ – *; CaCO_3 – ‡; Li_2CO_3 – •)

Waste glass as a feedstock for lithium metasilicate

Current environmental directives to preserve resources and divert waste streams have stimulated significant interest in mineral recycling and 'up-cycling' in added-value applications. Poor collection facilities and colour mismatch limit the supply of suitable glass cullet that can be effectively recycled as new container glass. In addition, large quantities of recycled cullet can alter the feedstock during glass manufacture causing variations in composition and redox chemistry, which can compromise the quality of the finished glass (Karamberi and Moutsatsou, 2005).

This preliminary study has demonstrated that lithium metasilicate can be prepared by hydrothermal reaction between waste container glass and lithium hydroxide solution at 100 °C. Minor proportions of calcium hydroxide, calcite, and lithium carbonate were also produced during the reaction. Percentage crystallinity and proportion of lithium metasilicate in the product both increased as functions of lithium hydroxide concentration. Lower concentrations of lithium hydroxide also promoted the formation of poorly crystalline tobermorite by increasing the solubility of calcium ions released from the glass. A previous study indicated that tobermorite, an ion-exchanger, can be synthesised from waste glass under similar hydrothermal conditions in 1, 2 and 4 M sodium hydroxide solution (Coleman et al., 2013). These studies have demonstrated that waste glass is a potentially versatile feedstock for a range of technologically significant silicate phases.

This research has also shown that Zn^{2+} ions can be taken up by lithium metasilicate, and that the extent of Zn^{2+} -uptake after 24 h by the waste glass-derived lithium metasilicate exceeds those of other synthetic silicate minerals reported in the literature (Coleman et al. 2009, Coleman 2010). These initial results indicate that the Zn^{2+} -bearing lithium metasilicate may be a suitable filler material for antimicrobial polymer composites. Further research is now underway to optimise the yield of the lithium metasilicate product phase and to evaluate the antimicrobial properties of its Zn^{2+} -bearing counterpart.

Conclusions

A novel hydrothermal route to the formation of a mixed product, principally comprising lithium metasilicate, from waste container glass has been demonstrated. Percentage crystallinity and proportion of lithium metasilicate in the reaction product were found to increase as functions of lithium hydroxide concentration. This research has also shown the lithium metasilicate phase can take up 6.4 mmol/g of Zn^{2+} ions after 24 h during batch sorption. Further work to optimise the yield and to appraise the antimicrobial properties of Zn^{2+} -bearing lithium metasilicate is now warranted.

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