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CHEMICAL ETCHING OF AlF-BASED GLASSES

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ABSTRACT

Aluminium fluoride based glass [AlF_3-M(II)F_2-xPO_3, M=Mg, Ca, Ba, Sr] fibres have potential for use as 1.3μm amplifiers, but successful application depends on improving their poor mechanical strength. Surface contamination of the preform is a major factor contributing to the lack of strength; it can be improved by chemical etching. As the glass components are highly unreactive, few etching studies have been reported in the literature. In this work, two multicomponent etches have been identified for the purpose and characterised. Optimum working compositions are 0.4M $AlCl_3.6H_2O$ / 1M HCl and 50% HF (48%) / 30% HNO_3 (68%) / 20% H_2O plus 3M H_3BO_3. Both yield fibres of significantly improved strength and quality, although the former etch tends to perform slightly better. Furthermore, an etch procedure has been developed for the aluminium chloride mixture which enables good strength fibre to be pulled in a controlled and reproducible manner.

INTRODUCTION

There has been considerable interest in fluoride fibres because of their optical performance [1][2][3]. Potential applications include long distance telecommunication systems, temperature or chemical sensing and power transmission [4]. Particular emphasis has been placed on fluorozirconate glass systems which are low loss, transmit further into the infrared, and can be more heavily doped with rare earth metal ions than silica. However, these glasses are limited by their poor chemical durability and mechanical strength [5]. As fibres are often stressed and subjected to a range of chemical environments (pH, temperature), it is important that their reliability is maintained over a realistic lifetime. This has resulted in the search for alternative glasses. Aluminium fluoride based glasses (ALF) have improved chemical stability, showing little degradation in aqueous environments, and can produce fibre with similar optical quality to ZBLAN [6]. In particular, the neodymium doped aluminium fluoride based glass, ALF1, [AlF_3-M(II)F_2-xPO_3, M=Mg, Ca, Ba, Sr] (T_g=430°C, T_x=560°C) is attractive for use as a 1.3μm optical fibre amplifier. However, for practical application, it must be possible to produce high quality optical fibres reproducibly.

Fabrication of ALF fibres is more difficult than ZBLAN because of the higher fibre drawing temperature (470°C<T<500°C; c.f. T~300°C in ZBLAN) which enhances the tendency to undergo surface crystallisation. Highly specific methods have had to be developed to prepare the ALF surface prior to fibre fabrication. Furthermore, this processing must yield fibres which maintain high mechanical strength in air to ensure reliability [7][8]. It is known that the mechanical strength of fluoride fibres largely depends on the surface state [1][9]. Removing the outer surface of the preform by mechanical or chemical polishing results in significantly improved fibres [1]. Mechanically polishing ALF preforms followed by a fine chemical etch, such as 0.4N solution $AlCl_3$ and HCl for 20 minutes at room temperature, appears to be the preferred route [6]. However, as mechanical polishing can leave debris and surface imperfections (eg. bubbles) an alternative chemical polishing technique would be preferable. A suitable etch has so far proved elusive; in general, the fluoride components are highly unreactive, resulting in few etching studies being reported in the literature [2],[3].

In this work, the question of designing and optimising a chemical etch for the aluminium fluoride based glass ALF1 is addressed. A system capable of removing a significant layer of glass (typically 0.5mm depth) in a realistic time period whilst generating an optical quality surface is identified and a procedure developed to give a reproducible maximum fibre strength.

EXPERIMENTAL PROCEDURE

The reported work is separated into two sections. The first section concerns etch design and the second focuses on etch procedure. In all experiments, ALF1 glass rods were used. All chemicals were from Aldrich (>99.9% purity) and were batched in a glovebox containing dry nitrogen. Melting took approximately 5 hours including a fluorination step, carried out in a covered 95%Pt/5%Au crucible under a flowing nitrogen atmosphere. The melts were quenched in air to give a cullet. Subsequently the cullet glass was remelted at 1000°C for 30 minutes and cast into a preheated brass-based mould (340°C). The rod (~120mm long, 10mm diameter) was annealed at 430°C for 1 hour before being allowed to cool at 30°C/hour to room temperature.

