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# FABRICATION AND OPTICAL CHARACTERIZATION OF DOPED GERMANOSILICATE FIBRES

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## ABSTRACT

This work assesses the incorporation of dopant ions such as  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$  and  $\text{Er}^{3+}$  into the core of germanosilicate optical fibres via modified-chemical-vapour-deposition plus solution doping fabrication techniques. We find that highly-charged smaller ions, like  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$ , behave similarly. These ions are more efficiently incorporated, assist in the incorporation of  $\text{Er}^{3+}$ , and have the same influence on the fluorescence spectra of  $\text{Er}^{3+}$ . The structural role of these ions appear to be their ability to provide nonbridging oxygens around  $\text{Er}^{3+}$ . The waveguide and lasing characteristics of  $\text{Er}^{3+}$  codoped with  $\text{Ta}^{5+}$  are presented.

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# FABRICATION AND OPTICAL CHARACTERIZATION OF DOPED GERMANOSILICATE FIBRES

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## ABSTRACT

This work assesses the incorporation of dopant ions such as  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$  and  $\text{Er}^{3+}$  into the core of germanosilicate optical fibres via modified-chemical-vapour-deposition plus solution doping fabrication techniques. We find that highly-charged smaller ions, like  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$ , behave similarly. These ions are more efficiently incorporated, assist in the incorporation of  $\text{Er}^{3+}$ , and have the same influence on the fluorescence spectra of  $\text{Er}^{3+}$ . The structural role of these ions appear to be their ability to provide nonbridging oxygens around  $\text{Er}^{3+}$ . The waveguide and lasing characteristics of  $\text{Er}^{3+}$  codoped with  $\text{Ta}^{5+}$  are presented.

## INTRODUCTION

The glass composition in standard modified-chemical-vapour-deposition (MCVD) fibre processing involves changing the ratios of any combination of  $\text{SiO}_2$  with  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$ . Solution doping<sup>1</sup> allows the flexibility of introducing optically-active ions, such as rare-earth (RE) ions, as well as codopant ions (CDIs) such as  $\text{Al}^{3+}$ . The dependence of the optical properties of RE ions on glass composition is well documented<sup>2</sup>. This is most evident in the variation in fluorescence bandwidth with glass composition. For example,  $\text{Er}^{3+}$ -doped aluminosilicate fibres give a broader  $\text{Er}^{3+}$  1.5  $\mu\text{m}$  fluorescence bandwidth compared to the fluorescence of  $\text{Er}^{3+}$ -doped germanosilicate fibres. Erbium is particularly interesting because it clearly demonstrates this relationship, owing to the large number of possible Stark levels available in the  $^4\text{I}_{13/2}$  metastable-state manifold and the  $^4\text{I}_{15/2}$  ground-state manifold.

This work identifies CDIs whose oxides have thermal properties compatible with the MCVD process in order to expand the choice of glass compositions presently available. We assess the efficiency of incorporating these CDIs by solution doping and their effect on the incorporation of  $\text{Er}^{3+}$ . The latter is an important consideration in tailoring the glass composition to optimize  $\text{Er}^{3+}$  fibre laser and fibre amplifier performances<sup>3</sup>.

We have prepared  $\text{Er}^{3+}$  codoped with  $\text{Ga}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ . The optical properties have also been determined. We find that increasing the number of nonbridging oxygens (NBOs) in the glass available for coordination with  $\text{Er}^{3+}$  increases the linewidth, thus  $\text{Ta}^{5+}$  behaves similarly to the commonly-used  $\text{Al}^{3+}$  and therefore provides an interesting alternative codopant to broaden and flatten the  $\text{Er}^{3+}$  spectrum. The lasing characteristics of  $\text{Er}^{3+}$  codoped with  $\text{Ta}^{5+}$  is presented.

## EXPERIMENTAL

All preforms were prepared by MCVD, using a cladding layer in all cases of  $\text{SiO}_2$ . The core deposition was carried out by depositing  $\text{SiO}_2$  and  $\text{GeO}_2$  at a low temperature to form a porous layer (hereafter to be referred to as the SiGe frit) in preparation for solution doping. Solutions were prepared from the chloride and nitrate salts dissolved in either deionized water or methanol. In each case  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$  was added to the CDI solutions. The SiGe frit was soaked in the solution for an

hour, after which the tube was dried and collapsed into a preform in the usual way.

