

XPS and NMR analysis on $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$

R K Pan^{1,2}, S Feng² and H Z Tao^{2,3}

¹School of Materials Science and Engineering, Hubei University, Wuhan 430062, China

²State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

E-mail: thz@whut.edu.cn

Abstract. $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) glass was prepared by the melt quenching method. The glass transition temperature (T_g) and the crystallization temperature (T_c) of C12A7 glass are about 1050 K and 1194 K, respectively, measured by the differential scanning calorimetry (DSC). The structure of C12A7 glass was investigated by X-ray photoelectron spectroscopy (XPS) as well as magic angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR). Analysis shows that Al coordination number is about four in C12A7 glass, in which AlO_4 tetrahedrons and bridging oxygens (BO) constitute the glass network. Ca^{2+} produces a few of non-bridging oxygens (NBO), which become neighbours of Al.

1. Introduction

Calcium aluminates $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ are main component materials in the Earth's mantle and aluminous cement, which have been focused by many researchers [1,2]. Calcium aluminates are very fragile glass former and do not contain typical network-forming cations. The structure of liquid $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ with $x=0.33, 0.5, 0.75$ was investigated in a laser heated aerodynamically levitation furnace by neutron and high energy x-ray diffractions [3]. Reports show that the coordination number (CN) of Al and Ca is around 4.1 and 5-6, respectively, and the bond length of Al-O and Ca-O is 1.765 Å and 2.38 Å, respectively [4]. This implies that Al is in tetrahedral coordination and Ca is in distorted octahedral sites.

C12A7 also can be used as transparent electride materials because there are 12 sub-nanometer-sized cages in every unit cell, which can accommodate electrons and get high electronic conductivity. H. Hosono prepared room-temperature-stable electrodes (C12A7:e^-) from C12A7 glass, which exhibits unique electronic properties such as high electronic conductivity [5]. C12A7 glass was annealed in reduced atmosphere to be crystallized. The temperature is important during the annealing process. In this paper, C12A7 glass was prepared. The glass transition temperature (T_g) and crystallization temperature (T_c) were determined by DSC test. The structure of C12A7 was discussed by XPS and NMR tests.

2. Experimental

2.1. Glass preparation

C12A7 glass samples were prepared by the conventional melt quenching method. The raw materials CaCO_3 and Al_2O_3 (99.9%) were thoroughly mixed and then melted in a corundum crucible. The



melting process was done at the temperature 1900 K for 10 h. The melt was quenched between two iron plates to obtain amorphous C12A7 samples.

2.2. DSC and XRD tests

T_g and T_c were determined using a standard calorimetric method. The calorimetric measurement was performed using a differential scanning calorimetric (DSC) instrument (STA 449 F1, Netzsch). The glass samples were cut to dimensions of approximately $4 \times 4 \times 0.8$ mm³ and the bottom surface was optically polished. The measurements were conducted in a purged argon atmosphere (40 mL/min). The upscan rate was 20 K/min. The crystalline structure of C12A7 samples after DSC test was analyzed by an X-ray diffractometer (Bruker, D8 Discover) with Cu K α radiation ($\lambda = 0.15405$ nm).

2.3. XPS test

XPS measurement was carried out on an X-ray photoelectron spectrometer (Thermo Scientific, VG Multilab 2000) with Al K α radiation ($h\nu = 1486.6$ eV) under UHV (1.33×10^{-8} Pa). The energy resolution was set to 0.5 eV for wide scans and 0.05 eV for narrow scans, respectively. The analyzer pass energy was set to 20 eV for narrow scans. All peaks are calibrated by the carbon deposit C 1s binding energy at 284.8 eV.

2.4. NMR test

²⁷Al MAS-NMR experiment of C12A7 glass was carried out using a 9.8 Tesla spectrometer (Bruker BioSpin GmbH) corresponding to a ²⁷Al resonance frequency of 104.26 MHz. The spinning speed was set at 12 kHz for the MAS rotor (4 mm ZrO₂). The recycle time is 1 s and pulse width is 0.9700 μ s.

3. Results and discussion

Figure 1 shows the DSC up-scanning curve of the C12A7 glass sample from 330 K up to 1370 K at 20 K/min. During heating, C12A7 glass experienced an obvious glass transition range from 1000 to 1100 K, and began to crystallize after 1120 K. The glass transition temperature is 1050 K. There are two sharp and intense crystallization peaks at 1194 K and 1280 K, respectively. The temperature gap between the offset of glass transition and the onset of crystallization is very narrow, which indicates that C12A7 glass might have relatively poor glass forming ability.

