

Preparation of Rare Earth Glasses

Summary

The finished glass contains SiO_2 , Rare Earth (R.E) oxide (generally RE_2O_3)*, CaO and Al_2O_3 .

The gel starting materials were prepared by mixing the required weights of standard solutions of aluminium, calcium and rare earth nitrates to produce a final weight of either 5g or 10g. Ethanol was then added to the nitrate mixture. This was to ensure the miscibility of tetraethyl orthosilicate (TEOS $\text{Si}(\text{OC}_2\text{H}_5)_4$), used for the silica component, which was added next. Concentrated ammonia (0.88vol NH_4OH) was then added with vigorous stirring to form a gelatinous precipitate of hydroxides. The mixture was then covered to prevent volatilisation of TEOS and left for at least 16 hours to ensure the complete hydrolysis of the TEOS.

The gels were then slowly dried, starting at 70°C and increasing the temperature slowly over several days to 180°C in an oven. This was followed by heating in an isomantle heater to around 400°C and finally roasting at 900°C .

When dry, the gels were ground up finely and small amounts were fused at around 1470°C and quenched in ice water.

When dry, the gels were ground up finely, placed in a large platinum crucible and fused using furnaces at around 1420 - 1550°C . They were then quenched in ice water. The fusions were carried out in controlled atmospheric conditions when required. Due to the small crucible size the fusion had to be done in several batches. Different oxides underwent a different number of fusions depending on the homogeneity after each fusion. If the homogeneity could be improved by further fusion the batches were bulked, ground and re-fused. This process could be repeated up to 5 times.

*Note- Cerium oxide can also be CeO_2

Praseodymium can form the mixed oxide Pr_6O_{11}

GEL STARTING MATERIALS

RARE EARTH SOLUTIONS

With the exception of cerium, all of the rare earth solutions used were obtained by dissolving the corresponding rare earth oxide. In the case of cerium, Ceric ammonium nitrate was used.

The rare earth solutions were prepared by first igniting the oxides at 900°C for around 2 hours. When cool, the required amount was weighed accurately into a 250ml beaker and enough water added to cover the powder. (15 ml was sufficient for around 10g of oxide.) This was followed by the addition of concentrated HNO_3 to dissolve the R.E. oxide. It was found that 15ml of conc. HNO_3 was usually enough to dissolve 10g of oxide but in some cases a bit extra was required. Care was taken when adding the acid since some R.E. oxides are quite reactive. A watch glass was held over the beaker during the acid addition thus preventing loss of material from the beaker in the case of a vigorous reaction and also protecting the pourer! The mixture was heated on a hotplate until the oxide was completely dissolved and then the beaker was transferred to a steam bath. The solutions were evaporated to dryness. The resultant R.E. nitrates were taken up in water and a small amount of 50% HNO_3 added (1ml to a 10g batch). The solutions were then transferred quantitatively to the appropriate volumetric flasks and diluted to the mark with water.

The Ceric ammonium nitrate solution was prepared by 'drying' the crystals at 110°C overnight and dissolving the required amount in water with a little conc. HNO_3 (10 ml in this case). This

solution was then transferred quantitatively to a volumetric flask and made up to the mark with water.

CALCIUM AND ALUMINIUM SOLUTIONS

The Aluminium solution was prepared by weighing the required amount of dry aluminium powder into a 250ml conical flask and adding enough water to cover it. Next, around 120ml of a 33 % (approx.) solution of HNO_3 was dripped slowly and with stirring onto the mixture. Since the reaction can be violent, the flask was placed in a water bath at room temperature to disperse the heat of the reaction. When reaction had ceased, the temperature of the bath was set to 40°C and then gradually increased, in 10 degree stages, to 95°C . When the aluminium powder was completely dissolved, the cooled solution was transferred quantitatively to a volumetric flask.

