School of GeoSciences

Research Facilities

Rare Earth Element (REE) Standards

Fourteen REE glasses, together with a Y glass, have been prepared as standard material for electron microprobe and other mico-beam techniques. A suite of these standards is available on request.

Each glass has a single REE in a Si-Al-Ca-O based matrix. The REE is present at a concentration of approximately 20wt% oxide and has been analysed independently by ICP, SIMS, AA as well as EMPA.

The preparation and analysis of the glasses has involved a number of staff over a period of 20 years. The major contributors are:

- E. Cairns
- P.C. Choi (University of Bristol)
- K. Fearnhead
- P. Hadden
- P. Hill
- S. Malik (University of Reading)
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University Homepage Schools & departments School of GeoSciences Facilities EMMAC: Microanalysis
Electron Probe REE Standards

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 gels were made in a similar manner to that described in Biggar and O'Hara (1969). 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 $Si(OC_2H_5)_4$), used for the silica component, which was added next. Concentrated ammonia (0.88vol NH_4OH) was then added to form a gelatinous precipitate of hydroxides. The mixture was then covered and left for at least 16 hours to ensure the complete hydrolysis of the TEOS.

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

When dry, the gels were ground up finely, placed in a large platinum crucible and fused using furnaces at around 1420-1550^{o}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

A detailed description of the Gel making process can be downloaded (by Elizabeth Cairnes) PDF

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, $(NH_4)_2Ce(NO_3)_6$ was used.

The rare earth solutions were prepared by first igniting the oxides at 900^{o}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. This was followed by the addition of concentrated HNO_3 to dissolve the R.E. oxide. The mixture was heated on a hotplate until the oxide was completely dissolved and then the beaker was transferred to a steam bath. The solution was 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 solution was then diluted to the required concentration.

The $(NH_4)_2Ce(NO_3)_6$ solution was prepared by 'drying' the crystals at

110^oC overnight and dissolving in water with 10ml concentrated HNO_3. This solution was then transferred quantitatively to a volumetric flask and made up to the mark with water.

ALUMINIUM SOLUTION

The Aluminium solution was prepared by accurately weighing the required amount of dry aluminium powder into a 250ml conical flask and adding enough water to cover. Next, around 120ml of a 33 % (approx.) solution of HNO_3 was dripped slowly and with stirring onto the mixture. When reaction had ceased, the temperature of the bath was set to 4O^oC and then gradually increased, in 10 degree stages, to 95^oC. When the aluminium powder was completely dissolved, the cooled solution was transferred quantitatively to a volumetric flask.

CALCIUM SOLUTION

The calcium solution was prepared by accurately weighing the required amount of calcium carbonate into a conical flask an adding approximately 100ml of water. Around 200ml of a 33% (approx.) solution of HNO_3 was then dripped slowly onto the mixture. 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' but the purity of each batch was measured prior to use. 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. 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. 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 gels were transferred to glass beakers for heating. The beakers were placed in an oven at 70^oC for 24 hours and then the temperature was gradually increased to 160^oC at around 10 degrees every 2-3 hours. The gels were left overnight at 160^oC.

A slow heating process removed the NH_4NO_3 over a period of approximately 36 hours. The heating was slow to avoid gel fragments contaminating other gels if large amounts of NH_4NO_3 were released explosively. Any vapour crystals which formed on the side of the beaker were knocked back into the beaker by gently tapping the sides.

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^oC and the heating was gradually increased, over several hours, until a temperature of 400^oC was achieved. The samples were left at this temperature overnight and, on removal, they were stored in a dessicator.

The gels were finally dried to constant weight. Next, the gel containers were loaded into a closed furnace at 400°C. 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.

FUSION OF GELS

FUSION PROCEDURE

The dry gels were placed in platinium crucibles and fusions were carried out in furnaces, in small quantities, under controlled atmospheric conditions (log fO_2 ~ -7.2) where necessary. The fusions took place between 1420-1550°C and were then quenched in water.

After fusion the glasses were checked for homogeneity by electron microprobe analysis (EMPA). If the glasses' homogeneity could be improved they underwent further fusions. Due to the small quantities used the fusions occurred in batches. Before re-fusing the batches were bulked together, ground and then re-fused. This process could be repeated up to 5 times before the final result was reached.