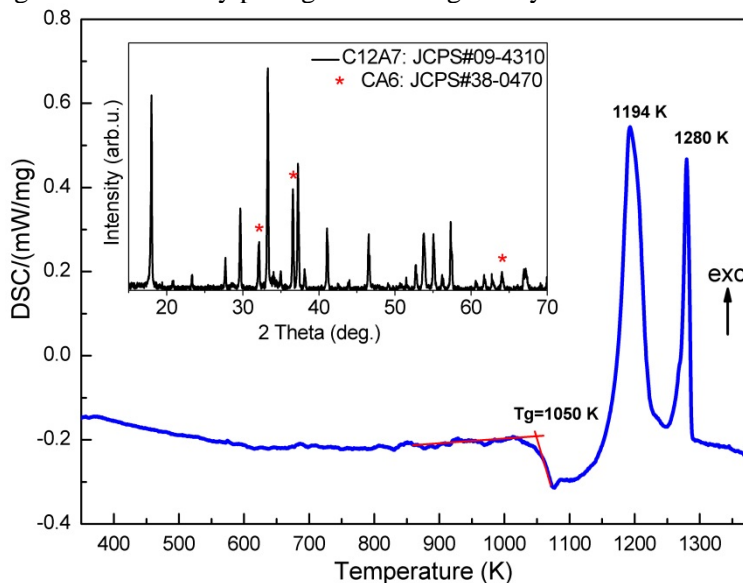


Figure 1. DSC curve of C12A7 glass sample from 350 to 1380 K up-scanned at 20 K/min. The inset is XRD pattern of C12A7 glass after DSC test.

To identify the peaks of crystallization, XRD measurement was done for the glass sample after DSC annealing. The inset in Figure 1 shows that there are two crystalline phases. The main phase is C12A7 and the other is CA6. So it can deduce that the first crystallization peak at 1194K is related to C12A7. The second peak at 1280 K is related to CA6. Reports give that the exothermic peak near 1090 K is due to the crystallization of CaO [6], the crystallization of γ -Al₂O₃ and formation of α -Al₂O₃ occur at about 1220 K [7]. The transformation of non-equilibrium CaO·Al₂O₃ to equilibrium C12A7 has up to the temperature 1320 K [8]. But these exothermic peaks with higher temperatures in above reports were got from annealing dried gels using sol-gel method, not glass samples. It seems the crystallization temperatures are much lower using crystallizing glass method than using sol-gel method.

Figure 2 shows the XPS survey spectrum of C12A7 glass sample, in which Ca, Al, and O can be detected. The stoichiometry verified well as the nominated C12A7, as calculated from Ca 2p, Al 2p and O 1s peak areas amounts.

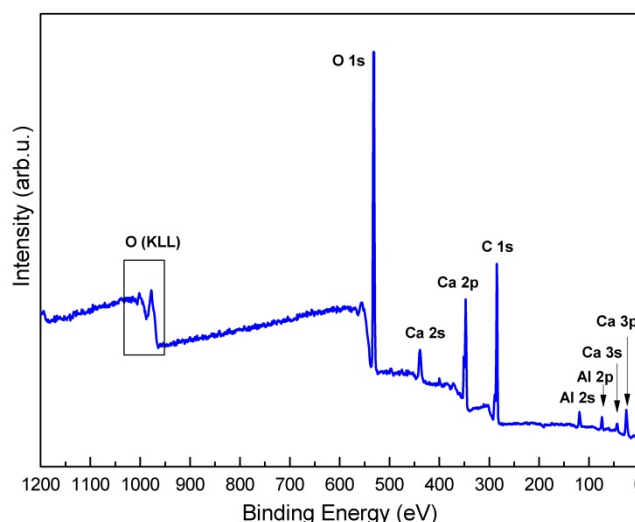


Figure 2. XPS survey spectrum of C12A7 glass.

Figure 3 shows the XPS spectra of O 1s, Ca 2p, Al 2s and Al 2p, respectively. The O 1s spectrum in Figure 3(a) can be clearly deconvoluted into two distinct contributions, which peaks are at around 531 eV and 531.7 eV, respectively. The high energy component is attributed to bridging oxygen (BO) atoms, while the low energy component is assigned to non-bridging oxygen (NBO) atoms [9]. The ratio of NBO/BO is about 1:4 by calculating the areas of deconvoluted O 1s XPS spectrum.

