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Lionel Montagne, K. Sharma, G.P. Kothiyal, F.O. Méar. Influence of V₂O₅ on a sealing glass and self-healing VB₂-glass composites. *Solid State Sciences*, 2021, 119, pp.106706. 10.1016/j.solidstatesciences.2021.106706 . hal-03610177

HAL Id: hal-03610177

<https://hal.science/hal-03610177v1>

Submitted on 22 Aug 2023

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Influence of V₂O₅ on a sealing glass and self-healing VB₂-glass composites

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Abstract

The effect of V₂O₅ addition on sealing properties of glasses with nominal composition (29-x)SiO₂-23SrO-32BaO-4Al₂O₃-10B₂O₃-2P₂O₅-xV₂O₅ (where x = 2; 4; 6 mol.%) is reported. The glass transition temperature (T_g) decreases, and flow temperature increases with an increase in V₂O₅ content. ²⁹Si and ³¹P MAS-NMR indicate that silicates are present mainly as Q² groups, while phosphates are present as Q⁰ groups. ²⁷Al MAS-NMR data shows that Al is 4-coordinated with oxygens, and ¹¹B NMR spectra show the presence of both BO₃ and BO₄ units. Composite materials were prepared by mixing glasses and vanadium di-boride VB₂ (15 vol.%). Sealing with Crofer-22 alloy was carried out with composite and revealed good bonding and tight interfaces.

Keywords

Sealing glass; Self-healing; NMR; Thermal properties; V₂O₅

1. Introduction

Glasses and glass-ceramics have been studied as promising sealants materials for Solid Oxide Fuel Cell (SOFC) [1, 2]. During working conditions, SOFCs are subjected to different thermal cycles, which can result in building of stress within the sealant materials and can lead to formation of micro-cracks [3, 4]. Therefore, in order to increase the life-time and performance of sealant, it is desired that the sealant materials are able to repair the damages arising due to long term operation of devices. Thus, studies have been reported on new materials and methodology to heal micro-cracks / damages, increase wettability and ensuring stronger bonding and mechanical strength [5]. The damages can be repaired when glass based sealant materials heated above its softening temperature and enables the glass to flow in micro-cracks. However, sufficient flow of glass takes place at high temperature, which can deteriorate the other components of the SOFCs. Nevertheless, the flow temperature of glass can be reduced by increasing modifying oxides in the glass formulation, ensuring the healing of micro-cracks at lower temperatures. V_2O_5 is interesting as it acts as an intermediate oxide and leads to decrease in glass flow temperature, and in addition it contributes to reduce the glass surface tension, which may result in good wettability and bonding with the sealing components [6].

Some studies have shown that the micro-cracks in glass can be healed using composite materials composed of active particles dispersed in the glass matrix. $MoSi_2$, SiC , B_4C , ZrB_2 , HfB_2 have been studied as active particles for healing of micro-cracks by their oxidation at higher temperatures [7, 8]. Coillot et al. [9] investigated the role of different active particle like B, B_4C , VB, V and VC for healing of cracks. The filling of cracks takes place through the particle oxidation and the formation of respective oxides when exposed to air; for example VB is oxidized to V_2O_5 and B_2O_3 and lead to filling of cracks. As VB particles form oxides at relatively

low temperature, healing of cracks is achieved at lower temperature, which is useful for some sealing applications with temperature sensitive materials.

In the present work, we report the influence of V_2O_5 addition on the properties of sealing glasses with nominal composition $(29-x)SiO_2-23SrO-32BaO-4Al_2O_3-10B_2O_3-2P_2O_5-xV_2O_5$ (where $x=2; 4; 6$ mol.%), and self-healing composites made of glass with 15 vol.% of VB_2 .

We have previously reported the beneficial effects of P_2O_5 on sealing properties of these glasses [10], and the substitution of part of P_2O_5 by V_2O_5 has also contributed in improving their sealing behavior with Crofer alloy [11]. In the present paper, considering the glass forming character of V_2O_5 , and the necessity to keep thermal characteristics of the sealing glass as low as possible, we decided to introduce V_2O_5 in substitution of SiO_2 in the glass compositions. Since under SOFC conditions the glass will be kept at high temperature (typically $800^\circ C$) for long time, it will generally crystallize to produce a glass-ceramic like material. This is why we also studied the evolution of the glasses after a heat treatment of 100 hours at $800^\circ C$.

The sintering and flow properties of the composites made of glass mixed with 15 vol.% of VB_2 have been studied by Hot-Stage Microscopy (HSM). Finally, we will present the sealing behavior of glasses and composites with Crofer 22 APU alloy.

2. Experimental methods

Glasses with nominal composition $(29-x)SiO_2-23SrO-32BaO-4Al_2O_3-10B_2O_3-2P_2O_5-xV_2O_5$, (where $x=2; 4; 6$ mol.%) were prepared by melt quench technique (Table 1). The carbonate or oxide precursor of 99.9% purity were mixed, ground and calcined at a maximum temperature of $900^\circ C$ in a Pt-Rh crucible. The calcined charge was then melted at $1450-1550^\circ C$. The melt was then poured on stainless steel plate. The glass samples were annealed at around $650^\circ C$ for 4

hours with slow heating rate of $1^{\circ}\text{C}\cdot\text{min}^{-1}$. Weight losses were carefully checked during thermal treatment, hence actual composition is considered to be similar to nominal one. The glass samples were heat treated at 800°C for 100h with heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$, which is the operating temperature for most of SOFC.

