GADOLINIUM AND HAFNIUM ALUMINO-BOROSILICATE GLASSES: Gd AND Hf SOLUBILITIES

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ABSTRACT

The solubilities of Hf and Gd in sodium alumino-borosilicate glasses based on the target compositions were examined and confirmed by electron microprobe analysis. The measured compositions of essentially crystal-free glasses are generally homogeneous and close to the target compositions. Therefore, the solubilities of Gd and Hf in sodium alumino-borosilicate glasses based on the target glass compositions are valid. However, for glasses containing quenched crystals (grown from the melt) and undissolved HfO_2 with overgrowths, the chemical compositions are often heterogeneous and may be significantly different from the target compositions. Precipitated crystalline phases include a rare earth silicate with the apatite structure ($NaGd_9(Si_{5.25}B)O_{26}$) in a gadolinium sodium alumino-borosilicate glass and a HfO_2 phase in hafnium sodium alumino-borosilicate glasses.

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INTRODUCTION

- Alumino-borosilicate glasses are proposed waste forms for the immobilization of plutonium-containing waste (this does not include the excess weapons plutonium that is to be converted to a crystalline ceramic) and miscellaneous spent nuclear fuels [1-4].
- New glass compositions in the four-component system (Na2O-B2O3-Al2O3-SiO2) with neutron absorbers (Gd and Hf) have been synthesized to study the effect of variation of the bulk composition on the solubility of Gd and Hf [5-7].

- The solubility limit is defined as the highest concentration of an element (e.g., Gd or Hf) in the glass above which crystallization or phase separation occurs [6]. Chemical heterogeneity and mass losses during glass synthesis may affect solubility determination.
- Therefore, it is necessary to directly determine distributions and contents of each individual element in the glasses and associated precipitated crystals.
- We present the compositional features of representative glasses and precipitated crystals as determined by EMPA.

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SAMPLES

- Thirteen Gd- or Hf-bearing glass samples, with or without precipitated phase, were studied (Table I).
- Precipitated crystals in some samples are not homogeneously distributed.
- Some samples examined here were not formed under the same conditions as the samples used in the solubility study.

Table I. Gd- and Hf-bearing sodium alumino-borosilicate glass samples.

Sample #	Description
Al15Gd18	Clear Gd glass. No observable crystals
B15Gd42	Clear Gd glass. No observable crystals
B15Gd48	Clear Gd glass with crystalline phase. Elements in crystals: Si, Al, Na, O and Gd
Na10Gd20	Clear Gd glass. No observable crystals
B15Hf30	Clear Hf glass. No observable crystals
B15Hf31	Clear Hf glass. No observable crystals
Na30Hf30	Clear Hf glass. No observable crystals
Na30Hf34	Clear Hf glass. No observable crystals
Na30Hf35a	Clear Hf glass with no crystals
Na30Hf35b	Different Hf glass from sample Na30Hf35a. Clear glass with euhedral HfO_2 crystals (up to tens of μm in size). Elements confirmed in crystals: Hf and O
PL0.35Hf8a	Clear Hf glass with bladed crystals radiating outward from undissolved HfO_2 particles. Heat-treated for one hour at 1560°C and one hour at 1450°C. Elements confirmed in crystals: Hf and O
PL0.35Hf8b	Hafnium glass with tiny crystals. Heat treated for 30 minutes at 1400°C after initially melted at 1560°C for one hour and one hour at 1450°C. Elements confirmed in crystals: Hf and O
PL0.85Hf32	Clear Hf glass with well-developed, hexagonal crystals. Heat-treated for one hour at 1560°C and three hours at 1350°C. Elements confirmed in crystals: Hf and O

ANALYTICAL METHODS

- Electron microbeam techniques: electron microprobe analysis (EMPA), backscattered electron (BSE) imaging, and energy dispersive X-ray spectroscopy (EDS).
- EMPA: to minimize volatilization of sodium in glass, enlarged beam sizes, lower beam current and shorter count times were used.

