Some Properties of Lithium Aluminium Silicate (LAS) Glass-Ceramics Used in Glass-Ceramic to Metal Compressive Seal for Vacuum Applications

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Abstract. We report here the preparation of LAS glass-ceramics and some studies on their thermo-physical properties and microstructure, for compressive seals in vacuum applications. Glass of composition 12.6Li₂O-71.7SiO₂-5.1Al₂O₃-4.9K₂O-3.2B₂O₃-2.5P₂O₅ was prepared by the conventional melt quench technique. Based on differential thermal analysis (DTA) data, glass samples were nucleated at 600°C for 2hr and were then crystallized at 800°C for 2-5hr. X-ray diffraction (XRD) spectra showed lithium disilicate to be the major phase. A dwell time of 3hr yielded a sample of good crystallinity. Dilatometric measurements of this sample on a thermo-mechanical analyzer (TMA) measured a thermal expansion coefficient (TEC) of 94.61x10⁻⁷°C⁻¹. Glass transition temperature (Tg), and dilatometric softening temperature (Tds) of the sample was recorded as 585°C and 830°C respectively. Considering TEC and Tds compression type seals were prepared with SS304 (TEC=172x10⁻⁷°C⁻¹) housing of length 15mm, outer diameter 30mm and inner diameter 15mm. After pre-heat treatment of the metal components, sealing was carried out under a protective atmosphere of flowing Argon gas. The finished seal was tested for leak tightness on a He leak detector. The seal was capable of withstanding a vacuum of 10⁻⁶ Torr; at a leak rate of 10⁻⁹ Torr l/s. Scanning electron microscopy (SEM) was carried out on LAS before and after fabrication of compressive seal to elucidate the effect of compressive stress and the presence of metal near the interface. We observe a significant difference in microstructure due to compressive stresses of sealing and due to the presence of metal. Energy dispersive analysis of X-rays (EDAX) revealed no interdiffusion of species from glass-ceramic to metal or vice-versa.

1. Introduction
The bonding of glasses with metals is a well-documented occurrence that has been exploited to improve aesthetics and wear durability of metals for a long time [1,2]. More recent technical application of glasses include the use of glasses to coat metals as a thermal barrier coating, with the aim of protecting the underlying metal from high temperature corrosive ambient, or in sealing to metal to form hermetic seals for use under vacuum, pressure and even in corrosive environments. While glass-to-metal (GM) seals have been fabricated between various glasses and metals [1], glass-ceramics offer a number of advantages such as tuneable thermal expansion coefficient (TEC), better chemical durability and generally enhanced mechanical properties [3]. Glass-ceramics (GC) belonging to the...
lithium aluminium silicate system are candidates for sealing to metals due to their excellent chemical
durability, wide range of TECs possible and excellent mechanical properties [4]. In this paper, we
report the fabrication of LAS glass-ceramic-to-SS304 compressive seals and some studies on the
properties of the LAS glass-ceramics. These studies are also expected to throw light on microstructure
changes occurring at the glass-ceramic to metal interface as a consequence of compressive stresses and
the presence of the metal housing.

2. Experimental procedure

2.1. Preparation of glass-ceramic and materials characterization

LAS glass of composition 12.6Li2O-71.7SiO2-5.1Al2O3-4.9K2O-3.2B2O3-2.5P2O5 was prepared by
conventional melt quench technique. Analytical grade precursors (Li2CO3, Al2O3, SiO2, B2O3,
NH4H2PO4 and KNO3) were mixed thoroughly and calcined in recrystallized alumina crucibles
according to a schedule determined by the decomposition temperatures of the precursors. To ensure
complete decomposition of nitrates and carbonates into oxides, the batch was weighed before and after
calcination to ensure weight loss. The calcined batch was melted under air ambient at 1500°C in a
raising and lowering hearth furnace (Model OKAY M/s Bysakh and Co. Kolkata) and held for 1-2hr
to ensure melt homogenisation. The melt was poured onto pre-heated graphite mould and annealed at
500°C for a 3 hr to relieve thermal stresses. The vitreous nature of the annealed glass was verified by
by powder XRD (Philips PW1710 X-Ray Diffractometer with collimated Cu Kα radiation).