The dopant ions were chosen so as to distinguish between the effect of size (ion radius) and field strength which is defined as the charge to radius ratio,  $Z/r$ . Except for the oxides of niobium, all the other oxides have boiling points greater than  $\text{SiO}_2$ . Most of the niobium was lost during the preform collapse and what remained gave a bluish tinge characteristic of the reduction of  $\text{Nb}^{5+}$ .

The fibre type and its associated core host glass composition (minus the  $\text{SiO}_2$  contribution), are summarized in Table II. The composition of the host glass was determined from the preform using a JEOL JSM 640D Scanning Electron Microscope (SEM) and TRACOR Series II x-ray and image analysis system. The concentration ratio of  $\text{CDI}/\text{Er}^{3+3+}$  in the glass is generally greater than 10. The fibre refractive index profile (RIP) was determined using York S14 refractive index profiler. From the RIP and SEM data, we obtain the change in refractive index per mole-%, to be .0017, .0045, .004 and .0073 for  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_3$ , respectively. This is consistent with published data<sup>4,5</sup>.

The fibre attenuation was obtained using the usual cut-back method. The background losses in these glasses for 10  $\mu\text{m}$  (multimode) fibres in the near infrared are about  $50 \pm 10 \mu\text{m}$ . In a single-mode fibre with cutoff at 930 nm (3.4  $\mu\text{m}$ ) the background loss increases to 150 dB/km. A similar level in background losses can be expected from the other fibres<sup>5</sup>.

## RESULTS AND DISCUSSION

### Fabrication Assessment

The ratio of the concentration of ions present in the preform to the concentration of ions in the solution from which it was derived is a measure of the efficiency of incorporating the ions into the SiGe frit. This ratio is expressed as  $C_{\text{glass}}/C_{\text{soln}}$  where  $C_{\text{glass}}$  is the atom-% of ion present in the core layer determined from SEM data and  $C_{\text{soln}}$  is the ion concentration in the soaking solution expressed in molarity. Normally, the frit porosity which depends primarily on the temperature at which the frit is deposited determines the efficiency of ion incorporation, however, as shown in Figure 1 when the frit conditions are kept similar, then  $C_{\text{glass}}/C_{\text{soln}}$  is also dependent on the cationic field strength. The larger the field strength, the greater is the ion incorporation. The dependence of the incorporation efficiency on ion field strength rather than size alone implies that the polarizability of the covalently bonded atoms of the frit, Si, Ge and O, are altered due to these high field strength ions making incorporation more favourable.

All the CDIs have oxides with boiling points higher than  $\text{SiO}_2$ . In germanosilicate preforms, SEM data and RIP measurements reveal that  $\text{Zr}^{4+}$ ,  $\text{Ta}^{5+}$  and  $\text{Al}^{3+}$  ions are retained in the core while  $\text{Er}^{3+}$  and  $\text{Ga}^{3+}$  burn-out. The depletion of  $\text{Er}^{3+}$  from the core when germania burns-out during processing has been previously observed<sup>3</sup> and ascribed to  $\text{Er}^{3+}$  associating with  $\text{GeO}_4$  centres. The depletion of  $\text{Ga}^{3+}$  from the core, however, occurs even in the absence of  $\text{GeO}_2$  as shown in Figure 2 and confirmed by SEM data, in agreement with Anoykin's result<sup>4</sup> on  $\text{SiO}_2/\text{Ga}_2\text{O}_3$  glass fibres. The  $\text{Ga}^{3+}$  loss is likely due to the reduction of  $\text{Ga}^{3+}$  and evolution of reduced gallia,  $\text{Ga}_2\text{O}$  is reported<sup>6</sup> to sublime at 500°C.