The calcium solution was prepared by accurately weighing the required amount of calcium carbonate into a conical flask and adding approximately 100ml of water. Around 200ml of a 33% (approx.) solution of nitric was then dripped onto the mixture slowly and with stirring. When the CaCO_3 was completely dissolved, the solution was transferred quantitatively to a volumetric flask.

TETRAETHYL ORTHOSILICATE

TEOS is used to supply the silica component of the gels. It is used 'straight from the bottle' and it is useful to know the purity of a particular batch before using it. TEOS is immiscible with water and in order to homogenise it, ethanol must be added to the mixture of aqueous nitrates.

PREPARATION OF GELS

The weight and volume of solutions required for each gel were calculated and these amounts were titrated into Teflon beakers. The beakers were placed on a top pan balance during titration so that the solutions could be measured by weight. This is done because the display on a balance can be read more accurately than the graduations on a burette. However, the volumes were noted as a cross check. To obtain a good, thick gel, it is important that the total solution volume is small and so the Al/Ca/ R.E. mixtures were evaporated down in a water bath to around 50 ml. Next, 20ml of ethanol was added and mixed thoroughly with the aqueous components before adding the TEOS. As soon as the TEOS was added, the mixture was stirred vigorously to ensure the complete homogenisation of the TEOS. If the TEOS is not completely homogenised, it rises to the surface and eventually forms a crust of SiO_2 . As soon as possible after the alcohol addition, 20ml of ammonia was added, again, with vigorous stirring, thereby forming the gel precipitates. The beakers were covered with loose fitting Teflon lids to prevent loss of TEOS by evaporation and then left to stand overnight before the drying procedure could begin.

DRYING THE GELS

The beakers were placed in an oven at 70°C , i.e. below the boiling point of ethanol, so that the ethanol was removed by slow evaporation rather than rapid boiling which could result in cross-contamination. For this reason also, the beakers were well spaced out in the oven in case any 'spitting' occurred. The oven was left at 70°C for 24 hours and then the temperature was gradually increased to 160°C at around 10 degrees every 2-3 hours. The gels were left overnight at 160°C .

Next, the gels were transferred to glass beakers. The transferrals were done over a large sheet of black, non-absorbent paper so that any material spilt was spotted easily and retrieved. The glass beakers were then placed in isomantle heaters to remove ammonium nitrate. The gels are capable of suddenly releasing large amounts of ammonium nitrate resulting in a shower of gel fragments which can contaminate other gels. To avoid this, the

heaters were initially set at a low heat and a setting of around 1.2 was used. The setting was increased by 0.2 every 2 hours (approx.) until a setting of 5.0 was reached. In this way, the NH_4NO_3 was removed by sublimation rather than melting and perhaps explosive boiling. Any vapour crystals which formed on the side of the beaker were knocked back into the beaker by gently tapping the sides.

After removal from the isomantles, the gels were roasted in an open furnace to remove the last traces of NH_4NO_3 . The beakers were placed in a furnace at 100°C and the heating was gradually increased, over several hours, until a temperature of 400°C was achieved. The samples were left at this temperature overnight and, on removal, they were stored in a desiccator.

The gels were then dried to constant weight. This was achieved by transferring them to weighed PALAU containers and covering them with loose fitting lids. Next, the containers were loaded into the furnace at 400°C and the furnace closed. The temperature was raised over several hours to 900°C and the samples were left at this temperature overnight. On cooling, the containers were weighed and the yield of dry gel recorded. The gels were then ground to a fine powder in an agate mortar and stored in bottles until required.

N.B. R.E. oxides are very hygroscopic and so too are the corresponding gels. Because of this, it was difficult to record the yields accurately.

Fusions were carried out in furnaces in small quantities under controlled atmospheric conditions where necessary. The fusions took place between 1420 - 1550°C and were then quenched by water. After fusion the glasses were checked for homogeneity. If the glasses could be improved they underwent further fusions. Due to the small quantities the fusions occurred in batches. Before refusing the batches were bulked together, ground and then refused. This process could happen up to 5 times before the final result was reached. The final product was often a mixture of many batches due to the quantities involved.

