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Effect of HNO_3 on crystalline phase evolution in lithium silicate powders prepared by sol–gel processes

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Abstract An interesting observation is reported on the dramatic effect of HNO_3 on crystalline phase evolution in the 33.3 mol% Li_2O–SiO_2 glass–ceramic (stoichiometric composition of lithium disilicate $Li_2Si_2O_5$, LS_2) prepared by sol–gel processes from tetraethylorthosilicate (TEOS) and lithium ethoxide precursors. Nitric acid (65%), in molar ratio HNO_3/TEOS $= 0.1$, was added either to the precursor sol or to 95 °C dried gel. The product, which is amorphous at temperatures below 450 °C, transforms into crystalline lithium metasilicate (Li_2SiO_3, LS) at around 550 °C (starting temperature $\sim$450 °C), instead of forming crystalline LS_2. Phase separation in the glassy phase may be responsible for the formation of lithium metasilicate. XRD, ^{29}Si MAS, and ^{7}Li static NMR were used to follow the crystallization evolution and network structures of the materials heat-treated at various temperatures.

Introduction

Lithium silicate ceramics found applications in areas such as CO_2 captures [1], lithium battery cathode materials [2], fast-ion conductors [3], and tritium breeding materials [4]. Phase evolution is significance in the control of the material performance. Preferential formation of lithium metasilicate (Li_2SiO_3, LS) in the crystallization of lithium silicate system has been a discrepant opinion and motivated intensive investigation for decades [5–9]. Nitric acid was used to suppress the formation of LS in sol–gel processing [10, 11]. The effect of nitric acid was assumed to dissolve LiOH produced by the reaction of lithium alkoxide and water, and consequently to improve the homogeneity of lithium ions' distribution [11]. Furthermore, nitric acid is also a common catalyst for TEOS hydrolysis [12]. Our previous work [13] shows that no LS phase formed during lithium disilicate $Li_2Si_2O_5$ (LS_2) synthesis by a sol–gel process in the absence of nitric acid. Because of the particular role of nitric acid, we used it in the preparation of lithium silicate powders by sol–gel processes. Contrary to our expectations, crystalline LS was formed rather than the anticipated LS_2. Here we report the dramatic effect of nitric acid and crystalline phase evolution in the lithium silicate system with composition corresponding to the stoichiometry of lithium disilicate $Li_2Si_2O_5$.

Experimental procedure

Materials preparation

The sol–gel processes are represented by the schematic flow chart in Fig. 1, which are based on the procedure described previously [13, 14]. Nitric acid was added in two ways in molar ratio HNO_3/TEOS $= 0.1$ and the processes are nominated as process 1 and process 2. Tetraethylorthosilicate (TEOS, 98% purity, supplied by Sigma–Aldrich, St. Louis, MO) was used as a precursor for silicon, lithium ethoxide as a precursor for lithium, and absolute ethanol as a solvent. Lithium ethoxide was synthesized by reaction of lithium metal with ethanol. The sol was prepared at ambient temperature ($\sim$21 °C) by mixing ethanolic solutions of TEOS

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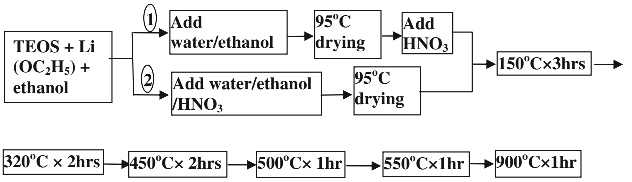

Fig. 1 Sol–gel processes and heat-treatment procedures in material preparation

(2.31 mol/L) and lithium ethoxide (0.87 mol/L) for 40 min with a magnetic stirrer to give Si/Li molar ratio corresponding to lithium disilicate, $Li_2Si_2O_5$. In process 1, a mixture of deionized water and ethanol ($H_2O/[4Si + Li] = 4.5$ in molar ratio, ethanol:water = 2:1 in volume) was then added to the TEOS/lithium ethoxide solution, resulting in gelation within a few minutes. After being held for overnight at ambient temperature the gels were dried at 95 °C. After cooled down to ambient temperature, 65% nitric acid (molar ratio $HNO_3/TEOS = 0.1$, and HNO_3 was pre-mixed with appropriate amount of ethanol for easy handing) was added into the gel by thoroughly grinding with an agate mortar and pestle. Alternately, in process 2, the nitric acid was added in the step where the mixture of water and ethanol was added to TEOS/lithium ethoxide solution; and after 95 °C dried, the gel was ground with the mortar as well but without addition of nitric acid. The ground powders were further heat-treated at different temperatures illustrated in Fig. 1 (heating rate 5 °C/min). The samples were subject to analyses after cooled down to ambient temperature from each treatment temperature.