The incorporation of  $\text{Er}^{3+}$  is affected by the presence of CDIs. When  $\text{Er}^{3+}$  is added as a codopant in SiGeAlEr type fibres, there is no depletion of  $\text{Er}^{3+}$  due to burn out. This is demonstrated in Table I which gives data for the concentrations of each component at the core centre and edge. This is consistent with the results of Reference 3. We postulate the same is true for  $\text{Er}^{3+}$  in SiGeTaEr fibres. Unfortunately, the data of Table I is difficult to obtain for this composition since to get measurable  $\text{Er}^{3+}$  signals with SEM, very high  $\text{Er}^{3+}$  concentrations are required which implies a large  $\text{Ta}^{5+}$  concentration and this produces devitrification (at a  $\text{Ta}^{5+}/\text{Er}^{3+}$  ion ratio  $< 8$ ). In these codoped fibres a better measure of the ability of codopant ions to assist in the retention of  $\text{Er}^{3+}$  in

the core can be obtained from the optical properties of  $\text{Er}^{3+}$  as discussed below.

Table I: SEM Result for Element Concentration in Weight% at the core for SiGeAlEr Preform

Element	Si	Ge	Al	Er
Edge of Core	83.51	7.13	5.59	3.77
Centre of Core	89.10	1.58	5.54	3.78

### Optical Properties

The fluorescence spectra of  $\text{Er}^{3+}$  around  $1.5 \mu\text{m}$  in the different glass compositions are shown in Figures 3 and 4 with the optical properties summarized in Table II. Figure 3 shows that the broadening of the  $\text{Er}^{3+}$  ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ )  $1.5 \mu\text{m}$  fluorescence bandwidth is not unique to codoping  $\text{Er}^{3+}$  with  $\text{Al}^{3+}$  since codoping with  $\text{Ta}^{5+}$  and  $\text{Ga}^{3+}$  can also result in fluorescence linewidth broadening. To understand the factors that contribute to linewidth broadening, the effect of CDI concentration was investigated. In Figure 4, increasing the  $\text{Ga}^{3+}$  ion concentration while maintaining the same  $\text{Er}^{3+}$  ion concentration, as in going from SiGaEr-A ( $\text{CDI}/\text{Er}^{3+} = 13$ ) to SiGaEr-B ( $\text{CDI}/\text{Er}^{3+} = 50$ ), results in an increase in bandwidth. A larger  $\text{CDI}/\text{Er}^{3+}$  ratio implies a greater number of NBOs in the glass available for coordination with  $\text{Er}^{3+}$  and this increases the linewidth. The broadening observed in SiGaEr-B agrees with the results reported in Reference 5 and listed as SiGaEr-C in Table I. In the SiGeTaEr and SiGeAlEr preforms, the number of NBOs are high since  $\text{CDI}/\text{Er}^{3+}$  ratios  $> 50$  in these glasses, thus, the broadening observed.

It is also interesting to note from Figure 4 that the spectra of SiGaEr-A and SiGeGaEr ( $\text{CDI}/\text{Er}^{3+} = 22$ ) are similar, the  $\text{Er}^{3+}$  concentration has been halved in the latter indicating perhaps that in gallate-germanosilicate preforms a higher  $\text{CDI}/\text{Er}^{3+}$  maybe needed to effect fluorescence linewidth broadening. By comparison, in  $\text{Er}^{3+}$ -doped tantalate-germanosilicate preforms when the  $\text{CDI}/\text{Er}^{3+} = 25$ , the fluorescence spectra is similar to the glass with  $\text{CDI}/\text{Er}^{3+}$  of 50 and in alumina-germanosilicate preforms when the  $\text{CDI}/\text{Er}^{3+} > 10$ , the fluorescence spectra remain unchanged. Finally, as in gallate-germanosilicate, zirconate-germanosilicate may require a higher  $\text{CDI}/\text{Er}^{3+}$  to effect fluorescence broadening since the spectra of SiGeZrEr ( $\text{CDI}/\text{Er}^{3+} = 22$ ) is similar to SiGeGaEr.

The dependence on  $\text{CDI}/\text{Er}^{3+}$  ratio and hence on the number of NBOs in doped germanosilicate preforms is summarized in Figure 5. For the same  $\text{Er}^{3+}$  ion concentration, the effective width is plotted against the number of NBOs which is equal to the atom-% times its charge. A straight line is arbitrarily drawn to indicate the trend, that increasing the number of NBOs in the glass result in increasing the effective linewidth.