(i) ETCH DESIGN

All fluorides (particularly group II) are highly unreactive. Theory would suggest a suitable etchant should contain a cocktail of chemicals based on either an acidic zirconium or aluminium solution or an HF/HNO_3 solution. In practise, using these guidelines, an etch was sought empirically which would remove material at a reasonable rate and leave a a good quality surface. A series of 11 single component etches and 18 multicomponent etches largely using readily available chemicals (as listed in Table 1) were tested over a range of temperatures (25 - 100°C) and varying times. In each case the solution was magnetically stirred. The glass rod was weighed before and after etching to enable etch rates to be determined and the surface was inspected using an optical microscope. Two candidate systems were identified: $AlCl_3.6H_2O$ / HCl and HF (48%) / HNO_3 (68%) / H_2O plus H_3BO_3. The concentrations of each component in these etches was varied and the etch rate - temperature profile determined.

Finally, fibres (125μm diameter) were pulled after etching with the most promising compositions (marked by (*) in Table 1) to examine strength and surface quality. The preforms were slowly rotated in the etch solution, which was maintained at 60°C for 60 minutes, followed by a 30 minute rinse in methanol in an ultrasonic bath.

(ii) ETCH PROCEDURE

The fabrication aim is to produce 125μm diameter fibres. In the trials, standard ALF1 preforms were etched in 0.4M $AlCl_3.6H_2O$ / 1M HCl before pulling fibre in a dry nitrogen atmosphere using an rf susceptor. During the etch, the preform was rotated using a standard overhead stirrer to ensure even removal of material. The experimental variables investigated were etch time, etch temperature, rinse procedure, etch reusability, speed of preform rotation and mould material (standard brass, nickel plated brass or naval brass). Fibres were analysed by bend testing the uncoated fibre and optical inspection.

Bend testing the fibre gave a measure of the strength which reflected the general state of the fibre surface. A fibre (~100mm) was loaded between 2 parallel metal plates (maximum separation 40mm). One plate remained stationary and the other was driven forwards at a rate of 3mm/minute until the fibre broke. The separation, D, was noted and the procedure repeated 15-20 times to allow statistical analysis [10] using the Weibull distribution for ranked data.

$$W = \ln[-\ln(R(S_i))] = m\ln(S) + \ln(\lambda)$$

$$R(S) = \frac{N+1-i}{N+1}$$

where m and λ are the Weibull shape and scale parameters and N is the number of data points. The breaking strain, S, is given by:

$$S = \frac{r}{0.42D}$$

where r is the radius of the fibre. If the Weibull model is applicable a log-log plot of -ln(R(S)) against S is linear and the slope, m, gives a measure of the fibre inhomogeneity. From a log-log plot of cumulative failure probability (F(S)=1-R(S)) against S, the median breaking strain, $S_{50\%}$, can be determined. A good fibre must have a large $S_{50\%}$ value and a high m value.

RESULTS AND DISCUSSION

The results and discussion are considered in two sections as outlined above.

Table 1: Etches for ALF Glass

(A) Single Component

Etch	Temp. /°C	Etch Rate /μm min^{-1}
H_2O	77	0.09
H_2O_2 (30 wt%)	55	0.10
HCl (37 wt%)	60 68	0.45 0.95
HNO_3 (68 wt%)	72	0.22
H_2SO_4 (96 wt%)	95	0.09
H_3PO_4 (85 wt%)	90	0.17
CH_3COOH (100%)	91	none
HF (25 wt%)	40	0.07
0.4M $AlCl_3.6H_2O$	60	0.97
0.8M $AlCl_3.6H_2O$	50	0.16
	60	0.37
	80	3.4
1M Na_2CO_3	25	none