Ca 2p narrow XPS spectrum in Figure 3(b) has two peaks at around 350.7 eV and 347 eV, which are related to Ca 2p_{1/2} and Ca 2p_{3/2}, respectively. Due to spin orbit splitting, Ca 2p XPS spectrum is clearly distinguishable two peaks. The narrow and sharp peaks indicate that Ca connected with O and without any hydrated specimen [10, 11]. There is a report shows that Ca 2p XPS peaks shift to lower binding energy in Pr_{1-x}Ca_xMnO₃ crystalline [12]. Comparing with that of glass sample, there are less O atoms around Ca in Pr_{1-x}Ca_xMnO₃ crystalline, which caused the peak position shift.

The Al 2s and 2p XPS spectra in Figure 3(c) and (d) have peak positions at around 118.8 eV and 74 eV, respectively, which are consistent with the reports [13, 14]. That indicates that the valence state of Al in C12A7 is as same as that of Al₂O₃. So we can conclude that only Ca-O bonds and Al-O bonds exist in C12A7 glass sample.

Figure 4 shows the NMR spectrum of C12A7 glass, in which a sharp and narrow peak (69.9 ppm) indicates that Al in C12A7 glass is in four-fold (tetrahedral) coordination connecting to oxygen. The asymmetric central peak is due to the effects of the second order quadrupolar interaction, which can not be averaged in the solid-state MAS-NMR. Using the method mentioned by P F McMillan et

al.[15], the isotropic chemical shift can be got: $\delta_{iso}=81.4$ ppm, which is nearly equal to the report in Ref.[15]. P F McMillan pointed out there was no evidence for Al in any other coordination state in the glasses with $\text{CaO}:\text{Al}_2\text{O}_3 \geq 1$, independent of the quench rate. So C12A7 glass can be described in terms of polymerization state of the aluminate framework with Ca^{2+} ions stuffing sites within the framework structure. It mainly contains some six-membered rings of AlO_4 tetrahedra, in which each AlO_4 group has two terminals or non-bridging. Al-O bonds and two bridging oxygens share in intertetrahedral Al-O-Al linkages to form Q^2 units.

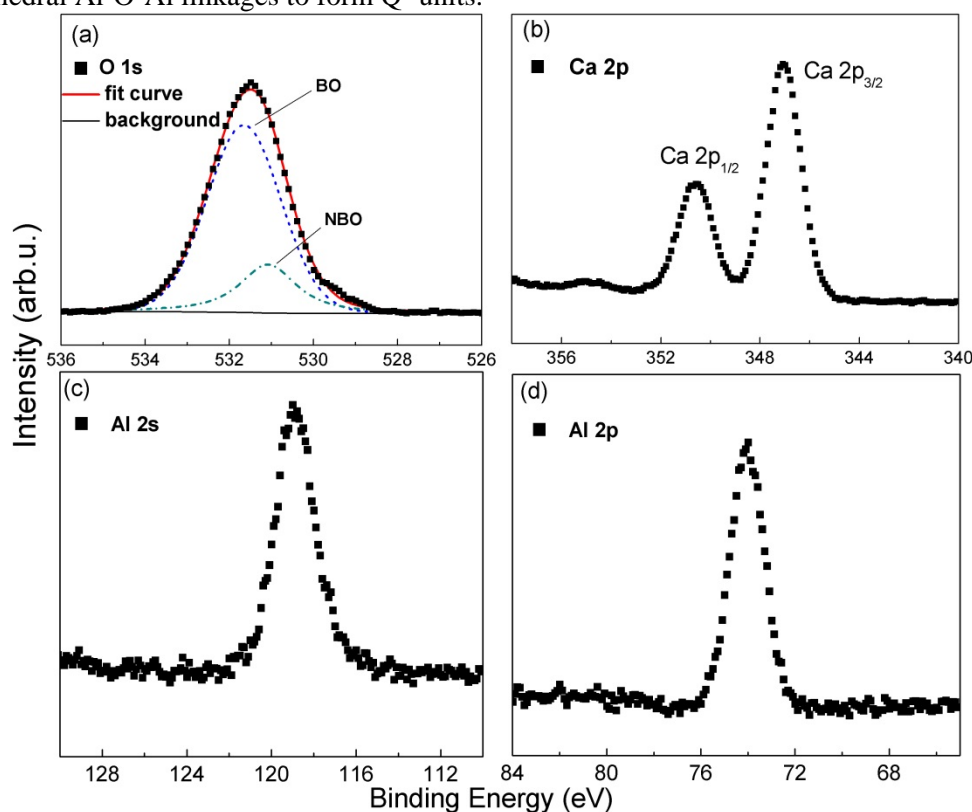


Figure 3. XPS spectra of O 1s (a), Ca 2p (b), Al 2s (c) and Al 2p (d), respectively.