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*	19.36	21.78	13.85	6.20	38.79
Erbium*	19.87	21.15	14.26	6.40	38.33
Holmium*	19.00	22.03	13.85	6.20	38.92
Ytterbium*	19.62	21.98	13.64	6.12	38.64
Europium*	19.94	19.60	15.54	7.01	37.91
Thulium*	22.87	17.44	16.28	7.30	36.11
Lutetium	19.62	22.11	16.51	6.08	38.68

*Recalculated values as 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.

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

Element	R.E Oxide	SiO2	CaO	Al2O3
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*	22.28	46.60	19.38	11.74
Erbium*	22.75	45.24	19.95	12.10
Holmium*	21.77	47.13	19.38	11.72
Ytterbium*	22.34	47.02	19.08	11.56
Europium*	23.09	41.93	21.74	13.24
Thulium*	26.12	37.30	22.78	13.80
Lutetium	22.31	47.29	18.91	11.49

* Recalculated values as 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.

References

Biggar (G.M) and O'Hara(M.J) 1969- A comparison of gel and glass starting materials for phase equilibrium studies, *Mineralogical Magazine*, June 1969, Vol 37, No 286

Contacts

A set of these REE standards is available on request free of charge to Universities and other educational establishments. Each glass fragment supplied will weigh between ~0.02-0.05g.

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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 $Si(OC_2H_5)_4$), 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 STARTIRG 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 4O°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 an 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 TE0S 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^{o}C and the heating was gradually increased, over several hours, until a temperature of 400^{o}C was achieved. The samples were left at this temperature overnight and, on removal, they were stored in a dessicator.

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^{o}C and the furnace closed. The temperature was raised over several hours to 900^{o}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 $1420\text{-}1550^{o}$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 l4.040l2g 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 24.3l8l9g 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 $[(NH_4)2Ce(N0_3)_6]$ 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 Pr_{6O11} in 50ml. This is equivalent to 9.70406g Pr_2O_3 per 50ml. (conversion factor = 0.9687). Solution weight was 65.19g.

Neodymium Solution

9.62332g Nd_2O_3 in 50ml. Solution was not weighed.

Tetra Ethyl Orthosilicate (TEOS)

Formula is $Si(C_2H_5O)_4$. Batch used was 9l77870D which was found to be 99.6% pure. Therefore 1g of this batch contains 0.2888g SiO_2.

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

Aluminium Solution

7.47446g Aluminium powder in 250ml. This is equivalent to 14.11925g Al_2O_3 per 250m1. The solution weight was 292.60g.

Calcium Solution

44.40818g $CaCO_3$ in 250m1. This is equivalent to 24.88634g CaO per 250m1. The solution weight was 300.22g.

TEOS

Batch number 9177870D used - as above.

Samarium Solution

9.78150g Sm_2O_3 in 50ml. Solution weight was 64.85g.

Dysprosium Solution

9.79645g DY_2O_3 in 50ml. Solution weight was 65.30g

Gadolinium Solution

9.95073g Gd_2O_3 in 50ml. Solution weight was 65.43g.

Yttrium Solution

9.893719 Y_2O_3 in 50ml. Solution weight was 68.19g.

Holmium Solution

4.95596g Ho_2O3 in 25ml. Solution weight was 32.65g.

Erbium Solution

9.93487g Er_2O_3 in 50ml. Solution weight was 65.77g

Thulium Solution

6.02663g Tb_4O_7 in 25 ml. This is equivalent to 5.89766g Tb_2O per 25ml. (conversion factor = 0.9786). Solution weight was 34.2lg.

Ytterbium Solution

4.88757g Yb_2O_3 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 $A1_2O_3$ per 250ml. The solution weight was l17.90g.

Calcium Solution

10.05647g $CaCO_3$ in l00ml. This is equivalent to 5.63565g CaO per l00ml. The solution weight was 111.46g.

Europium Solution

3.72241g Eu_2O_3 in 25ml. Solution weight was 30.97g.

Thulium Solution

2.90739g Tm_2O_3 in 25ml. Solution weight was 29.57g.