Analyses

X-ray diffraction (XRD) was performed with a D8 Advance Bruker X-Ray Diffractometer using Cu Kα radiation. Scans were recorded in the (2θ) range 10–40° with scan rate 0.02°/s. The crystalline phases were identified by electronic comparison of diffraction patterns with reference patterns using Diffrac-plus software “EVA” module.

NMR spectra were recorded using a Bruker Avance 300 MHz spectrometer. For ^{29}Si MAS, the spinning rate was 5 KHz, the resonance frequency was 59.6 MHz, the pulse angle was 30°, and the delay time between pulses was 60 s for gels heat-treated at temperatures <500 °C (with 900 scans recorded) and 500 s for gels heat-treated at temperatures ≥500 °C (100 scans). For ^7Li static, 16 scans were recorded at resonance frequency 116.6 MHz, pulse angle 30°, and delay time 10 s.

Results and discussion

XRD pattern (Fig. 2) revealed that the prepared powders are amorphous and start to crystallize at 450 °C. The initial crystallization phase is lithium metasilicate Li_2SiO_3, rather than the expected lithium disilicate $Li_2Si_2O_5$ which is reported in literature [10, 11, 13]. That means addition of the nitric acid hereby did not suppress the formation of Li_2SiO_3 but conversely promoted its formation. The material however can fully transfer to $Li_2Si_2O_5$ upon higher temperature treatment, for example at 900 °C. ^{29}Si NMR spectra (Fig. 3) show that the main peaks at temperatures ≤450 °C are the broad humps centred at −92 to −95 ppm whose structural units are disorded Q^3 (Q^n denotes an SiO_4 tetrahedral unit with n bridging oxygen atoms, and here $n = 3$), which are attributed to the XRD amorphous phases, and meanwhile small peaks at around −105 to −110 ppm relative to Q^4 were also detectable. The Q^2 units at the positions around −74 ppm appear after 500 °C treatment for process 1 and after 450 °C treatment for process 2.

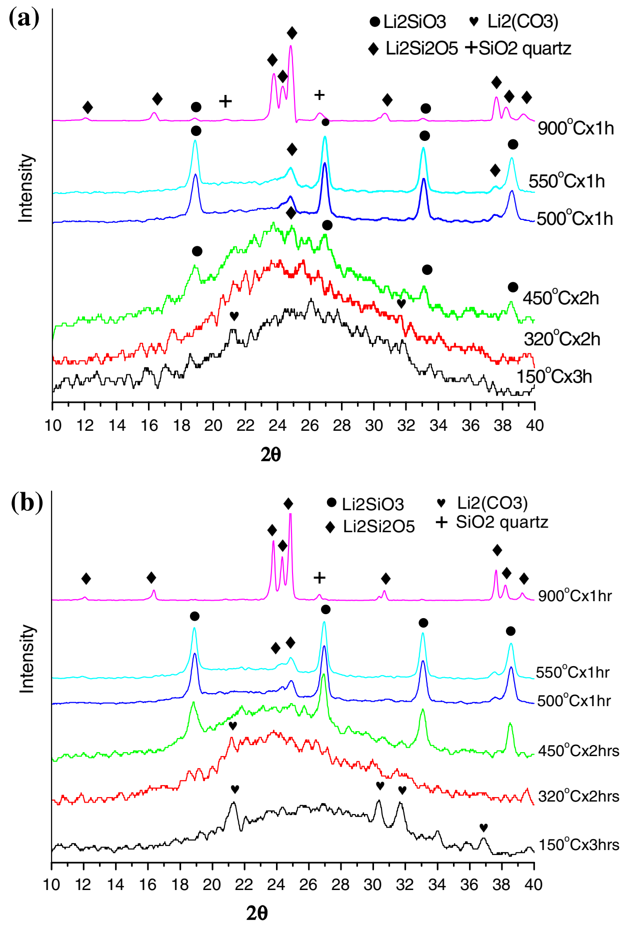

Fig. 2 X-ray powder diffraction patterns for materials prepared using (**a**) process 1; (**b**) process 2

In principle, the theoretical structural units of lithium metasilicate Li_2SiO_3 (or $Li_2O{\cdot}SiO_2$) are Q^2, and the units for lithium disilicate $Li_2Si_2O_5$ (or $Li_2O{\cdot}2SiO_2$) are Q^3, and the Q^4 units correspond to silica SiO_2. Therefore, the