Table 1. Nominal compositions (mol.%) of glass samples.

Sample	SiO ₂	BaO	SrO	B ₂ O ₃	Al ₂ O ₃	V ₂ O ₅	P ₂ O ₅
V2	27	32	23	10	4	2	2
V4	25	32	23	10	4	4	2
V6	23	32	23	10	4	6	2

As prepared glasses were powdered and mixed with 15 vol.% VB₂ particles. The particles were mixed in slurry (ethanol) for uniform mixing in pestle and mortar. In order to simulate the sealing condition, the composites were heated to 800°C temperature in N₂ ambient pressure for 6h and thereafter structural changes were studied using XRD and MAS-NMR.

Differential Thermal Analysis (DTA) was carried out in temperature range of 30°C to 950°C with heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ in an air ambient using a TG-DTA instrument (Model SETSYS, Setaram, France). Thermal Expansion Coefficient (TEC) was measured in the temperature range of 30° to 900°C using Thermal Mechanical Analysis (TMA) instrument (Model TMA-92, Setaram, France).

X-ray powder diffraction (XRD) were done using Cu K α radiation and a scanning 2θ range from 10° to 60° with 0.02° resolution (Bruker D8 diffractometer).

^{29}Si , ^{27}Al , ^{11}B and ^{31}P MAS-NMR spectra were recorded at 2.34, 18.8, 18.8 and 9.4T, respectively, on Bruker AVANCE spectrometers, with 4 mm probes at 12.5 kHz spinning speed, except for ^{29}Si for which a 7 mm probe at 5kHz was used. The Larmor frequencies were 19.8, 104.2, 128.4, 162.3 MHz for ^{29}Si , ^{27}Al , ^{11}B and ^{31}P respectively. For ^{31}P , the pulse duration was 1.6 μs ($\pi/6$), and the recycle delay was 120 s. For ^{11}B , the pulse duration was 2 μs ($\pi/6$), and the recycle delay was 10 s. For ^{27}Al , the pulse duration was 1.5 μs ($\pi/8$), and the recycle delay was 2 s. For ^{29}Si , the pulse duration was 1.6 μs ($\pi/5$), and the recycle delay was 180 s. All relaxation delays were chosen long enough to enable relaxation at the field strength that was used. The ^{29}Si chemical shifts are relative to tetramethylsilane (TMS) at 0 ppm, those of ^{27}Al are relative to AlCl_3 at 0 ppm, those of ^{11}B nuclei are given relative to BPO_4 at 3.6 ppm and those of ^{31}P are relative to 85% H_3PO_4 at 0 ppm.

For studying the adhesion / bonding, sealing with Crofer 22 APU alloy was carried out at a maximum temperature of 1000°C employing the sandwich geometry. Microstructure near the interface was investigated using EPMA (Electron Probe Micro Analysis) instrument (Tescan Vega MV2300T/40) and line scan was carried out across the interface for the observation of element diffusion.

3. Results

The bubble-free and transparent glasses with yellowish tinge were obtained. The glass-composites having 15 vol.% VB_2 turned blackish.

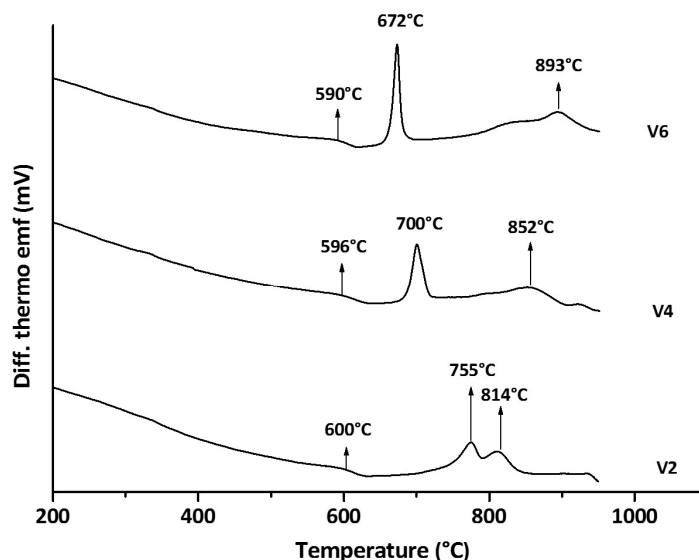


Figure 1. DTA plots of glasses.