Lutetium Solution

2.73351g Lu_2O_3 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	SiO2	CaO	Al2O3
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	SiO2	47.35	47.02
	CaO	18.96	19.08
	Al2O3	11.49	11.56
	Yb2O3	22.20	22.34
Ho/1	SiO2	47.76	47.13
	CaO	49.15	19.38
	Al2O3	11.58	11.72
	Ho2O3	21.51	21.77
Tb/1	SiO2	47.50	46.60
	CaO	19.05	19.38
	Al2O3	11.54	11.74
	Tb2O3	21.90	22.28
Er/1	SiO2	47.67	45.24
	CaO	19.06	19.95
	Al2O3	11.56	12.10
	Er2O3	21.71	22.75
Eu/1	SiO2	48.43	41.93
	CaO	19.31	21.74
	Al2O3	11.76	13.24
	Eu2O3	20.50	23.09
Tm/1	SiO2	47.62	37.30
	CaO	19.03	22.78
	Al2O3	11.53	13.80
	Tm2O3	22.31	26.12

Yttrium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	52.33	-	-	21.00	-	-	12.70	-	-	13.97	-	-	**100.00**		
ICP Analysis	50.34	52.05	48.63	21.01	20.98	20.60	12.54	12.47	11.92	12.41	14.07	10.79	**96.30**	91.94	99.57
EPMA Analysis	51.80	52.39	51.29	20.89	21.21	20.57	12.85	13.05	12.68	13.71	13.99	13.40	**99.25**	97.94	100.64
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Lanthanum	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	55.80	-	-	17.07	-	-	10.52	-	-	16.60	-	-	**99.99**		
ICP Analysis	47.49	54.99	36.95	16.54	17.13	15.35	10.04	10.00	9.59	15.89	16.56	14.88	**89.96**	76.77	98.68
EPMA Analysis	56.10	56.74	55.20	16.84	17.20	16.53	10.99	11.23	10.70	16.51	16.83	16.26	**100.45**	98.68	102.01
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Cerium (III)	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	53.72	-	-	16.44	-	-	10.13	-	-	19.71	-	-	**100.00**		
ICP Analysis	52.17	54.07	49.36	16.24	16.76	15.57	9.76	9.72	9.50	17.02	19.75	10.15	**95.19**	84.59	100.30
EPMA Analysis	53.35	53.78	53.00	16.01	16.17	15.77	10.16	10.27	10.06	19.44	19.60	19.25	**98.96**	98.08	99.82
Wet Chemical	-	-	-	-	-	-	-	-	-	19.84	19.95	19.68	-		
Praseodymium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	56.02	-	-	17.14	-	-	10.56	-	-	16.27	-	-	**99.99**		
ICP Analysis	52.29	54.35	48.83	17.87	18.20	16.90	11.23	11.63	10.91	16.21	17.20	15.37	**97.60**	92.02	101.39
EPMA Analysis	54.90	56.59	52.46	17.00	18.02	16.20	10.65	11.36	10.16	16.46	17.56	15.69	**99.03**	94.51	103.54
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Neodymium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	55.59	-	-	17.02	-	-	10.49	-	-	16.89	-	-	**99.99**		
ICP Analysis	52.60	54.27	50.50	16.59	17.03	15.41	10.51	10.45	9.72	16.26	18.11	15.00	**95.96**	90.64	99.86
EPMA Analysis	54.15	54.88	53.18	17.04	17.39	16.86	10.41	10.73	10.15	17.10	17.47	16.84	**98.70**	97.04	100.47
Wet Chemical	-	-	-	-	-	-	-	-	-	16.49	16.61	16.31	-		

