

Investigation of elemental diffusion during the drawing and heat treatment of glass optical fibres

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Using high-resolution X-ray analysis, elemental mobility during fibre drawing and the subsequent heat treatment were studied in germanium-doped, erbium-doped and cadmium-sulpho-selenide-doped optical fibres. It was found that all but the monovalent cations were effectively immobile in the silica matrix. There was also some evidence for reduced erbium volatility due to aluminium doping in some fibres.

1. Introduction

The optical properties of optical fibres are controlled by compositional variations across the fibre core. These compositional variations are carefully tailored during the various processes of fibre manufacture [1] in order to produce fibres with the required properties.

In the fibres investigated, the refractive-index profile of the core region was controlled by germanium doping. Erbium was added to some fibre cores to confer optical-gain properties on the fibre for all-optical amplification applications. Glass-containing semiconducting particulates of Cd(S,Se) was used in the cores of some other fibres to facilitate all-optical switching.

The aim of the investigation described in this paper was to determine the degree of diffusion of these various compositional elements which occurred during the process of fibre drawing and during subsequent heat treatment. It is obviously important that the compositional arrangement so carefully engineered into the fibre preform is maintained in the fibres pulled from it.

As typical monomode optical fibres have cores with diameters in the region of 5 μm , the standard $\sim 1 \mu\text{m}$ resolution technique of electron-probe microanalysis on bulk samples is clearly inadequate. To circumvent this problem, the analyses were performed on very thin transverse films by transmission electron microscopy (TEM). The resultant combination of low beam spread in the sample and high-quality condenser lenses improved the available spatial resolution of the analysis to $\sim 85 \text{ nm}$.

The results of the analysis of germanium-doped fibres were published in an earlier paper [2] where it was found that no diffusion of germanium was evident at the core boundary. This paper, therefore, will

concentrate on the two other types of fibres investigated, erbium-doped and semiconductor-doped fibres.

2. Experimental procedure

Thin transverse section of optical fibres were prepared using a technique described in a previous paper [2]. These samples were then analysed using a JEOL 100CX transmission electron microscope equipped with a scanning transmission electron microscopy (STEM) unit and a LINK 860 energy-dispersive analyser. To facilitate the acquisition of compositional linescans, the analyser was connected to a computer via an analogue/digital serial interface. The data were collected using specially written software.

3. Experimental results

3.1. Erbium-doped fibres

Figs 1 and 2 show X-ray linescans for two types of erbium-doped optical fibres. Both were pulled from the same preform but they were pulled to different final fibre diameters. In order to separate the effects due to variations in sample thicknesses and densities from those due to genuine variations in erbium-concentration, the data were gathered from a background window which was equal in width to the erbium window. Both the peak and the background information are reproduced on the figures as raw data, along with a processed peak-minus-background plot and a plot of the germanium concentration to show the position of the core centre. The detection of aluminium would be expected, but in practice the small aluminium peak is masked by the tails of the much larger silicon (SiK) and germanium (GeL) peaks.

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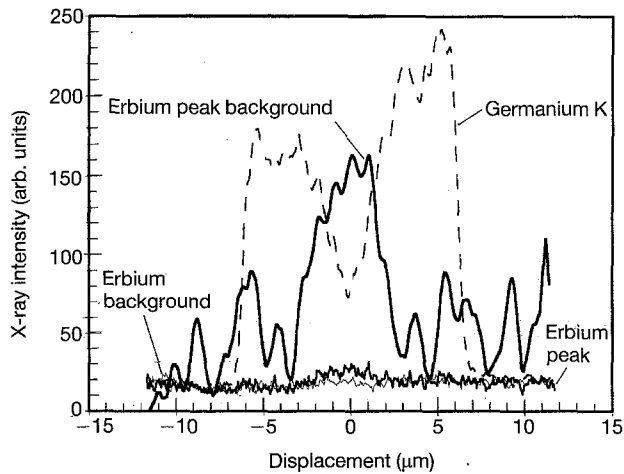


Figure 1 Erbium and germanium concentration profiles for an erbium-doped fibre core.

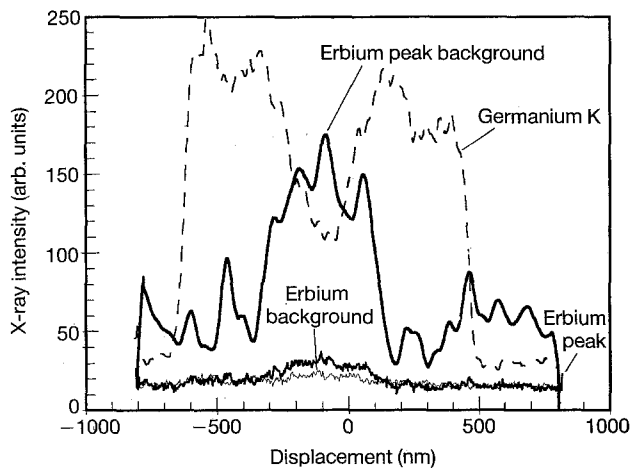


Figure 2 Erbium and germanium concentration profiles for an erbium-doped fibre core.