The similarities in the optical properties of  $\text{Er}^{3+}$  codoped with  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$  imply that the environment experienced by  $\text{Er}^{3+}$  in these glasses are similar. Our results are consistent with the structure proposed in Reference 7. An important conclusion from their EXAFS result is the identification that all the oxygen neighbours of  $\text{Nd}^{3+}$  in aluminosilicate glass are NBOs. The slight shift in  $\lambda_{\text{peak}}$  of the  $\text{Er}^{3+}$  fluorescence in the presence of  $\text{Ta}^{5+}$  and  $\text{Al}^{3+}$  reflects these largely ionic bonds made with NBOs<sup>8</sup> due to the nephelauxetic effect. The broad bandwidth in these glasses is likewise consistent with bonding with NBOs. This is because the ionic bonds made with NBOs have a larger polarizability than the mostly covalent Si-O-Si bonds of bridging oxygens (BOs) and this contributes to the homogeneous broadening in SiGeAlEr type fibres<sup>9</sup> because the effective fluorescence linewidth measured at room temperature is a measure of the of the overall Stark splitting. Thus, the resultant effect of bonding with largely NBOs is that the anionic field around  $\text{Er}^{3+}$

is more negative than it would be if its coordination requirements was satisfied by bonds made with BOs. The larger field increases the Stark splitting in both metastable and ground states, which contributes to the broadening of the fluorescence spectrum. This agrees with an earlier report<sup>10</sup> which showed that the fluorescence spectrum of Er<sup>3+</sup>-doped ionic sulphate glass, composition 59.5ZnSO<sub>4</sub>-40K<sub>2</sub>SO<sub>4</sub>-0.5Er<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, resembles the fluorescence spectrum of Er<sup>3+</sup> in aluminosilicate fibres in both  $\lambda_{\text{peak}}$  and  $\Delta\lambda_{\text{eff}}$ .

The fluorescence lifetimes in Table II were obtained from decay curves which all exhibited single exponential decay. The shorter Er<sup>3+</sup> lifetimes in alumina- and tantalate-doped germanosilicates is, as with their fluorescence spectra, related to its environment. The effect of NBO nearest oxygen neighbours is a reduction in lifetime of the <sup>4</sup>I<sub>13/2</sub>-state which may be indicative of increase coupling with the phonon energy via the NBO bonds so that nonradiative decay contributes to the lifetime.

Table II: Summary of Optical Properties\*

Preform Sample	Composition mole %	$\tau_f$ (ms $\pm$ 5%)	$\lambda_{\text{peak}}$	$\Delta\lambda_{\text{eff}}$
SiGeEr	5.0GeO <sub>2</sub>	11.3	1535	35
SiGeGaEr	5.5GeO <sub>2</sub> -0.55Ga <sub>2</sub> O <sub>3</sub>	11.2	1533	43
SiGeGaZr	5.5GeO <sub>2</sub> -1.1ZrO <sub>2</sub>	11.2	1534	41
SiGeAlEr	3.2GeO <sub>2</sub> -3.2Al <sub>2</sub> O <sub>3</sub>	10.5	1530	57
SiGeTaEr	4.6GeO <sub>2</sub> -1.5Ta <sub>2</sub> O <sub>5</sub>	10.3	1531	60
SiGaEr-A	0.55Ga <sub>2</sub> O <sub>3</sub>	11	1534	42
SiGaEr-B	2.1Ga <sub>2</sub> O <sub>3</sub>	10.6	1532	48
SiGaEr-C	2.8Ga <sub>2</sub> O <sub>3</sub>	10.8	1532	50

\*  $\tau_f$  is the fluorescence lifetime,  $\lambda_{\text{peak}}$  is the maximum peak wavelength and  $\delta\lambda_{\text{eff}}$  is the effective linewidth equal to the area of the fluorescence band/intensity at the maximum

### Lasing Characteristic

The lasing properties for fibre type SiGeTaEr were determined for a fibre with a Er<sup>3+</sup> ion concentration of 550 ppm. The fibre has an N.A. of 0.21 and a cut-off wavelength of 950 nm. The fibre attenuation at the 982 nm diode laser pump wavelength was 5.5 dB/m and the fibre background loss was 0.2 dB/m. Fibre lasers of 1.12 m in length were constructed by butting cleaved fibre ends against plane dielectric mirrors<sup>11</sup>. The input mirror had a reflectivity of 99.8% over the 1.5-1.6  $\mu\text{m}$  range while transmitting 90% of the pump light; the output mirror had a reflectivity of 50%.