Samarium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	48.55	-	-	19.44	-	-	11.81	-	-	20.20	-	-	**100.00**		
ICP Analysis	45.11	47.17	43.05	18.97	19.17	18.53	11.80	11.41	10.92	19.51	20.65	18.98	**95.39**	91.48	98.40
EPMA Analysis	49.48	11.87	11.63	19.22	49.80	48.89	11.74	19.37	19.05	19.52	19.91	19.16	**99.96**	98.73	100.94
Wet Chemical	-	-	-	-	-	-	-	-	-	21.23	21.97	20.57	-		
Europium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	41.93	-	-	21.74	-	-	13.24	-	-	23.09	-	-	100.00		
ICP Analysis	41.95	43.82	38.86	21.95	22.08	21.30	13.69	13.40	12.63	22.15	23.53	19.38	99.74	92.16	102.84
EPMA Analysis	40.35	41.37	39.67	21.85	22.08	21.62	12.00	12.18	11.76	22.76	22.08	21.62	96.96	94.66	97.70
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Gadolinium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	48.16	-	-	19.29	-	-	11.71	-	-	20.85	-	-	**100.01**		
ICP Analysis	43.81	45.68	43.80	19.48	19.18	17.87	12.09	11.69	10.93	20.42	32.22	18.74	**95.80**	91.34	108.77
EPMA Analysis	47.57	48.15	46.92	19.10	19.46	18.61	12.06	12.24	11.83	20.60	21.40	19.90	**99.33**	97.26	101.26
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Terbium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	46.60	-	-	19.38	-	-	11.74	-	-	22.28	-	-	**100.00**		
ICP Analysis	32.09	32.09	32.09	18.93	19.13	18.27	11.01	22.40	11.84	22.07	23.30	21.58	**84.11**	83.78	96.92
EPMA Analysis	44.95	45.43	44.34	19.35	19.50	19.16	11.80	11.95	11.60	22.46	22.80	22.18	**98.56**	97.28	99.69
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Dysprosium	**Weight %**														
	SiO_2	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al_2O_3**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	47.87	-	-	19.21	-	-	11.63	-	-	21.30	-	-	**100.01**		
ICP Analysis	45.59	48.19	42.99	18.69	18.69	18.13	12.01	12.31	10.89	20.54	21.22	20.04	**96.84**	92.05	100.41
EPMA Analysis	47.25	47.70	46.92	18.79	19.21	18.55	11.43	11.74	11.31	21.07	21.38	20.28	**98.54**	97.06	100.03
Wet Chemical	-	-	-	-	-	-	-	-	-	21.60	21.90	21.27	-		

Holmium	**Weight %**														
	SiO$_2$	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al$_2$O$_3$**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	47.13	-	-	19.38	-	-	11.72	-	-	21.77	-	-	**100.00**		
ICP Analysis	46.39	48.68	44.10	18.91	18.92	18.43	11.53	11.32	10.85	20.40	21.60	19.43	**97.22**	92.80	100.52
EPMA Analysis	45.72	46.04	45.36	18.98	19.37	18.76	11.72	11.82	11.57	21.70	22.06	21.34	**98.12**	97.02	99.29
Wet. Chemical	-	-	-	-	-	-	-	-	-	21.38	21.64	21.38	-		
Erbium	**Weight %**														
	SiO$_2$	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al$_2$O$_3$**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**		
Starting Gel Composition	45.24	-	-	19.95	-	-	12.10	-	-	22.72	-	-	**100.01**		
ICP Analysis	44.33	46.03	42.62	19.14	19.68	16.67	11.78	11.76	9.98	20.64	22.51	17.41	**95.89**	86.69	99.98
EPMA Analysis	44.38	44.84	43.95	19.57	19.84	19.28	12.36	12.53	12.15	22.43	22.96	21.72	**98.74**	97.10	100.17
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Thulium	**Weight %**														
	SiO$_2$	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al$_2$O$_3$**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	37.30	-	-	22.78	-	-	13.80	-	-	26.12	-	-	100.00		
ICP Analysis	26.77	27.07	22.96	21.78	22.39	21.17	13.43	13.43	12.04	25.13	26.77	26.77	87.12	82.95	89.67
EPMA Analysis	35.43	35.66	35.14	22.79	23.21	22.52	14.41	14.53	14.31	25.18	25.57	24.67	97.80	96.65	98.97
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Ytterbium	**Weight %**														
	SiO$_2$	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al$_2$O$_3$**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	47.02	-	-	19.08	-	-	11.56	-	-	22.34	-	-	**100.00**		
ICP Analysis	41.25	47.67	43.81	19.16	18.92	18.26	11.80	11.30	10.78	22.06	22.59	21.12	**94.26**	93.97	100.48
EPMA Analysis	46.47	47.31	34.86	19.02	19.42	18.86	11.45	12.17	11.27	22.41	23.14	21.79	**99.35**	86.77	102.04
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		
Lutetium	**Weight %**														
	SiO$_2$	**Max**	**Min**	**CaO**	**Max**	**Min**	**Al$_2$O$_3$**	**Max**	**Min**	**REE Oxide**	**Max**	**Min**	**Total**	**Min Total**	**Max Total**
Starting Gel Composition	47.29	-	-	18.91	-	-	11.49	-	-	22.31	-	-	**100.00**		
ICP Analysis	42.64	42.64	42.64	19.41	20.69	18.58	11.25	12.64	10.78	22.11	23.70	20.96	**95.41**	92.96	99.66
EPMA Analysis	46.93	47.25	46.55	19.31	19.52	19.12	11.74	11.83	11.60	22.56	22.91	21.99	**100.55**	99.25	101.50
Wet Chemical	-	-	-	-	-	-	-	-	-	-	-	-	-		