(B) Multi Component

Etch	Temp. /°C	Etch Rate /μm min^{-1}
80% H_3PO_4 (85%) 16% CH_3COOH (100%) 4% HNO_3 (68%)	25 72	none 0.10
50% H_2O_2 (30%) 50% H_2SO_4 (96%)	etch as prep >100	none; only active when hot - shatters sample
20% H_2O_2 (30%) 80% H_2SO_4 (96%)	etch as prep approx. 100	none; less vigorous than above - shatters sample
50g $(NH_4)_2S_2O_8$ per 1ℓ H_2SO_4 (96%)	25 72	none none
Convol pH 10 buffer solution	80	none
aqua regia	25	none
(i) 2M NH_4F + 2M $NaNO_3$ (ii) 10M NaOH (iii) 1M Na_2CO_3 in 30% HNO_3 (68%)	25 50	none 0.03
(i) 10M NaOH (ii) 1M Na_2CO_3 in 30% HNO_3 (68%) $^{(*)}$	40 70	0.07 0.17
0.4M $ZrOCl_2.xH_2O$ in 1M HCl $^{(*)}$	35 65	0.07 1.47
xM $AlCl_3.6H_2O$ in yM HCl (x=0.2, 0.4, 0.8, 1.2 M) (y=1 to 16.5M) $^{(*)}$	25 to 80	fairly composition independent <0.1 to >3.5
0.8 M $AlCl_3.6H_2O$ in 2.2M H_2O_2	32 60	0.13 0.74
0.8 M $AlCl_3.6H_2O$ in 8.8M H_2O_2	51 68	0.38 0.75
50% HF(48%): 20% HNO_3 (68%): 20% HCl (37%): 10% H_2O	40	0.17
50% HF(48%): 30% HNO_3 (68%): 20% H_2O	60	0.21
50% HF(48%): 50% HNO_3 (68%)	40 70	0.02 0.13
50% HF(48%): 10% HNO_3 (68%): 40% H_2O	40 70	0.03 0.19
50% HNO_3 (68%): 50% H_2O saturated with H_3BO_3 $^{(*)}$	60 80	3.49 8.91
50% HF(48%): x% HNO_3 (68%): (50-x)% H_2O saturated with H_3BO_3 (x=0 to 50%) $^{(*)}$	40 to 80	composition dependent 0.25 to 6.0

(i) ETCH DESIGN

ALF1 glass proved to be highly chemically resistant (see Table 1). With the exception of $AlCl_3.6H_2O$ solutions and HCl (37%), all the other single component etches (concentrated mineral acids, NaOH, Na_2CO_3, H_2O_2) had unacceptably slow rates of material removal (<0.1μm/min) even at elevated temperatures. Similarly, the majority of multicomponent etches had little or no etching capability. The two exceptions were xM $AlCl_3.6H_2O$ in yM HCl (x=0.2, 0.4, 0.8, 1.2 M; y=1 to 16.5M) and 50% HF(48%): x% HNO_3 (68%): (50-x)% H_2O saturated with H_3BO_3 (x=0 to 50%) when used at elevated temperatures. At room temperature, both etches had very low rates of material removal (<0.1μm/min.). It has been reported elsewhere [2],[3] that a pH10 buffer solution at 80°C etches ALF fibre, but this work was unable to reproduce the result. As the etch combining $AlCl_3.6H_2O$ and HCl gave faster etch rates and improved surface quality of the preform compared to the single components etches, they were not pursued further.

The $AlCl_3.6H_2O$/HCl composition is prepared by dissolving $AlCl_3.6H_2O$ in HCl. Etch rates are largely independent of component concentrations within the ranges $0.2M \leq [AlCl_3.6H_2O] \leq 1.2M$ and $0.5M \leq [HCl] \leq 12.0M$ but they are highly temperature dependent, enabling useful operation in the range 40°C (~0.2µm/min) to 80°C (~3.5µm/min) (or higher). Etches containing lower concentrations of the components yield optically polished preforms more reproducibly. A working composition of 0.4M $AlCl_3.6H_2O$ / 1M HCl has been adopted which can be reused a minimum of 3 times with no resulting surface deterioration.