DTA plots of glass samples are shown in Figure 1. The sample V2 showed a weak endothermic shift around 600°C that corresponds to glass transition, and two exothermic peaks around 775°C (T_{c1}) and 814°C (T_{c2}) corresponding to crystallization. As reported in Table 2, with increase of V_2O_5 content, glass transition and crystallization temperatures shifted to lower temperature. The exothermic peaks are observed at 700°C (T_{c1}) and 672°C (T_{c2}) for samples V4 and V6 samples, while the glass transition temperature decreased to 590°C when V_2O_5 content is increased to 6 mol.%. However, the peak corresponding to second crystallization (T_{c2}) temperature has shifted to higher temperature with increase in V_2O_5 content. TEC values of glass samples are reported in Table 2. TEC of V2 glass was found around $12.10^{-6} K^{-1}$. TEC value increased to $13.10^{-6} K^{-1}$ when V_2O_5 content increased to 6 mol.%.

Table 2. Thermo-physical properties of the glasses (with T_g ($\pm 2^\circ C$) Glass transition temperature, T_s ($\pm 2^\circ C$) Softening point, T_c ($\pm 3^\circ C$) Maximum crystallization peak, TEC ($\pm 0.2.10^{-6} K^{-1}$)

Thermal expansion coefficient, $T_{\text{shrinkage}}$ ($\pm 2^\circ\text{C}$) Shrinkage temperature, T_{flow} ($\pm 3^\circ\text{C}$) Flow temperature).

Sample	TEC	T_g	T_c		T_s	$T_{\text{shrinkage}}$	T_{flow}
			T_{c1}	T_{c2}			
V2	12.0	600	755	814	654	720	1145
V4	12.7	596	700	852	641	770	1107
V6	13.1	590	672	893	638	785	1108

The HSM plots of the different glass and composite samples are shown in Figure 2. The sintering temperatures do not vary significantly when V_2O_5 content is increased up to 6 mol.%. V2 glass shows a gradual change in slope and maximum shrinkage was observed around 720°C . The maximum shrinkage and flow temperatures increased with an increase of V_2O_5 content. HSM plots have also indicated an increase of maximum shrinkage temperature of glass samples when VB_2 was added.

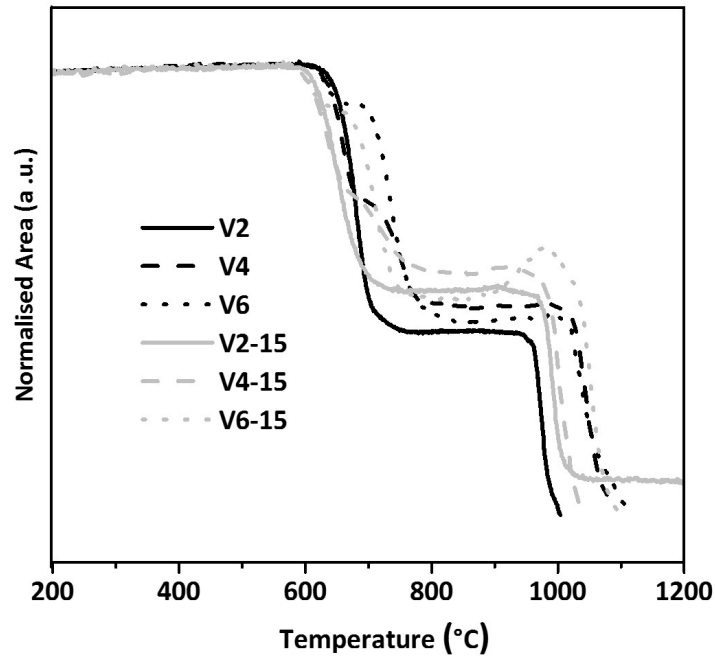


Figure 2. HSM plots of different glass and glass-composite samples.

In order to simulate the operating temperature of SOFC, glass samples were heat treated at 800°C for 100h. XRD patterns of glass samples after controlled heat treatment at 800°C for 100h are shown in Figure 3. V2 glass after heat treatment shows the formation of $\text{BaAl}_2\text{Si}_2\text{O}_8$ as major crystalline phase. The appearance of BaSiO_3 and Sr_2SiO_4 phases were also observed. $\text{BaAl}_2\text{Si}_2\text{O}_8$ remains the major crystalline phases when V_2O_5 content is increased to 6 mol.%, though, the relative content of Sr_2SiO_4 phase also increased.

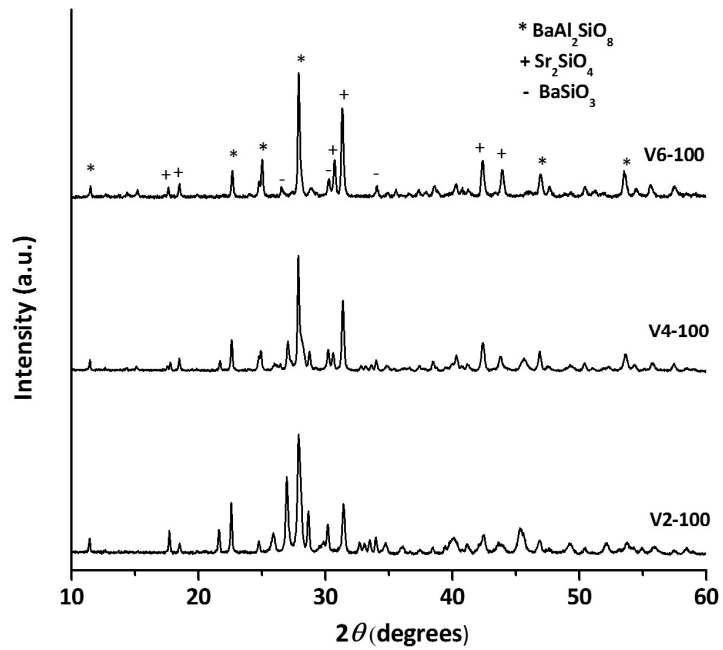


Figure 3. XRD plots of glass samples after heat treatment at 800°C for 100h.