SOLOUTIONS USED IN PREPARATION OF RARE EARTH GLASSES

Concentrations

Cerium, Lanthanum, Praseodymium and Neodymium gels.

Aluminium Solution

7.43257g Aluminium powder in 250ml. This is equivalent to 14.04012g Al_2O_3 per 250ml. (conversion factor = 1.8890) Solution weight was 292.77g.

Calcium Solution

43.39434g CaCO_3 in 250ml. This is equivalent to 24.31819g CaO per 250ml. (conversion factor = 0.5604). Solution weight was 299.36g.

Lanthanum Solution

9.97660g La_2O_3 in 50ml. Solution was not weighed.

Cerium Solution

27.72614g Ceric ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ per 200ml. This is equivalent to 8.30397g Ce_2O_3 in 200ml. (conversion factor = 0.2995). Solution weight was 222.02g.

Praseodymium Solution

10.01761g Pr₆₀₁₁ in 50ml. This is equivalent to 9.70406g Pr₂O₃ per 50ml. (conversion factor = 0.9687). Solution weight was 65.19g.

Neodymium Solution

9.62332g Nd₂O₃ in 50ml. Solution was not weighed.

Tetra Ethyl Orthosilicate (TEOS)

Formula is Si(C₂H₅O)₄. Batch used was 9177870D which was found to be 99.6% pure. Therefore 1g of this batch contains 0.2888g SiO₂.

Samarium, Dysprosium, Gadolinium, yttrium, Holmium, Erbium, Terbium, and Ytterbium gels

Aluminium Solution

7.47446g Aluminium powder in 250ml. This is equivalent to 14.11925g Al₂O₃ per 250ml. The solution weight was 292.60g.

Calcium Solution

44.40818g CaCO₃ in 250ml. This is equivalent to 24.88634g CaO per 250ml. The solution weight was 300.22g.

TEOS

Batch number 9177870D used - as above.

Samarium Solution

9.78150g Sm₂O₃ in 50ml. Solution weight was 64.85g.

Dysprosium Solution

9.79645g Dy₂O₃ in 50ml. Solution weight was 65.30g

Gadolinium Solution

9.95073g Gd₂O₃ in 50ml. Solution weight was 65.43g.

Yttrium Solution

9.893719 Y₂O₃ in 50ml. Solution weight was 68.19g.

Holmium Solution

4.95596g Ho₂O₃ in 25ml. Solution weight was 32.65g.

Erbium Solution

9.93487g Er₂O₃ in 50ml. Solution weight was 65.77g

Thulium Solution

6.02663g Tb₄O₇ in 25 ml. This is equivalent to 5.89766g Tb₂O per 25ml. (conversion factor = 0.9786). Solution weight was 34.21g.

Ytterbium Solution

4.88757g Yb₂O₃ in 25ml. Solution weight was 32.67g.

Europium, Thulium and Lutetium gels.

Aluminium Solution

3.53156g Aluminium powder in 100ml. This is equivalent to 6.67112g Al₂O₃ per 250ml. The solution weight was 117.90g.

Calcium Solution

10.05647g CaCO₃ in 100ml. This is equivalent to 5.63565g CaO per 100ml. The solution weight was 111.46g.

Europium Solution

3.72241g Eu₂O₃ in 25ml. Solution weight was 30.97g.

Thulium Solution

2.90739g Tm₂O₃ in 25ml. Solution weight was 29.57g.

Lutetium Solution

2.73351g Lu₂O₃ in 25ml. Solution weight was 29.40g.