EMP Summary Data Table

Element	**Al_2O_3** (Wt%)	**Si_2O_3** (Wt%)	**CaO** (Wt%)	**REE_2O_3** (Wt%)	Total (Wt%)
Y	12.85	51.80	20.89	13.71	**99.25**
Deviation from theoretical	*1.01*	*0.99*	*0.99*	*0.98*	
La	10.99	56.10	16.84	16.51	**100.44**
	1.04	*1.01*	*0.98*	*0.99*	
Ce	10.16	53.35	16.01	19.44	**98.96**
	1.00	*0.99*	*0.97*	*0.99*	
Pr	10.65	54.90	17.00	16.46	**99.03**
	1.00	*0.98*	*0.99*	*1.01*	
Nd	10.41	54.15	17.04	17.10	**98.69**
	0.99	*0.97*	*1.00*	*1.01*	
Sm	11.76	49.27	19.30	19.64	**99.96**
	0.99	*1.01*	*0.99*	*0.97*	
Eu	12.00	40.35	21.85	22.76	**96.96**
	0.91	*0.96*	*1.00*	*0.99*	
Gd	12.06	47.57	19.10	20.60	**99.32**
	1.03	*0.99*	*0.99*	*0.99*	
Tb	11.80	44.94	19.35	22.46	**98.55**
	1.00	*0.96*	*1.00*	*1.01*	
Dy	11.43	47.25	18.79	21.07	**98.50**
	0.98	*0.99*	*0.98*	*1.04*	
Ho	11.71	45.72	18.98	21.70	**98.10**
	1.00	*0.97*	*0.98*	*1.00*	
Er	12.36	44.38	19.57	22.43	**98.74**
	1.18	*0.80*	*1.15*	*1.35*	
Tm	14.40	35.43	22.79	25.17	**97.79**
	1.04	*0.95*	*1.00*	*0.96*	
Yb	11.45	46.47	19.02	22.40	**99.30**
	0.99	*0.99*	*1.00*	*1.00*	
Lu	11.74	46.93	19.31	22.56	**100.55**
	1.02	*0.99*	*1.02*	*1.01*	

	Theortical	AD Bristol			AD RH			LiB			Malik	Malik	Malik
	REE Oxide	REE Oxide	S.D	No. of	REE Oxide	S.D	No. of	REE oxide	S.D	No. of	REE Oxide	S.D	No. of
	Wt %	Wt %		results	Wt %		results	Wt %		results	Wt %		results
Y	**13.97**	11.41	0.06	4	12.45	0.14	3	11.81	0.12	2	13.96	0.52	9
La	**16.60**	15.88	0.18	3	15.30	0.08	3	16.11	0.24	4	16.26	0.08	9
Ce	**19.71**	16.09	0.14	3	19.75	0.09	3	14.89	0.22	3	17.34	0.10	9
Pr	**16.27**	16.74	0.16	3	15.37	0.19	3	16.66	0.22	3	16.08	0.06	9
Nd	**16.89**	15.89	0.10	3	15.00	0.21	3	17.23	0.10	3	16.92	0.03	9
Sm	**20.20**	19.55	0.11	13	19.13	0.29	3	19.47	0.18	2	20.11	0.23	9
Eu	**23.09**	22.70	0.18	3	19.38	0.08	3	23.21	0.18	3	23.31	0.16	9
Gd	**20.85**	20.88	0.19	3	19.47	0.14	3	20.85	0.18	2	20.46	0.18	9
Tb	**22.28**	22.64	0.09	2	21.66	0.49	3	21.94	0.07	1	22.03	0.25	9
Dy	**21.30**	20.29	0.18	3	20.45	0.04	3	20.46	0.15	2	20.98	0.14	9
Ho	**21.76**	19.63	0.26	3	20.02	0.21	3	20.55	0.24	2	21.39	0.16	9
Er	**22.72**	19.45	0.11	3	19.13	0.17	3	21.77	0.16	2	22.23	0.14	9
Tm	**26.12**	-	-	0	22.96	0.12	2	27.07	0.16	1	25.37	0.38	9
Yb	**22.34**	21.95	0.27	3	21.12	0.17	3	23.16	0.23	3	22.00	0.14	9
Lu	**22.31**	23.70	0.05	1	21.96	0.09	2	20.96	0.30	1	21.82	0.23	9