^{29}Si NMR spectra of the glass samples are shown in Figure 4-a. The spectra of V2 to V6 glasses show a broad feature in the -70 to -100 ppm range, which can be attributed to a distribution of Q^3 and Q^2 structural units as reported in other aluminosilicate glasses [10, 11].

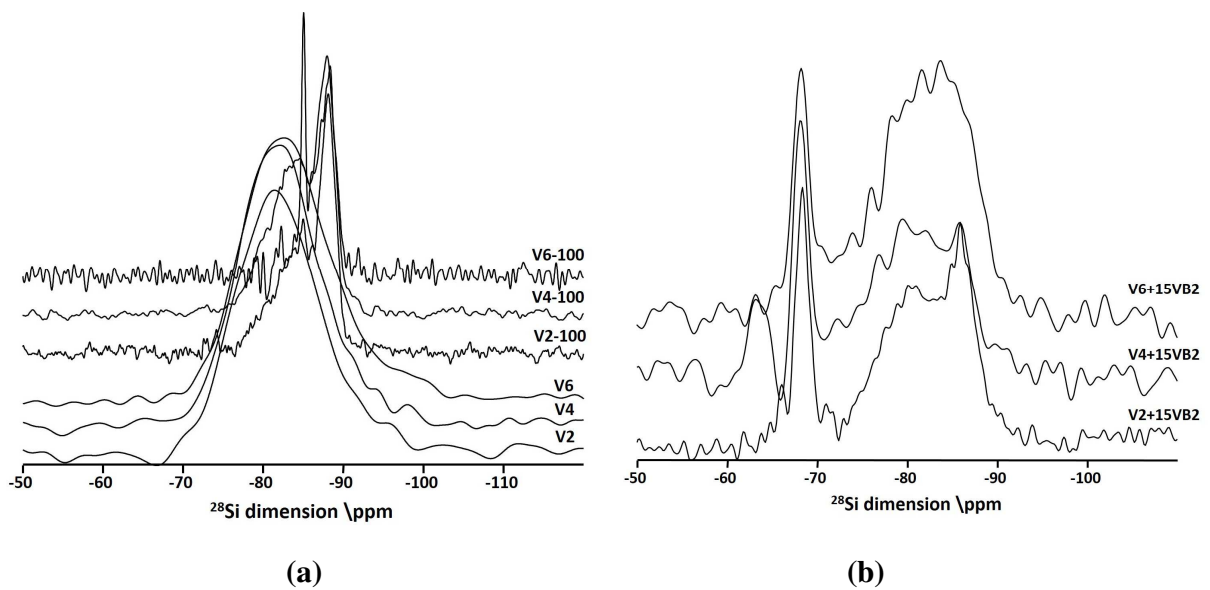


Figure 4. ^{29}Si MAS-NMR spectra of different (a) Glass and glass heat treated at 800°C for 100h samples and (b) Glass-composites.

^{29}Si NMR spectra of heat-treated glass samples show two narrow peaks superposed on a broad resonance assigned to the residual glassy phase. These resonances become sharper with increase V_2O_5 content, consistent with an increase in crystalline content as observed with XRD. The resonance at -85 ppm is possibly assigned the formation of barium or strontium meta-silicate $(\text{Ba,Sr})\text{SiO}_3$ [12], the other resonance at -88 ppm corresponds to the crystallization of the $(\text{Ba,Sr})\text{Al}_2\text{Si}_2\text{O}_8$ phase [11-13].

The NMR spectra of glass-composites are perturbed by the intermetallic character of VB_2 . They show the same broad resonances as for the glasses, meaning that composite preparation did not alter their structure significantly; in addition, some sharp resonances are also observed (Figure 4-b). The resonance at -68 ppm is a characteristic of barium or strontium orthosilicate $(\text{Ba,Sr})_2\text{SiO}_4$. The other resonance at around -88 ppm is also seen in heat-treated glass, and it is thus assigned to the crystallization of the aluminosilicate phase $(\text{Ba,Sr})\text{Al}_2\text{Si}_2\text{O}_8$.

^{11}B NMR spectra of the samples are shown in Figure 5, those of the composites are also affected by the presence of VB_2 . The spectra of both glasses and heat-treated glass consist of two resonances centered on 16 ppm and 1 ppm. The resonances can be assigned to BO_3 and BO_4 units, respectively [12]. In addition to these resonances, ^{11}B NMR spectra of glass-composites also show the presence of resonance around at 50 ppm due to the presence of VB_2 .