The optimum composition, 0.4M $AlCl_3.6H_2O$/1M HCl is analogous to the $ZrOCl_2.xH_2O$/HCl etch for ZBLAN [1]. As water attacks the glass, the cations dissolve but a high concentration of fluoride ions is released. This exceeds the low fluoride ion solubility limit and hence the ions precipitate on the preform surface. In the presence of acidic aluminium salts stable fluoride complexes are formed, thus preventing precipitation and favouring further glass removal.

For the $HF/HNO_3/H_3BO_3$ composition, etch rates are highly dependent on both the concentrations of HF and HNO_3 and the temperature [40°C (0.1-0.5µm/min) to 80°C (3-8µm/min)]. Optically polished preforms can be reproducibly produced provided a fresh etch solution is used. The optimum etch composition (by volume) is 50% HF (48%) / 30% HNO_3 (68%) / 20% H_2O plus 3M H_3BO_3.

The etch is thought to have a multiple attack mechanism. In the presence of HF, the soluble ion AlF_6^{3-} is formed. In addition, orthoboric acid acts as a complexing agent for fluoride ions, preventing fluoride precipitation on glass dissolution as described above. Also, HNO_3 dissolves those group II fluorides which are insoluble in HF.

Both etches behave according to the basic reaction mechanisms described in standard undergraduate textbooks. As both involve the formation of a soluble fluoride complex, the etch solution will only dissolve a finite quantity of glass before they become exhausted. This limit has not yet been quantified.

A practical etch rate is essential but the resultant fibre must be of good quality (strong, low loss, defect free). Preliminary fibre pulling trials revealed that etching significantly improves the fibre strength and quality over fibre pulled from unetched preforms. The etching removes a contaminated *skin* from the outside of the preform. The nature of this *skin* is currently unknown. Its thickness (amount of material needed to be removed) is addressed in the next section. Qualitatively, for the same etch procedure, the fibre strength depended more on the etch composition than the etch rate. Without etching, fibre drawing was unsuccessful and the preform tended to crystallise. With etching the best fibres (from the two favoured etches) were stable, regular and strong. The $AlCl_3.6H_2O$/HCl composition tends, on average, to perform slightly better. The etching process is most effective if carried out immediately prior to fibre pulling.

(ii) ETCH PROCEDURE

Preforms were etched in 0.4M $AlCl_3.6H_2O$ / 1M HCl following a variety of procedures before immediately loading into the pulling tower and performing a standard fibre pulling operation. Approximately 100m of uncoated 125µm diameter fibre was collected in 20m bands. Several sections of each band were bend tested. Subsequent Weibull analysis showed the model was applicable with data correlations all lying in the range 0.96 to 1.0.

Initially, a single step etch procedure was adopted. Slowly rotating preforms were etched at 55°C for differing times (30 - 150 mins.) before rinsing in methanol in an ultrasonic bath for 30 minutes. The etch rate was ~1.5µm/min and generally the resultant preform surface was improved although not all defects were removed. Fibre pulling tended to lack control, the fibre had variable tension and the preform always showed some neck crystallisation. Although the fibre strength and quality showed significant improvement over fibre from an unetched preform, it was sometimes lumpy and still very weak and brittle often making bend testing impossible. The time of etching bore little relationship to the fibre strength and the results were not reproducible. The fibre strength deteriorated rapidly when left in air overnight.

These results were obviously unsatisfactory and a different approach was therefore necessary. Comparison with ZBLAN data showed a much higher etch rate of 18µm/min. corresponding to a 1mm reduction in preform diameter [1]. The aim was to achieve a similar amount of surface material removed. After much investigation a two step etch procedure was adopted to completely remove the contaminated surface. Step 1 was x mins etch (x=30 - 120mins) at 80-95°C rapidly rotating the preform followed by 60 mins ultrasonic rinse in methanol. Step 2 was y mins etch (y=0, 30, 60 mins) at 55°C slowly rotating the preform followed by 30 mins ultrasonic rinse in methanol.To avoid thermally shocking the preform, it was placed in or removed from the etch at ≤50°C. In the initial coarse step the surface material was rapidly removed, whereas the second fine step removed loose surface material and polished the preform to give a good surface.