Tables I–III show the apparent concentrations from spot analyses of fibre cores with insufficiently high concentrations of dopants to permit the acquisition of linescans. Tables I and II show the results from fibres doped with aluminium and Table III shows the analysis of a fibre without such doping. Aluminium was not detected in either of the aluminium doped fibres for the reasons outlined above.

3.2. Semiconductor-doped fibres

Fig. 3 shows the zinc-concentration profiles measured on three samples of a semiconductor-doped fibre after various heat treatments. The traces have been normalized along the x-axis.

Fig. 4 shows the concentration profiles for germanium, potassium and sodium. The potassium and germanium data were acquired using the energy-dispersive analyser in the usual way. To acquire the sodium data it was necessary to use a wavelength-dispersive analyser on a JEOL electron-probe microanalyser to separate the closely spaced sodium (NaK) and zinc (ZnL) peaks. This data was then transferred to the computer for processing.

Fig. 5 shows potassium-concentration profiles for three samples of the same fibre in the untreated state, after heat treatment at 550 °C for 8 h and after

TABLE I Apparent concentrations of elements in an erbium- and aluminium doped fibre core

Element	Net Integral	Concentration (at %)
Silicon	242 410	48.91
Erbium	54	0.1
Germanium	253 203	51.08

TABLE II Apparent concentrations of elements in an erbium-doped fibre core

Element	Gross Integral	Net Integral	Concentration (at %)
Silicon	3942 190	337 505	64.43
Erbium	10 917	80	0.2
Germanium	205 199	186 218	35.55

TABLE III Apparent concentrations of elements in an erbium- and aluminium doped fibre core

Element	Net Integral	Concentration (at %)
Silicon	143 433	68.92
Erbium	0	0
Germanium	64 693	31.08

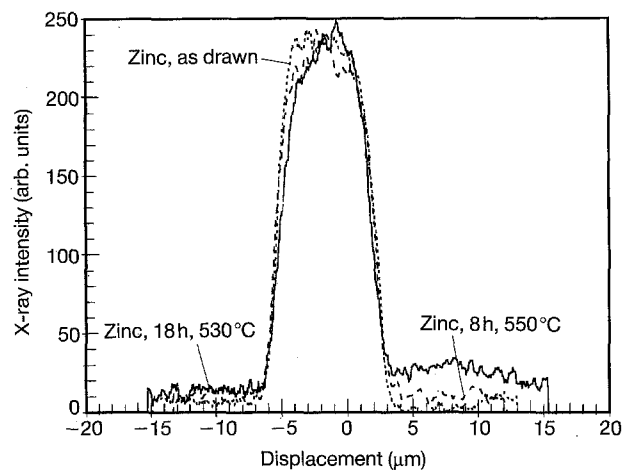


Figure 3 Zinc-concentration profiles for a semiconductor-doped fibre after a variety of heat treatments.

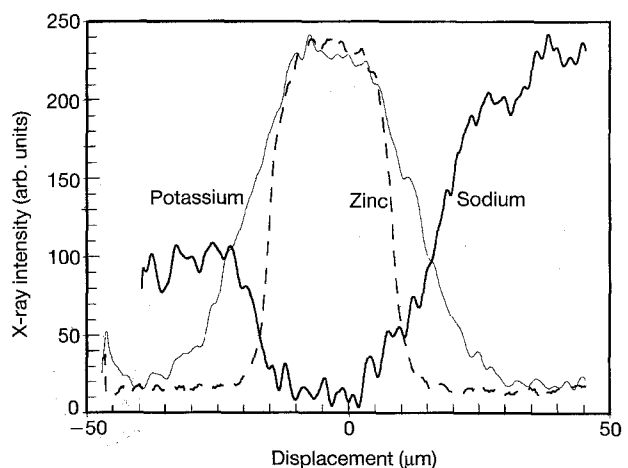


Figure 4 Linescans showing diffusion profiles of sodium and potassium in a semiconductor-doped optical fibre.