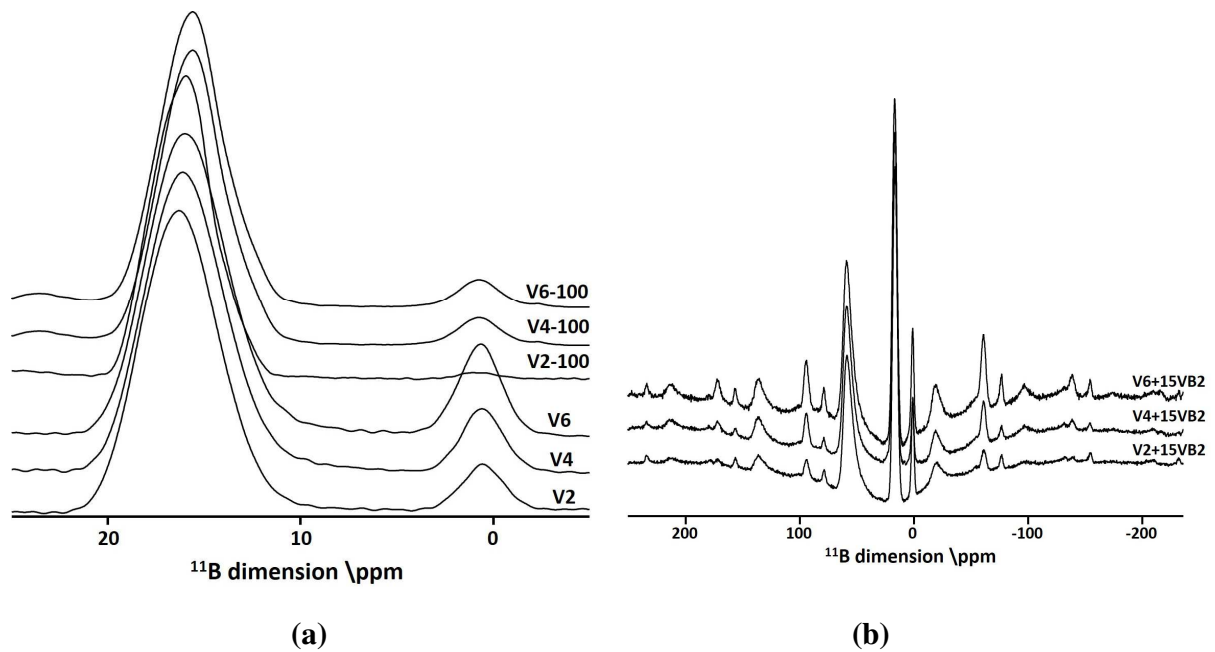


Figure 5. ^{11}B MAS-NMR spectra of different (a) Glass and glass-ceramic (heat treated at 800°C for 100h) samples and (b) Glass-composites.

^{27}Al NMR spectra of glasses and glass-composites are reported in Figure 6. The spectra of the glasses consist of a broad resonance centered at ~ 65 ppm, typical of aluminum coordinated with 4 oxygens, as expected in such glasses. After heat-treatment the resonance is much narrower, thus indicated that almost all of Al is involved in the crystalline phases. ^{27}Al spectra of the composites show the same feature as in glasses, but some crystallization may have already occurred during densification as shown by the narrower resonance of V6+15VB₂ composite.