Table 2: Fibre strength data after two step etch procedure for varying etch times

Mins at 80°C	Mins at 55°C	S_{50}(%)	m
60	0	0.64	7.60
60	60	0.76	5.66
90	60	1.00	5.10

Etch rates of up to 8µm/min were achieved if the temperature was allowed to rise to 95°C giving 1.0-2.0mm reduction in preform diameter depending on the etch time. The glass glistened (comparatively dull prior to etching), had improved transparency and all surface problems were removed (checked using a white light source). Table 2 gives typical fibre strength results as a function of etch time. Preforms undergoing the high temperature etch always gave stronger fibres. These data were reproducible. Hence, the coarse etch step should be for at least 90 minutes and an additional fine etch step is required to achieve a total reduction ≥1mm in preform diameter and the best fibre strength.

Fibre pulling was easily controlled and highly reproducible. Scanning electron microscope results confirmed there was no preform surface crystallisation. The fibre tension showed only very minor fluctuations, probably due to inhomogenities in the glass. All the fibre pulled was relatively strong although the early fibre tended to be slightly stronger.

Table 3: Fibre strength data as a function of fibre age

Age of Fibre	S_{50}(%)	m
as pulled	1.12	4.81
1 day	1.00	5.10
3 days	1.05	6.20
1 week	1.02	4.57
2 weeks	1.05	6.69

Fibre strength variations on extended exposure to an air environment were investigated and results are given in Table 3. Typically, there is <10% reduction in median strength after 2 weeks in air. Also, the data spread remains constant implying there is no selective degradation. Weaker fibres typically tended to show more degradation in air than stronger fibres as there are more imperfections open to attack. These results are consistent with minimal surface corrosion confirming ALF1 is fairly stable in the atmosphere.

As expected, fibre strength also depended on preform history. Fibre pulled from similarly etched preforms showed the strength was a function of the material of the preform mould (see Table 4). The strongest fibres resulted from fibres cast in a nickel coated brass mould, closely followed by those cast in a naval brass mould. These are both superior to using a standard brass mould. In addition, it was noted that preforms from a naval brass mould etched at a slower rate.

This suggests the nature of the surface *skin* was determined by the mould. Although fibre strength was variable, all fibres showed similar uniformity.

Table 4: Fibre strength data as a function of preform mould material

Max. Etch Temperature /°C	Preform Mould Material	S_{50}(%)	m
55	Ni Brass	0.82	5.97
80	Ni Brass	1.40	4.21
	Naval Brass	1.00	5.10
	Brass	0.86	6.02

Overall, these results are very encouraging. The strength data represents the strongest fibres possible as preform rods were used and not a core/clad structure. However, it is thought that coating would result in strong fibres, possibly comparable with ZBLAN. This would also minimise the data spread.

CONCLUSION

ALF1 proved to be highly chemically resistant at room temperature. This is very positive for the fibre which is therefore predicted to be essentially inert and hence, environmentally friendly.

However, an etch, 0.4M $AlCl_3.6H_2O$ / 1M HCl, has been identified which chemically polishes ALF1 preforms resulting in dramatically improved fibre strength. The minimum etch requirement is 90 minutes at 85°C, 30 minute rinse in methanol followed by 60 minutes at 55°C and a final 30 minute methanol rinse. This reduces the preform diameter by at least 1mm. Subsequent fibre pulling is controlled and reproducible. Reasonably strong uncoated fibres are obtained although the strength also depends on the preform history (particularly mould sensitive). In terms of fabrication, several preform mould materials may appear suitable but the final selection should be influenced by fibre strength considerations. Furthermore, the fibres appear largely resistant to air attack. Thus, the nature of the preform surface is no longer the limiting factor to achieving high quality ALF1 fibres.

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