The laser output spectra showed two discrete wavelengths in the range 1.53  $\mu\text{m}$  and 1.55  $\mu\text{m}$  with the 1.53  $\mu\text{m}$  seven times more intense. The fibre lasing characteristics are shown in Figure 6 where it is seen that the threshold is 2.5 mW and the slope efficiency is 37%. This corresponds to a quantum efficiency (QE) of 0.83. A QE of unity has been reported for Er<sup>3+</sup> -doped (150 ppm) in SiO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> - P<sub>2</sub>O<sub>5</sub> fibre<sup>11</sup>. One possible reason for the lower QE of the fibre laser is that the Er<sup>3+</sup> ion concentration is higher than the optimum level and some of the metastable Er<sup>3+</sup> ions are lost to cooperative upconversion<sup>12</sup>.

## CONCLUSION

In MCVD plus solution doping, the larger the cationic field strength, the greater is the cation incorporation into the glass from solution. Ions with small field strengths, such as  $\text{Er}^{3+}$ , associate with  $\text{GeO}_4$  sites and are poorly incorporated. Furthermore, these ions burn out with germania during preform processing. Ions with larger field strengths, such as  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$ , can associate with  $\text{SiO}_4$  sites and incorporate more efficiently. There is no depletion of these ions from the core during preform processing. Furthermore, codoping  $\text{Er}^{3+}$  with highly-charged smaller ions, like  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$ , assist in the incorporation and retention of  $\text{Er}^{3+}$  in the core. The presence of these codopant ions also dramatically changes the  $\text{Er}^{3+}$  ion optical properties, as is evident from the fluorescence bandwidth broadening. The structural role of  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$  appears to be their ability to provide NBOs around  $\text{Er}^{3+}$ . Since  $\text{Al}^{3+}$  and  $\text{Ta}^{5+}$  incorporate more efficiently, they are able to break Si-O-Si-network bonds and create NBOs. For example, each  $\text{Al}_2\text{O}_3$  incorporated potentially breaks three Si-O-Si bonds and creates six NBOs. This is markedly different from the poor incorporation of  $\text{Er}^{3+}$  in binary germanosilicate glass, where clustering has always been a problem<sup>3</sup>. Clustering is indicative of the need of cations to share NBOs<sup>13</sup>.

In general, ions with  $Z/r < 4$  will be poorly incorporated and have a tendency to cluster in germanosilicate glass. This can be alleviated by codoping these ions with highly-charged smaller ions. Several of the interesting optically-active transition metal ions have  $Z/r < 4$ .

SiGeTaEr type fibres provide a new host glass for  $\text{Er}^{3+}$ . The advantage of this glass is the potentially higher numerical aperture that can be obtained with smaller codopant ion levels.  $\text{Er}^{3+}$ -doped aluminosilicate and alumina-germanosilicate fibres used as erbium doped fibre amplifiers have a problem with  $\text{H}_2$  ingress in undersea systems giving a significant hydrogen-induced loss<sup>14</sup>, thus there is huge interest in alternative bandwidth-broadening co-dopants.

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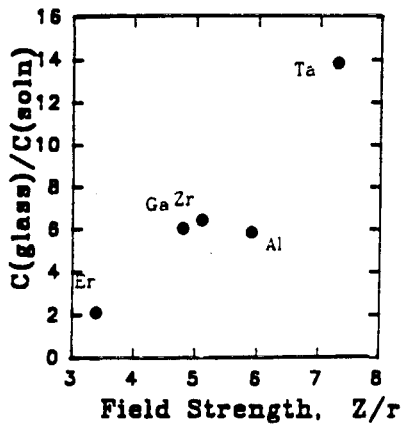