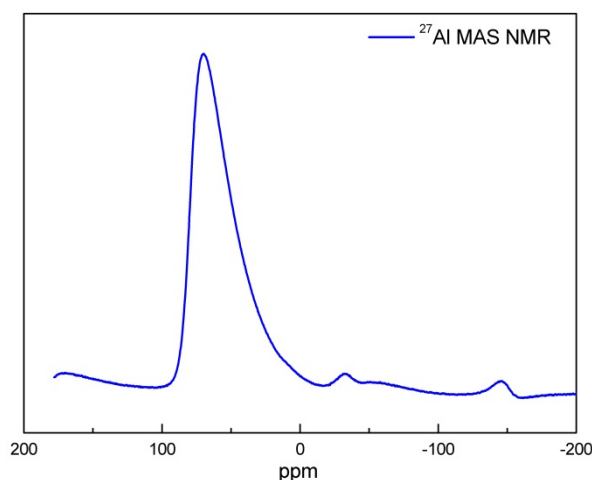


Figure 4. ^{27}Al MAS-NMR spectrum for C12A7 glass tested at room temperature.

4. Conclusions

In this work, C12A7 glass was prepared. DSC and XRD tests indicate that the glass transition temperature and the crystallization temperature of C12A7 are about 1050 K and 1194 K, respectively. The ability of glass formation of C12A7 is poor. Analysis on XPS and NMR indicates that Al coordination number is about four in C12A7 glass. And AlO_4 tetrahedron and bridging oxygens (BO) constitute the glass network. Ca^{2+} produces a few of non-bridging oxygens (NBO), which become the neighbours of Al.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (no. 51272072) and the funding of State Key Laboratory of Silicate Materials for Architectures (SYSJJ2016-14).

References

- [1] Jerebtsov D A and Mikhailov G G 2001 *Ceram. Inter.* 27 25-28
- [2] Drewitt J W E, Hennet L, Zeidler A, Jahn S, Salmon P S, Neuville D R and Fischer H E 2012 *Rev. Lett.* 109 235501
- [3] Drewitt J W E, Jahn S, Cristiglio V, Bytchkov A, Leydier M, Brassamin S, Fischer H E and Hennet L 2012 *J. Phys.: Condens. Matter* 24 099501
- [4] Neuville D R, Henderson SG, Cormier L and Massiot D 2010 *Am. Miner.* 95 1580–1589.
- [5] Hosono H, Kim S W, Miyakawa M, Matsuishi S and Kamiya T 2008 *J Non-Cryst. Solids* 354 2772-2776
- [6] Meng Q, Lin J, Fu L, Zhang H, Wang S and Zhou Y 2001 *J. Mater. Chem.* **11** 3382-6
- [7] Assem E E 2005 *J. Phys. D: Appl. Phys.* **38** 942-5
- [8] Sung Y M and Dunn S A 1996 *J. Mater. Sci.* **31** 4741–4
- [9] Chowdari B V R, Rao G V S and Lee G Y H 2000 *Solid State Ionics* 136–137 1067–1075
- [10] Voigts F, Bebensee F, Dahle S, Volgmann K and Friedrichs W M 2009 *Surface Science* 603 40–49
- [11] Comans R N J, Eighmy T T and Shaw E L 1996 *Surf. Sci. Spectra* 4 150-156
- [12] Dalai M K, Kundu R, Pal P, Bhanja M, Sekhar B R and Martin C 2011 *J Alloys Compd.* **509** 7674–7676
- [13] Benito N, Díaz D, Vergara L, Galindo R E, Sánchez O and Palacio C 2011 *Surf. Coat. Tech.* 206 1484–1489
- [14] Brand J V D, Sloof W G, Terryn H and Wit J H W 2004 *Surf. Interface Anal.* **36** 81–88
- [15] McMillan P F, Petuskey W T, Coté B, Massiot D, Landron C and Coutures J P 1996 *J Non-Cryst. Solids* 195 261-271