DTA measurements on glass powders were performed on a Setaram 92-15 TG/DTA apparatus that
was calibrated using the melting points of high purity indium and zinc. The non-isothermal
experiments were performed by heating approx. 40mg of the sample in Pt crucibles under protective
ambient, using empty Pt crucible as reference. A heating rate of 10° K/min was employed in the range
25-1000°C. Based on DTA data, a two step process was employed to convert glasses into glass-
ceramics. Samples were heated at 60°C/hr to 600°C and held there for 2hr. This was followed by
heating at the same rate to the crystal growth temperature of 800 °C (T2). Samples were held at that
temperature for various time durations from 2-5 hr and were then cooled in the furnace to room
temperature. Glass as well as glass-ceramic samples were made flat by polishing and used for thermo-
mechanical analysis (TMA) (Model 92-12 M/s Setaram, France). TMA was employed to measure the
TEC, glass transition temperature (Tg), and dilatometric softening temperature (Tds) of all samples.

Glass and glass-ceramic pieces were mirror polished and used for micro-hardness measurements by
a Vicker’s micro-hardness tester (Model VMHT 30M M/s Leica). In all cases, an indentation load
of 100g for 10s was employed unless specifically mentioned otherwise. Vicker’s micro-hardness number
(VHN) was calculated by measuring the diagonal length of the indentation made in the sample by a
square base pyramidal indenter, according to equation 1 [5]:

\[
\text{VHN} = 2F d^{-2} \sin \left( \frac{\theta}{2} \right)
\]

where, F is the applied load, d is the diagonal length of the indentation and \(\theta\) (=136°) is the angle of
the pyramidal indenter. The VHN numbers reported are the averaged values for at least 10
indentations. Density of all glass and glass-ceramics was measured by using the Archimedes principle
using distilled water as the immersion fluid. The formula used for calculating density (\(\rho\)) was:

\[
\rho = \frac{W_a}{W_b - W_a}
\]

where, \(W_a\) is the sample weight in air, while \(W_b\) is the sample weight in water. All weights were
measured on a single scale electronic balance with an accuracy of ±0.02g. Powder XRD in the range
10°≤θ≤70° was carried out to identify the crystalline phases formed in all glass-ceramics. Etched
(10% HF for 10s) samples were coated with gold and imaged using SEM (Vega MV 2300T/40) to
study phase morphology. EDAX attachment was employed to discern the chemical compositions of the various phases evolved.

2.2. Seal fabrication/characterization

We used SS304 housing of length 15 mm, outer diameter 30 mm and inner diameter 15 mm for seal fabrication. The steel housings were thoroughly cleaned and were then degreased in organic solvent. The housings were fired in wet H\(_2\) at 975°C for 30 min to achieve good oxide layer growth of desired thickness and texture. The housings were then mounted on a graphite jig and filled with crushed LAS glass frit. The whole assembly was then securely placed on a suitable support in the sealing furnace.

Seal fabrication was carried out under flowing Ar to prevent oxidation of the graphite jig. The loaded assembly was heated to about 950°C and held there for 45 minutes to allow the glass to melt and wet the metal. In the cooling cycle, the assembly was then cooled in the furnace to 800°C. After holding at 800°C for 60 minutes, the assembly was cooled to 610°C and held there for 60 minutes. Subsequently, after annealing at 450°C for 30 minutes, the assembly was allowed to cool in the furnace to room temperature. In the heating cycle, after the 950°C step, the assembly was cooled to 610°C and held for 60 min. Subsequently, heating to 800°C was carried out. After holding at 800°C for 60 min, the assembly was annealed at 450°C for 30 min before cooling in the furnace to room temperature. The seals were tested for leak tightness and leak rate on a He leak detector set-up. After checking vacuum leak tightness and measuring leak rate, the seal fabricated in heating cycle was sectioned using a Buehler ISOMET 4000 linear precision saw, coated with gold and imaged using SEM. EDAX line scan was performed across the metal glass-ceramic interface to study interdiffusion of elements.

3. Results and discussion

After annealing, clear transparent bubble free glasses were obtained. DTA curve of the as annealed glass is given is figure 1.