Figure 1  
Ion Incorporation

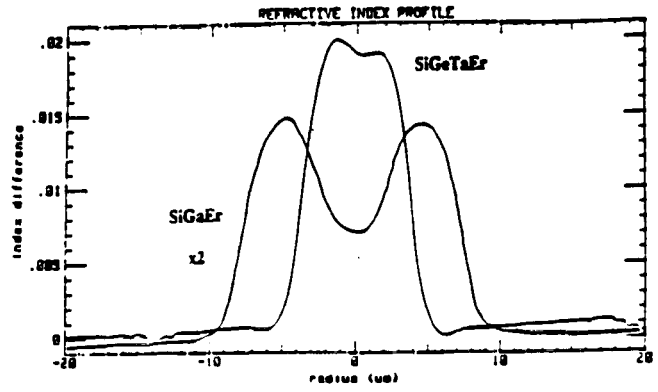
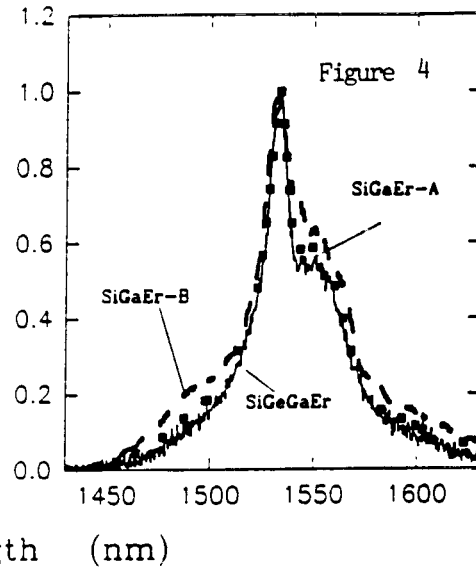
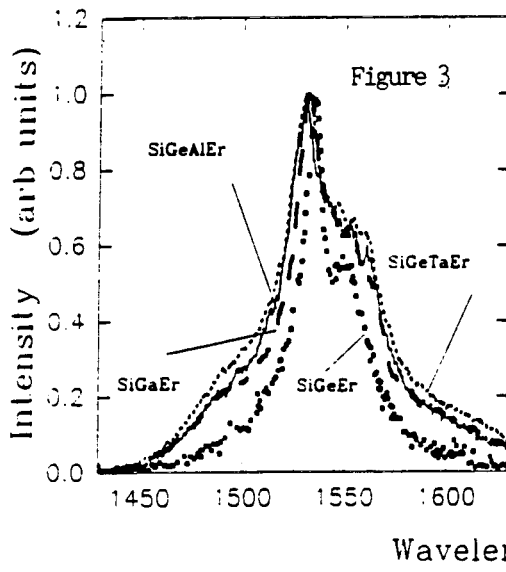


Figure 2  
Refractive Index Profile



Figures 3 and 4 : Erbium Fluorescence Spectra

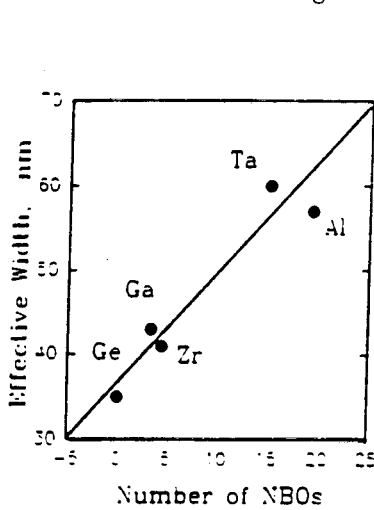


Figure 5  
Width vs NBO

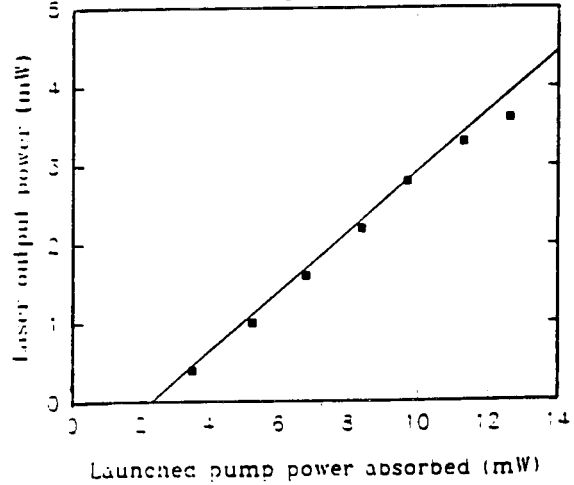


Figure 6  
Laser Characteristic for SiGeTaEr