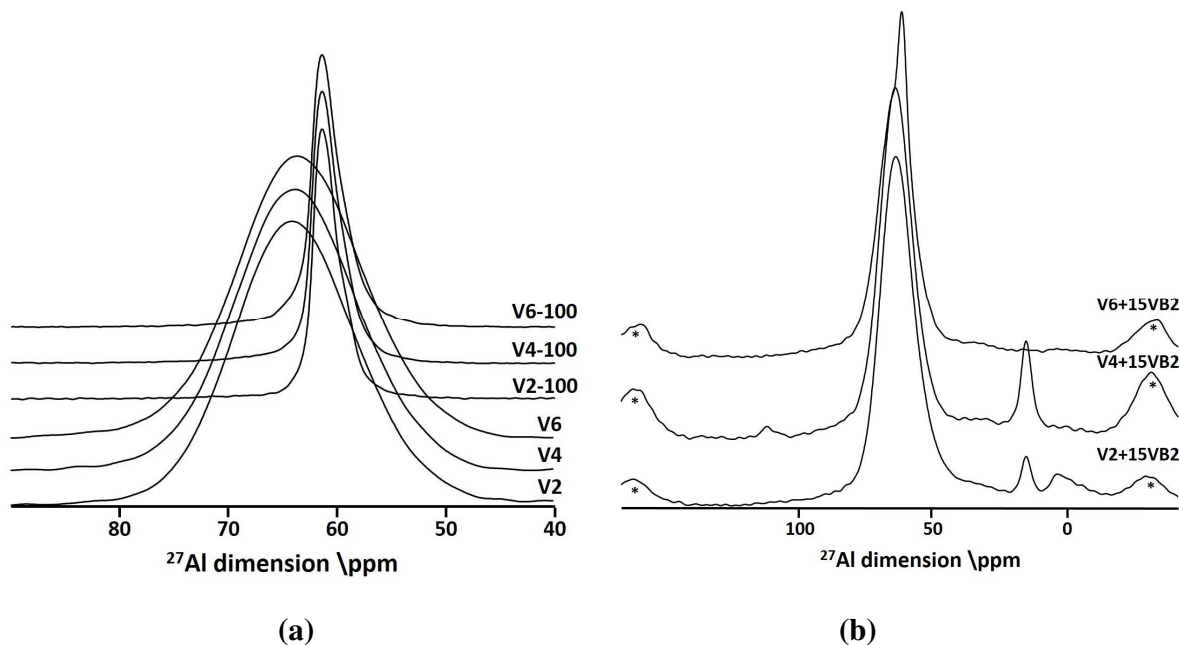


Figure 6. ^{27}Al MAS-NMR spectra of different (a) Glass and glass-ceramic (heat treated at 800°C for 100h) samples and (b) Glass-composites. Asterisk represent spinning side bands.

^{31}P NMR spectra of the glass and heat-treated glass samples are shown in Figure 7-a. A main broad resonance is observed at ~ 3 ppm, which is assigned to Q^0 (orthophosphate units) [11, 12]. After heat-treatment, the presence of a narrower peak around 4-5 ppm indicates the crystallization of $(\text{Ba},\text{Sr})_3(\text{PO}_4)_2$ [15]. This phase has not been detected on XRD diffractograms, probably owing to their very low amount since P_2O_5 content is 2 mol.% in the glasses. The chemical shift observed is close to that of Q^0 units in $\text{Sr}_3(\text{PO}_4)_2$ crystal (3 ppm) [12, 16]. Nevertheless, the large width of the resonance suggests that the some of the orthophosphate anions are also balanced by Ba^{2+} as the chemical shift of $\text{Ba}_3(\text{PO}_4)_2$ crystal has been reported around ~ 9 ppm.

^{31}P NMR spectra of the glass-composites are shown in Figure 7-b. A main resonance is observed around 3 ppm as seen for glass samples; however, a resonance around 25 ppm is also observed, which could not be assigned.

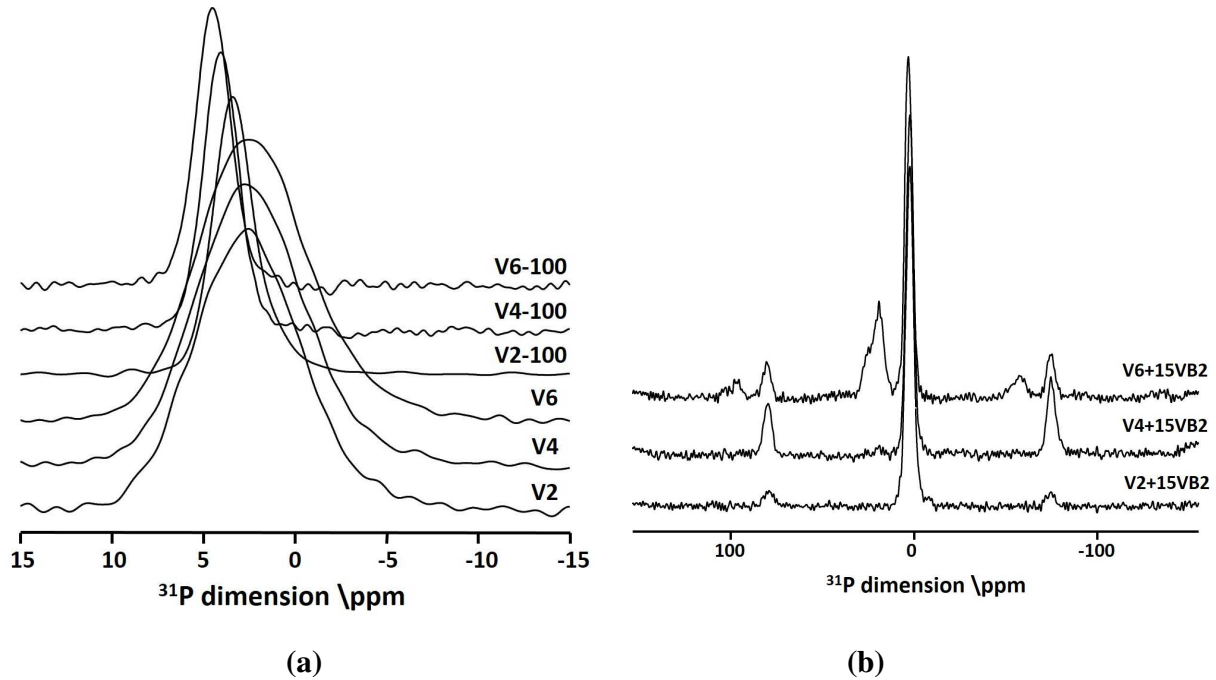


Figure 7. ^{31}P MAS-NMR spectra of different (a) Glass and glass-ceramics (heat treated at 800°C for 100h) samples and (b) Glass-composites.