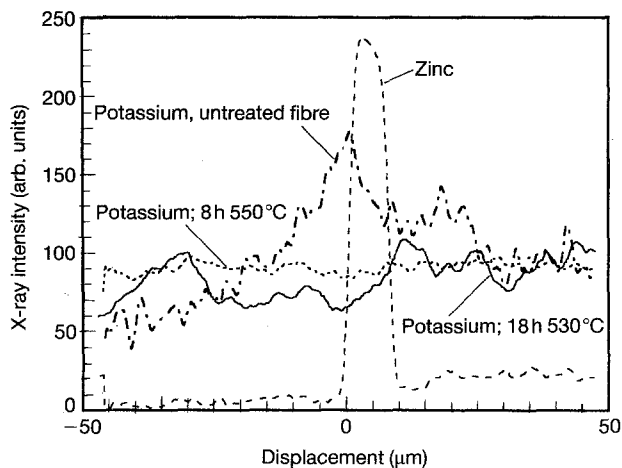


Figure 5 Concentration profiles for zinc and potassium in a semiconductor-doped fibre after a variety of heat treatments.

treatment at 530 °C for 18 h. The zinc-concentration profile is also reproduced to show where the core would be expected to be.

Table IV shows the chemical analyses of various glasses used in the manufacture of the semiconductor-doped fibres investigated.

4. Discussion

4.1. Erbium-doped fibres

The aim in examining the erbium-doped fibres was to investigate the effectiveness of attempts to confine erbium in the central-core region. During the collapse phase of preform manufacture, volatile species tend to be lost. This effect causes a dip in the concentration in the central region of the germanium linescans [3]. Erbium is just such a volatile species, but there is evidence for interaction between erbium and non-bridging oxygen in alumina introduced into the silicate lattice [4]. Alumina has a very low vapour pressure, even at the temperatures encountered during the collapse phase of MCVD preform production, and unlike germanium it does not form a volatile suboxide. These fibres were manufactured in an attempt to utilise these effects to increase the maximum concentration of erbium attainable in the fibre cores.

The initial linescans for erbium and aluminium in these fibres showed two similar peaks in the core centre. It was found, however, that the aluminium peak was an artefact caused by an increase in the specimen density and by an increase in specimen thickness due to a reduction in the sputtering rate during ion-beam thinning caused by the aluminium content.

The evidence for this included the fact that when viewed by (TEM), the central core region was darker than the rest of the core; this is the reverse of the normal situation. A further contributory problem was the fact that the aluminium peak lies on the shoulder of the silicon peak, and the core-centre germanium depletion is matched by a consequent increase in the silicon concentration. Point analyses of the core region showed a marked erbium peak but no

TABLE IV Chemical analyses of Schott RG630 filter glass, Hoya H640 filter glass and glass used for fibre cladding

Element	Concentration/ Mass%		
	Schott RG630	Hoya H640	Cladding Glass
Silicon	22	27	32
Zinc	18	11.6	
Potassium	17	15.7	2
Sodium	0.2	2.2	21
Cadmium	0.5-1	0.5-1	
Sulphur	0.2	0.2	
Selenium	0.2	0.2	
Aluminium			2.6
Calcium			3.7
Barium			0.3

aluminium peak, and so neither the aluminium linescans nor the point analyses have been reproduced in this paper.

It can be seen in the unprocessed linescans (the erbium peak and background) at the bottoms of Figs 1 and 2 that the erbium concentration is convincingly higher in the middle of the scan. This supports the conclusion that aluminium can improve the retention of erbium. In order to gather further supporting evidence, some other fibres were obtained: two with aluminium doping and one without. In the case of these fibres, the level of doping was reduced from ~ 1 wt%, to ~ 0.1 wt%, which is a more normal rare-earth concentration in such fibres, to avoid undesirable ion-ion interactions [5]. This level of doping was too low for meaningful linescans to be produced, so the spot analyses in Tables I-III were obtained.

It can be seen from the apparent concentration analyses for the aluminium-doped fibres in Tables I and II that there is some evidence for erbium in the cores, whereas in the fibre containing no aluminium there is not. However, from the differences between the net integral and gross integral columns in Table II, it is possible to calculate the standard deviation of the analysis. This shows that the erbium peaks, if any are present, are only in a region one standard deviation in height, and so they have only a 68% possibility of being genuine. Each analysis was repeated three times, however, and each time a one standard deviation peak was detected for erbium in the aluminium-doped fibres, and no peak was detected in the aluminium-free fibres.

The large variations in the measured germanium concentration may be due to the large gradient of the germanium-concentration profile in the central depletion region. This evidence supports the belief that aluminium is helpful in confining erbium in fibre cores, but it cannot be considered conclusive.