![DTA curve of LAS glass exhibiting two crystallization exotherms.](image)

The DTA curve of the glass exhibits two well-defined exothermic events. The exotherm at ~ 610°C arises due to the crystallization of lithium metasilicate (Li\(_2\)Si\(_2\)O\(_5\)) and cristobalite while the exotherm at ~ 800°C arises due to formation of lithium disilicate (Li\(_2\)Si\(_2\)O\(_5\)) [6,7]. Based on DTA data,
glasses were crystallized to yield glass-ceramics. The properties of the parent glass and glass-
ceramics obtained are summarised in Table 1.

| Sample Name | tₜ (hr) | TEC(×10⁻⁶/°C) | Tₙ (°C) | µH (GPa) | Density (g/cc) |
|-------------|---------|---------------|--------|---------|---------------|
| LAS 1G      | 0       | 10.5          | 543.83 | 5.73    | 2.40          |
| LAS 1a      | 2       | 8.397         | 573.21 | 6.47    | 2.39          |
| LAS 1e      | 2.5     | 9.062         | 551.05 | 6.65    | 2.41          |
| LAS 1b      | 3       | 9.461         | 584.75 | 6.62    | 2.40          |
| LAS 1c      | 4       | 8.896         | 544.90 | 6.79    | 2.41          |
| LAS 1d      | 5       | 8.962         | 582.45 | 6.84    | 2.41          |

From the data given in table 1, we notice that the parent glass has a higher TEC than the
glass-ceramics obtained from it. Also, the microhardness of the parent glass is significantly less than
that of the glass-ceramics. We also observe that 3hr dwell time results in sample with highest TEC.
While a large change in TEC and micro-hardness occurs on devitrification, there is no notable change
in the density. The XRD patterns of various LAS glass-ceramics are shown in figure 2. The major
phase revealed in XRD is lithium disilicate along with some aluminium silicate, the fraction of which
seems to increase with time.

![XRD patterns of LAS glass-ceramics after various dwell times at 800°C.](image)

**Figure 2.** XRD patterns of LAS glass-ceramics after various dwell times at 800°C.
The XRD pattern of sample given a dwell time of 3 hr seems to show the highest crystallinity. Verification of this conjecture is provided by SEM. SEM micrograph of annealed glass-ceramic sample given a dwell time of 3 hr reveals an ovoidal microstructure of lithium disilicate of average grain size of 150-200 µm (figure 3a). The microstructure of the glass-ceramics close to the GC to metal interface developed after seal formation is shown in figure 3b. This picture shows the microstructure of the metal (left) and the glass-ceramic (right) at the interface. It was also interesting to note that the microstructure of the glass-ceramics was markedly affected by the presence of the SS304 housing as shown in figure 3b.

Figure 3a. Microstructure of the glass-ceramic in the absence of the metal housing.

Figure 3b. Microstructure of glass-ceramic in the presence of the metal housing. To the left while glass-ceramic is to the right.
It is evident from the microstructure that the average crystallite size is smaller (~100-150 µm) in the glass-ceramic in intimate contact with metal as compared to the glass ceramic formed in the absence of the metal housing. Figure 4 shows a micrograph of the interface at higher magnification. The appearance of the microstructure at the interface is somewhat undulating. Compressive stresses during the crystallization process slow down the grain growth leading to a finer microstructure and smaller crystallites [8]. This observation agrees with reports that the presence of the metal in contact with the GC influences the microstructure and the TEC [1].

EDAX line scans run along the glass-ceramic to metal interface showed no interdiffusion of species from glass-ceramic-to-metal or vice versa thus confirming that sealing was occurring due to compressive forces.

LAS glass-ceramic-to-metal seal fabricated according to the procedure detailed earlier, was found capable of withstanding a pressure of $10^{-6}$ Torr at a leak rate of $10^{-9}$ Torr l s$^{-1}$.

**Figure 4.** SEM micrograph of the glass-ceramic at 5Kx magnification. The microstructure shows undulations resulting from compression.

**4. Conclusion**

Transparent bubble free LAS glasses were obtained by conventional melt quench technique. Crystallization dwell time of 3hr yielded highly crystalline samples. The major phase was lithium disilicate. LAS glass-ceramic to SS304 compressive seal was fabricated. The seal withstood vacuum of $10^{-6}$ Torr at a He leak rate of $10^{-9}$ Torr l s$^{-1}$. It is observed that proximity with metal housing has a marked impact on the microstructure of the glass-ceramic especially close to the interface. The effects of compression are readily visible in SEM images as smaller crystallite size and an undulating microstructure near the interface. EDAX did not reveal any interdiffusion of species. It would be quite interesting to observe the effect of compressive stresses due to seal fabrication on the crystalline phases formed in the compressive type seal. The use of LAS seals is expected to be more environmentally safe as compared to Pb containing seals [9].
5. References

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