^{51}V NMR spectra of glasses and glass-composites are shown in Figure 8. A broad resonance is observed at ~ 590 ppm in glass samples, which is close to that measured in $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Ba}_2\text{V}_2\text{O}_7$ crystal [12]. After heat-treatment, the resonance becomes much narrower, meaning that most of V^{5+} is included in crystalline phases, despite they could not be detected with XRD. Considering the close structural properties of V^{5+} and P^{5+} , it can be suggested that V^{5+} is included in the phosphate phases in substitution of P^{5+} . ^{51}V NMR spectra could not be recorded for the composites because of the strong signal perturbation by VB_2 .

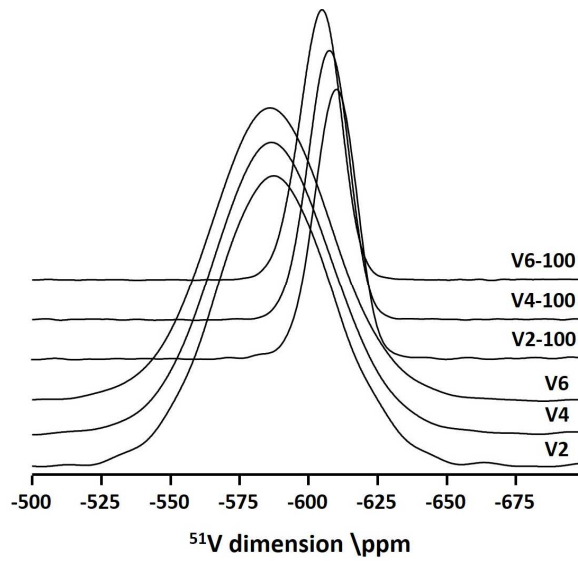


Figure 8. ^{51}V MAS-NMR spectra of different glass and glass-ceramic (heat treated at 800°C for 100h) samples.

Figure 9 shows SEM pictures of the interfaces of glasses with Crofer-22 APU. The seals of glass samples with metal part were found good as no bubble or crack was observed. The V2 glass shows the formation of small crystallites of $1\text{-}2\ \mu\text{m}$ and of needle shape. The samples V4 and V6 showed the same microstructure with bigger crystallites sizes, which increases from $1\text{-}2\ \mu\text{m}$ to around $5\ \mu\text{m}$ when V_2O_5 content was increased.

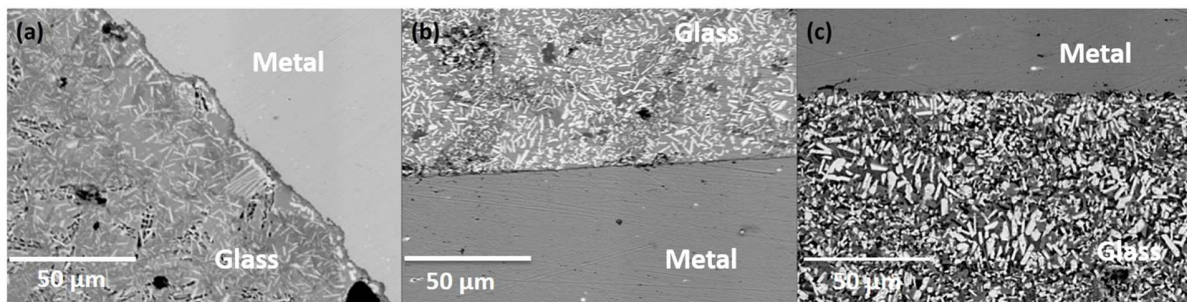


Figure 9. Microstructure near the interface of glass samples with Crofer 22 APU (a) V2 (b) V4 (c) V6.

As will be discussed below, V2 glass was considered as the best glass composition for the sealing application. Thus V2 glass with 15 vol.% VB₂ composite was used for sealing with Crofer 22 APU interconnect. The microstructure at interface of the seal gives evidence for a good bonding with no bubble or crack (Figure 10-a). Elemental mapping (Figure 10-b) of the seal shows an enrichment of Cr and V at the interface, and an interdiffusion of Fe, Sr and Ba across the boundary is also observed, but in limited amount.