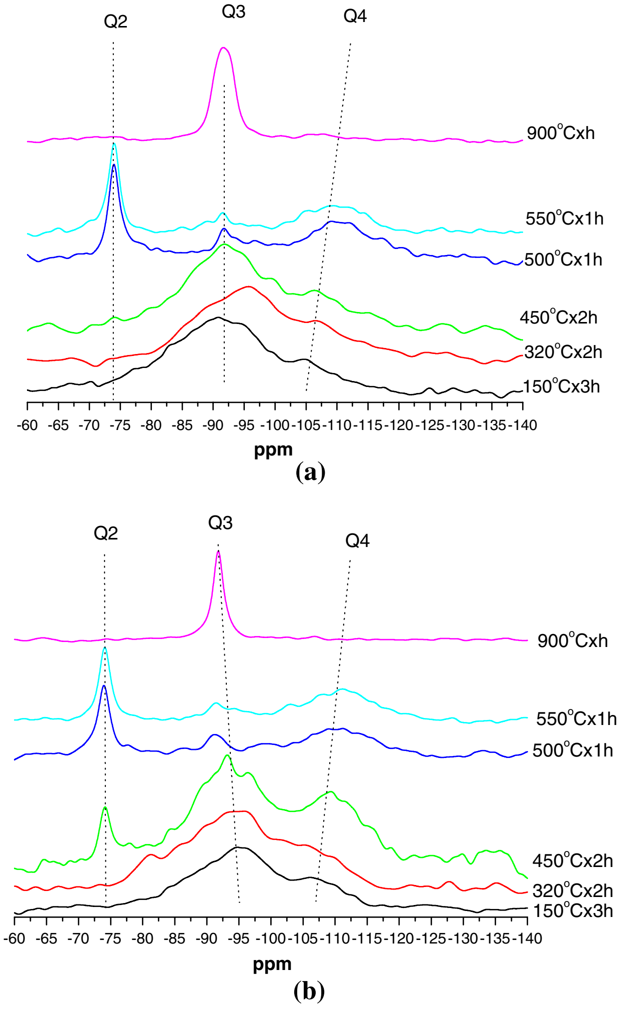

Fig. 3 ^{29}Si NMR spectra for materials prepared using (**a**) process 1; (**b**) process 2

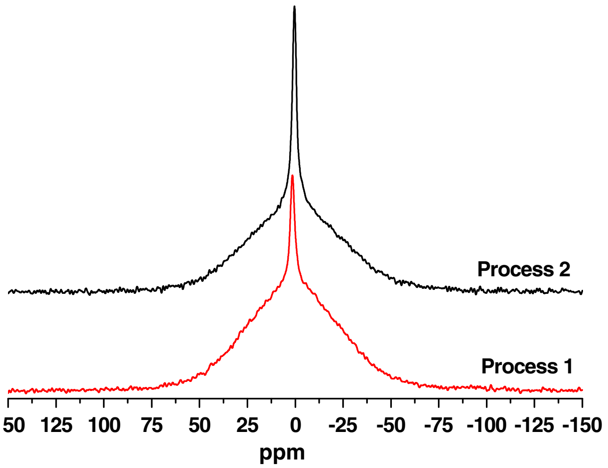

Fig. 4 ^{7}Li static NMR spectra for materials prepared heat-treated at 150 °C for 3 h

prepared powders treated at 150 °C composed of the majority of amorphous phase which is corresponding to $Li_2Si_2O_5$ with disorded units of Q^3, and additionally a petty magnitude of SiO_2-rich clutches of Q^4. Lithium ions are relatively rich in the surrounding areas of the SiO_2-rich clutches. These Li-rich areas afterwards evolve into crystalline lithium metasilicate with Q^2 units. Though they are not reflected in ^{29}Si MAS NMR spectra in Fig. 3 before their crystallization at temperature 500 °C for process 1 and 450 °C for process 2, the Li-rich areas are reflected in ^{7}Li static spectra shown in Fig. 4 where the sharp peaks superimposed on the broad peaks at 150 °C are attributed to the Li^+ ions of hydrous $LiNO_3$ [15]. Existence of SiO_2-rich areas and Li-rich areas indicate the occurrence of phase separation in the amorphous status.