Theoretical Composition of rare earth glasses (wt. percent element)

Element	R.E	Si	Ca	Al	O
Lanthanum	14.15	26.08	12.20	5.57	41.99
Cerium (III)	16.83	25.11	11.75	5.63	40.68
Praseodymium	13.90	26.19	12.25	5.59	42.06
Neodymium	14.48	25.99	12.16	5.55	41.81
Samarium	17.42	22.70	13.89	6.25	39.74
Dysprosium	18.56	22.38	13.73	6.15	39.19
Gadolinium	18.09	22.51	13.79	6.20	39.42
Yttrium	11.00	24.46	15.01	6.72	42.81
Terbium	19.03	22.20	13.61	6.10	39.05
Erbium	18.99	22.28	13.62	6.12	38.99
Holmium	18.78	22.33	13.69	6.13	39.07
Ytterbium	19.50	22.13	13.55	6.08	38.74
Europium	17.70	22.64	13.80	6.22	39.64
Thulium	19.11	22.26	16.60	6.10	38.93
Lutetium	19.62	22.11	16.51	6.08	38.68

Some of the gels produced gave yields of less than the theoretical values. The most likely explanation for this is evaporation of non-hydrolysed TEOS. The compositions of these gels have been recalculated to take this into account. These values are tabulated below.

Element	R.E	Si	Ca	Al	O
Ytterbium	19.62	21.98	13.64	6.12	38.64
Holmium	19.00	22.03	13.85	6.20	38.92
Terbium	19.36	21.78	13.85	6.20	38.79
Erbium	19.87	21.15	14.26	6.40	38.33
Europium	19.94	19.60	15.54	7.01	37.91
Thulium	22.87	17.44	16.28	7.30	36.11

Theoretical Composition of rare earth glasses (wt. percent oxide)

Element	R.E Oxide	SiO ₂	CaO	Al ₂ O ₃
Lanthanum	16.60	55.80	17.07	10.52
Cerium (III)	19.71	53.72	16.44	10.13
Praseodymium	16.27	56.02	17.14	10.56
Neodymium	16.89	55.59	17.02	10.49
Samarium	20.20	48.55	19.44	11.81
Dysprosium	21.30	47.87	19.21	11.63
Gadolinium	20.85	48.16	19.29	11.71
Yttrium	13.97	52.33	21.0	12.70
Terbium	21.90	47.50	19.05	11.54
Erbium	21.71	47.67	19.06	11.56
Holmium	21.51	47.76	19.15	11.58
Ytterbium	22.20	47.35	18.96	11.49
Europium	20.50	48.43	19.31	11.76
Thulium	21.82	47.62	19.03	11.53
Lutetium	22.31	47.29	18.91	11.49

Some of the gels produced gave yields of less than the theoretical values. The most likely explanation for this is evaporation of non-hydrolysed TEOS. The compositions of these gels have been recalculated to take this into account. The 'new' values are below.

Recalculated Compositions

Theoretical Recalculated

		Theoretical	Recalculated
Yb/1	SiO ₂	47.35	47.02
	CaO	18.96	19.08
	Al ₂ O ₃	11.49	11.56
	Yb ₂ O ₃	22.20	22.34
Ho/1	SiO ₂	47.76	47.13
	CaO	49.15	19.38
	Al ₂ O ₃	11.58	11.72
	Ho ₂ O ₃	21.51	21.77
Tb/1	SiO ₂	47.50	46.60
	CaO	19.05	19.38
	Al ₂ O ₃	11.54	11.74
	Tb ₂ O ₃	21.90	22.28
Er/1	SiO ₂	47.67	45.24
	CaO	19.06	19.95
	Al ₂ O ₃	11.56	12.10
	Er ₂ O ₃	21.71	22.75
Eu/1	SiO ₂	48.43	41.93
	CaO	19.31	21.74
	Al ₂ O ₃	11.76	13.24
	Eu ₂ O ₃	20.50	23.09
Tm/1	SiO ₂	47.62	37.30
	CaO	19.03	22.78
	Al ₂ O ₃	11.53	13.80
	Tm ₂ O ₃	22.31	26.12