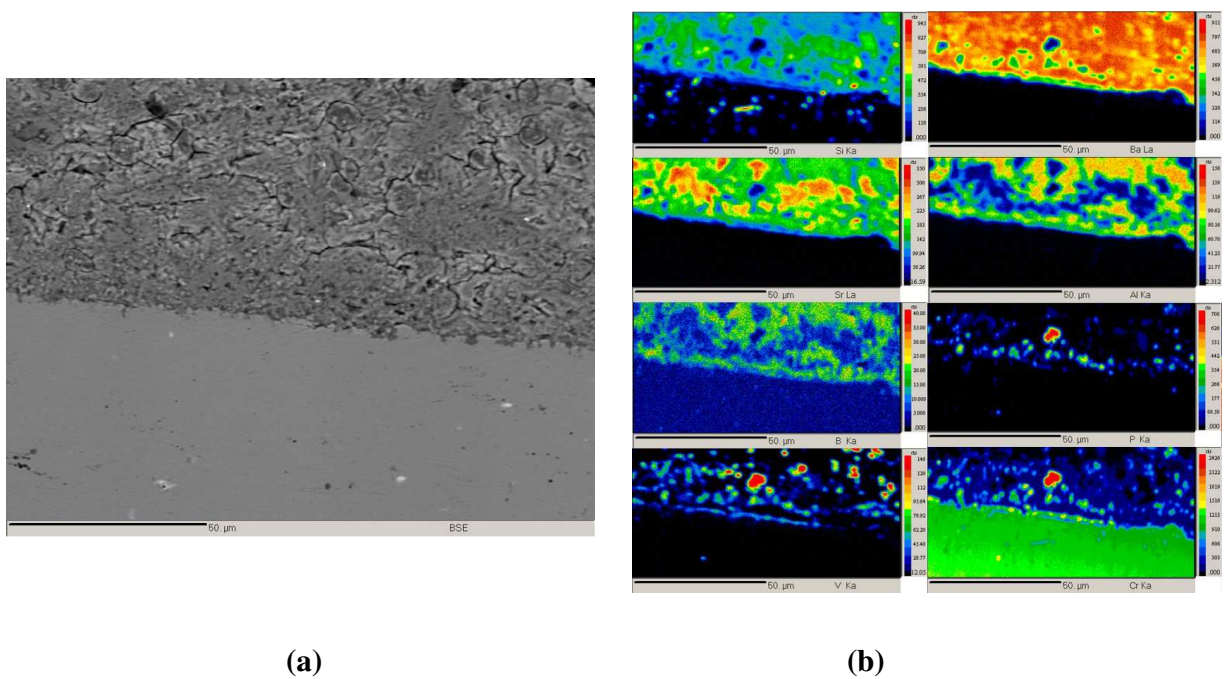


Figure 10. (a) Microstructure near the interface of V2 glass-composites with Crofer 22 APU and (b) Elemental mapping of the interface of V2 glass-composites with Crofer 22 APU.

4. Discussion

We observed that TEC values of glass samples show a limited increase with addition of V₂O₅ in substitution of SiO₂, which enables to keep their value quite close to that of Crofer 22 APU alloy (Table 2). Concurrently, T_g and softening temperatures are also decreased, which is beneficial as

the sealing with metallic interconnect could be operated at a temperature of 1000°C compatible with the other SOFC components.

DTA plots of glass samples show that V₂O₅ addition facilitates the glass crystallization as it acts as a nucleating agent [6, 18]. Indeed, peak crystallization temperature decreased from 755°C to 672°C when V₂O₅ content was increased from 2 to 6 mol.%. However, for sealing application, it is required that the densification of glass takes place before a significant crystallization occurs [19]. Glass V2 attains the maximum shrinkage at a temperature of 720°C (Figure 2), which is well below the crystallization temperature of 755°C. The samples V4 and V6 show the attainment of maximum shrinkage (770-785°C), however the peak crystallization temperature in the samples are observed at lower temperature ($T_c = 700-672^\circ\text{C}$). This means that the crystallization would take place before the attainment of maximum shrinkage in the glass samples, and this explains why the V2 glass composition was selected for the sealing application.

NMR spectroscopic studies carried out on the glass samples reveal the amorphous nature of the materials. The local structure of the main network forming elements (Al and B) is not affected by the introduction of V₂O₅ in the glasses, and also not significantly during the densification of the composites (with VB₂). After heat treatment, NMR analysis of the glasses has shown the formation of (Ba,Sr)Al₂Si₂O₈ and Sr₂SiO₃ as major crystalline phases, which is found in agreement with XRD analysis of the samples. Nevertheless, some residual glassy phase is still present after heat treatment, which is beneficial to ensure a tight interface with the bonded metal.

The SEM pictures of the sealed glasses has shown an increase in the size of crystallites when the V₂O₅ content is increased. This is attributed to the lowering of crystallization temperature of glasses with increase of V₂O₅ content, and this is in accordance with the nucleating character of

V₂O₅. The seals made with V₂ glass and VB₂ showed good adhesion to Crofer22 APU alloy, and limited element diffusion is measured at the interface.

5. Conclusions

HSM and DTA experiments led to the conclusion that glass with 2 mol.% V₂O₅ is better than those with 4 and 6 mol.%. Indeed, V₂O₅ addition enables the lowering of the glass transition temperature, but it also leads to decrease in peak crystallization temperature, this is why 2% V₂O₅ content was found as an optimum value to carry out densification before crystallization occurs. The local structure of the major elements in glasses (Si, Al, B, P) did not changed with addition of V₂O₅ and during the composite elaboration. Finally, the composite seal made with the V₂ glass and VB₂ revealed good interface with Crofer22 APU alloy.

Acknowledgements

The authors thank the IFCPAR for funding this work vides projectnumber 4008-1. The FEDER, Région Nord Pas-de-Calais, Ministère de l'Education Nationale de l'Enseignement Supérieur et de la Recherche, CNRS, and ULILLE are acknowledged for funding of NMR spectrometers.

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