4.2. Semiconductor-doped fibres

The semiconductor-doped fibres investigated were manufactured from commercial coloured-filter glasses (Hoya H640 and Schott RG630) and commercial glass tubing. A rod of the core material was placed in the

tube of cladding material, and both together pulled down into the fibre in the usual way. This method tends to produce oval cores with some fluctuation in the core diameters. As it was intended to compare the element-concentration profiles of several samples of the same fibre after a variety of heat treatments, this fluctuation made direct comparison of the core diameters difficult. To circumvent this problem, the low-noise linescans for zinc were normalized to a common apparent diameter and their shapes were compared (Fig. 3). It can be seen that there are no readily apparent differences in the shapes of the three profiles, and so it was concluded that no significant diffusion of zinc took place, and so the normalization parameters used for zinc could be used for the other linescans.

Initial linescans of a fibre with a 2 μm core of Schott RG630 glass showed all elements to be distributed as expected from the chemical analyses with the exceptions of sodium and potassium. From the analyses in Table IV, the potassium concentration would be expected to be at a maximum in the fibre core and the sodium concentration to be at a minimum. In fact, the potassium profiles seemed to be entirely homogenous, and the sodium linescans showed a distinct peak.

The reason for this anomalous result in the case of the sodium profile was found to be an overlap between the sodium K_{α} line at 1.04 keV and the zinc L_{α} line at 1.10 keV. These peaks are considerably more closely spaced than the energy resolution of an energy dispersive analyser, but they are well within the resolution of a wavelength-dispersive system (WDS). Consequently, it was decided to use a JEOL JXA 840 electron-probe microanalyser equipped with WDS to examine a sample of optical fibre. As the spatial resolution of this machine was too poor to give useful results for the 2 μm cores of the first fibres analysed, a sample of a fibre with a core diameter of 25 μm was obtained. This was manufactured using the same cladding glass as the first fibres, but with a core of Hoya H640 glass (Table IV). Analysis of this fibre in the TEM again showed the sodium profile to be the inverse of that expected, and so this fibre was seen as a good large-scale analogue of the fibres with smaller cores.

TEM analysis of this larger fibre showed a clear profile of diffused potassium. This suggested an explanation for the previous failure to acquire a potassium-concentration profile in the small-core fibres. In the larger fibre (Fig. 4) the potassium has diffused 20 μm from the core region delineated by the zinc profile. Where the fibre core itself has dimensions about this size, the concentration in the core is not markedly diminished, but in a core with a cross-sectional area two orders of magnitude smaller such a degree of mobility will reduce the core-concentration enrichment to undetectable levels.

It can also be seen in Fig. 4 that the wavelength-dispersive detector is able to resolve the sodium K_{α} peak and to detect a concentration profile for sodium which is more similar to that which would be predicted from the core-glass analyses.

As sodium and potassium are both present as monovalent cations in the silica matrix, conservation of charge neutrality demands that they both diffuse at

a common rate [6]. Therefore the sodium and potassium ions would be expected to mirror each other, as appeared to be the case.

Due to the difficulties inherent in the acquisition of sodium profiles and the high degree of symmetry between the sodium and potassium profiles it was decided to concentrate on potassium diffusion.

No evidence was found for diffusion of any elements other than sodium and potassium.

To further investigate diffusion of potassium, another fibre was obtained which had undergone a variety of heat treatments to form microcrystallites of semiconductor in the core. These treatments were 18 h at 530 $^{\circ}\text{C}$ and 8 h at 550 $^{\circ}\text{C}$. Untreated fibre was also examined. As these samples came from different parts of the fibre it was necessary to normalize all the linescans using the assumed undiffused zinc profiles. In Fig. 5 it can clearly be seen that potassium has diffused out of the core during fibre drawing in the case of the fibre which was not heat treated. The linescans of the heat-treated fibres show no potassium peak, and so it must be assumed that the potassium concentration has equilibrated during heat treatment.

The time-temperature cycle during fibre drawing is represented by a complicated integral [7, 8], as is the equation governing preform neck-down [9]. To provide a mathematical model for diffusion during fibre drawing, it would be necessary to solve Fick's equation in a co-ordinate-system shrinking according to one integral and with a time-temperature cycle governed by another. As all three of these equations are usually solved by numerical methods, it seems unlikely that an analytical solution could be found. An empirical approach, however, is developed in [10].

5. Conclusion

These investigations have shown that the majority of elements present in commercial-glass optical fibres do not show significant mobility during either fibre drawing or subsequent heat treatment.

There is evidence that aluminium is effective in reducing the volatility of erbium during the collapse phase of fibre-preform production, since the presence of erbium was indicated in fibre cores doped with aluminium and was not detected in (otherwise similar) cores lacking this element.

The only elements found to have any significant mobility during fibre drawing and heat treatment were sodium and potassium in semiconductor fibres. This may be of some importance if the kinetics of the semiconductor crystallization process are sensitive to the composition.

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