Due to its high susceptibility to water, lithium ethoxide immediately reacts with added water to produce lithium hydroxide (see reaction (1)). Because of its strong alkalinity, lithium hydroxide can base catalyse the hydrolysis of TEOS (illustrated by reaction (2)). In addition, LiOH can directly participate in reactions with TEOS or its hydrolysis products shown in reactions (3) and (4). By these reactions, the Li^+ ions but probably not all of them are incorporated into $[SiO_4]$ network to form Q^3-Li units, where one of the four Si–O bonds in one $[SiO_4]$ unit is broken to compensate the charge of the Li^+ cation. When nitric acid is added (in process 2), however, the LiOH react with HNO_3 to produce $LiNO_3$ (illustrated in reaction (5)), though the numbers of Li^+ involved in this reaction are fewer. The formation of $LiNO_3$ disturbs the homogeneity of Li^+ distribution, causing the configuration of Li-rich areas and Si-rich areas (phase separation). The Li-rich areas will evolve to LS clusters (Q^2) which act as seeds to eventually produce the crystalline phase of lithium metasilicate. Similarly, in case where the nitric acid was added into 95 °C dried gel (process 1), the Li^+ which did not completely attached to $[SiO_4]$ network reacted with NO_3^- to form $LiNO_3$. In addition, the formation of crystalline Li_2CO_3 detected by XRD (Fig. 2) is due to the reaction of Li(OH) with atmospheric CO_2.

$$LiOC_2H_5 + H_2O \rightarrow LiOH + C_2H_5OH \qquad (1)$$

$$Si(OR)_4 + H_2O \overset{Li(OH)}{\rightarrow} (OR)_3SiOH + ROH \qquad (2)$$

$$(OR)_3SiOH + LiOH \rightarrow (OR)_3SiO\text{-}Li + H_2O \qquad (3)$$

$$(OR)_3SiOR + LiOH \rightarrow (OR)_3SiO\text{-}Li + ROH \qquad (4)$$

$$Li(OH) + HNO_3 \rightarrow LiNO_3 + H_2O \qquad (5)$$

where R represents C_2H_5.

In summary, this study indicates that the addition of nitric acid (HNO_3/TEOS = 0.1 in molar ratio) in the preparation of $Li_2Si_2O_5$ by sol–gel processes did not suppress the formation of Li_2SiO_3 but promoted the formation of Li_2SiO_3 instead. Phase separation in the gels, evidenced by the Q^4 unit emergence in ^{29}Si MAS-NMR spectra (Fig. 3) and the sharp peaks imposed on the broad peaks of ^{7}Li static NMR spectra (Fig. 4), is probably responsible for the change in phase evolution. This, on the other hand, supports the opinion of preferential crystallization of lithium metasilicate in lithium silicate system.

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References

1. Nakagawa K, Ohashi T (1998) J Electrochem Soc 145:1344. doi: 10.1149/1.1838462
2. Nyten A, Abouimrane A, Armand M, Gustafsson T, Thomas JO (2005) Electrochem Commun 7:156. doi:10.1016/j.elecom.2004.11.008
3. Klein LC (1989) J Non-Cryst Solid State Ionics 32/33:639. doi: 10.1016/0167-2738(89)90339-1
4. Johnson CE, Kummerer KR, Roth E (1988) J Nucl Mater 155–157:188. doi:10.1016/0022-3115(88)90240-1
5. Soares PC Jr, Zanotto ED, Fokin VM, Jain H (2003) J Non-Cryst Solids 331(1–3):217. doi:10.1016/j.jnoncrysol.2003.08.075
6. James PF, Iqbal Y, Jais US, Jordery S, Lee WE (1997) J Non-Cryst Solids 219:17. doi:10.1016/S0022-3093(97)00247-0
7. Iqbal Y, Lee WE, Holland D, James PF (1998) J Non-Cryst Solids 224:1. doi:10.1016/S0022-3093(97)00453-5
8. Dupree R, Holland D, Mortuza MG (1990) J Non-Cryst Solids 116(2–3):148 doi:10.1016/0022-3093(90)90687-H
9. Holland D, Iqbal Y, James PF, Lee WE (1998) J Non-Cryst Solids 232–234:140. doi:10.1016/S0022-3093(98)00381-0
10. Li P, Ferguson BA, Francis LF (1995) J Mater Sci 30(16):4076. doi:10.1007/BF00360711
11. Dupree R, Holland D, Mortuza MG, Smith ME, Chen A, James PF (1990) Magn Resonance Chem 2:S89. doi:10.1002/mrc.1260281315
12. Klein LC (1985) Ann Rev Mater Sci 15:227
13. Zhang Bo, Bhattacharyya D, Easteal AJ, Edmonds NR (2007) J Am Ceram Soc 90:1592. doi:10.1111/j.1551-2916.2007.01561.x
14. Zhang B, Nieuwoudt M, Easteal AJ (2008) J Am Ceram Soc, OnlineEarly articles, 4-April-2008. doi:10.1111/j.1551-2916.2008.02389.x
15. Szu S-P, Klein LC, Greenblatt M (1990) J Non-Cryst Solids 121(1–3):90. doi:10.1016/0022-3093(90)90111-X