	Theortical	AD Bristol			AD RH			LiB		
	Al2O3	Al2O3	S.D	No. of	Al2O3	S.D	No. of	Al2O3	S.D	No. of
	Wt %	Wt %		results	Wt %		results	Wt %		results
Y	**12.70**	12.66	0.12	4	11.92	0.07	3	12.54	0.30	2
La	**10.52**	10.13	0.11	3	10.00	0.03	3	10.04	0.18	4
Ce	**10.13**	9.86	0.10	3	9.72	0.03	3	9.76	0.12	3
Pr	**10.56**	11.70	0.10	3	10.91	0.07	3	11.23	0.17	3
Nd	**10.49**	10.24	0.09	3	10.16	0.07	3	10.51	0.14	3
Sm	**11.81**	11.70	0.26	3	10.92	0.09	3	11.80	0.17	2
Eu	**13.25**	13.45	0.25	3	12.63	0.01	3	13.69	0.27	3
Gd	**11.71**	12.27	0.15	3	11.08	0.04	3	12.09	0.24	2
Tb	**11.72**	12.34	0.16	2	10.96	0.13	3	11.01	0.14	1
Dy	**11.63**	12.42	0.12	3	10.89	0.03	3	12.01	0.26	2
Ho	**11.72**	11.49	0.09	3	10.85	0.06	3	11.53	0.19	2
Er	**12.09**	11.33	0.12	3	10.96	0.08	3	11.78	0.26	2
Tm	**13.79**	-	-	0	12.04	0.06	2	13.43	0.20	1
Yb	**11.56**	11.56	0.13	3	10.78	0.04	3	11.80	0.16	3
Lu	**11.49**	12.64	0.08	1	10.78	0.00	2	11.25	0.30	1

	Theortical	AD Bristol			AD RH			LiB		
	CaO	CaO	S.D	No. of	CaO	S.D	No. of	CaO	S.D	No. of
	Wt %	Wt %		results	Wt %		results	Wt %		results
Y	**21.00**	21.07	0.33	4	20.98	0.16	3	20.99	0.37	2
La	**17.07**	16.12	0.29	3	17.13	0.07	3	16.36	0.29	4
Ce	**16.44**	15.94	0.16	3	16.76	0.06	3	16.04	0.37	3
Pr	**17.14**	18.16	0.30	3	18.20	0.16	3	17.25	0.42	3
Nd	**17.02**	16.15	0.26	3	17.03	0.16	3	16.59	0.26	3
Sm	**19.44**	19.13	0.44	3	19.17	0.18	3	18.62	0.34	2
Eu	**21.74**	22.21	0.49	3	21.98	0.03	3	21.65	0.26	3
Gd	**19.29**	19.81	0.21	3	19.18	0.10	3	19.45	0.34	2
Tb	**19.38**	19.49	0.35	2	19.04	0.33	3	18.27	0.17	1
Dy	**19.21**	18.92	0.29	3	18.13	0.02	3	19.02	0.36	2
Ho	**19.38**	18.79	0.36	3	18.92	0.10	3	19.02	0.58	2
Er	**19.95**	18.30	0.29	3	19.31	0.08	3	19.80	0.47	2
Tm	**22.78**	-	-	0	21.17	0.06	2	22.39	0.26	1
Yb	**19.08**	18.83	0.31	3	18.92	0.09	3	19.74	0.27	3
Lu	**18.91**	20.69	0.30	1	18.95	0.02	2	18.58	0.36	1

AD= Acid Digest
LiB= Lithium Metaborate Fusion
RH= Royal Holloway