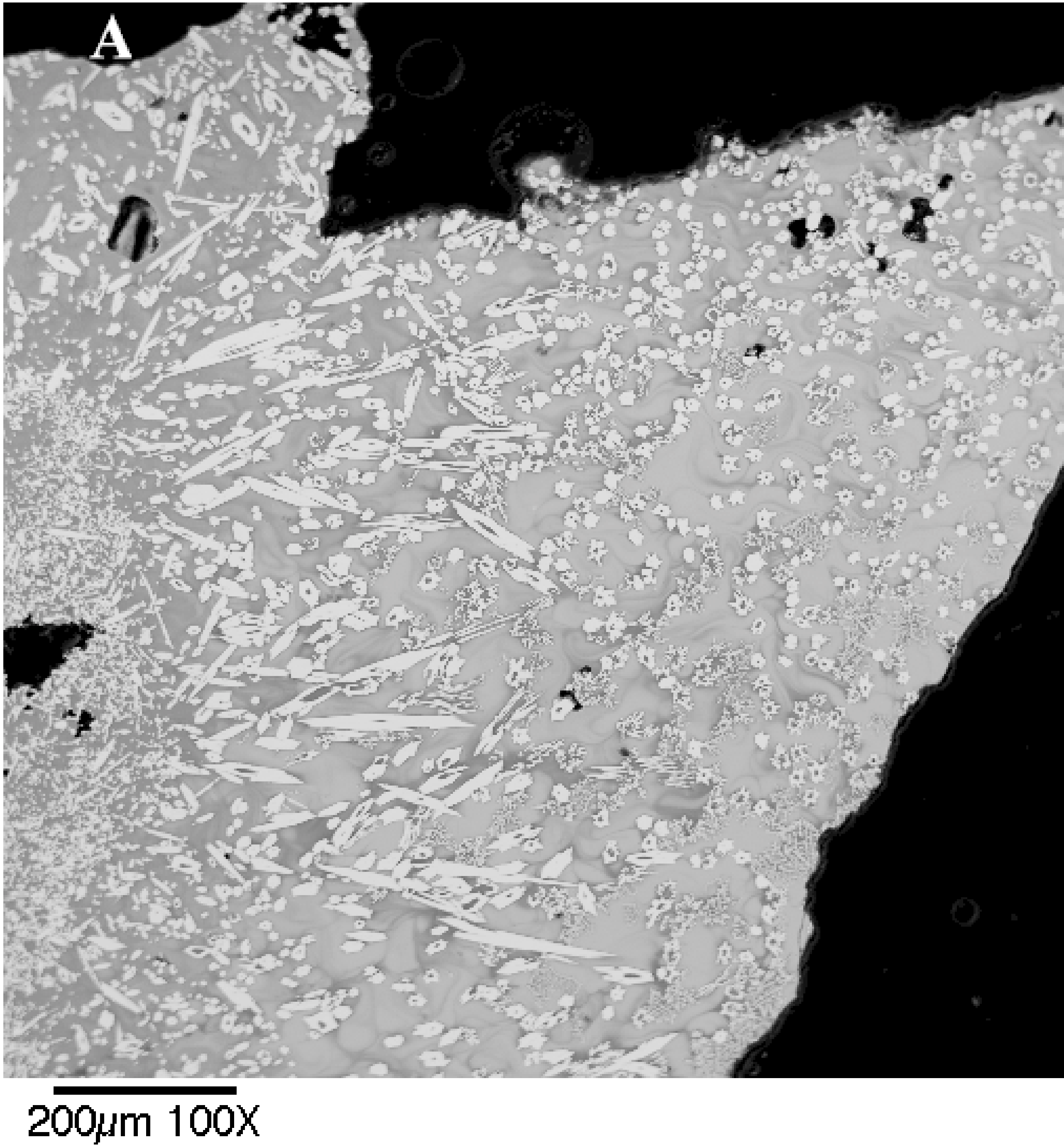
- Optimized procedure is beam size 15 x 15 μm^2, beam current 6 nA, accelerating voltage 15 kV, peak and background counting times of 10 and 5 seconds, B by difference, and O by charge balance
- Standards were SiO_2 for Si, andalusite (Al_2SiO_5) for Al, albite ($NaAlSi_3O_8$) or jadeite ($NaAlSi_2O_6$) for Na, Gd phosphate ($GdPO_4$) for Gd, and metallic Hf for Hf. Glass standards were not used due to alkali loss.

Characteristics of samples and morphology of precipitated crystals

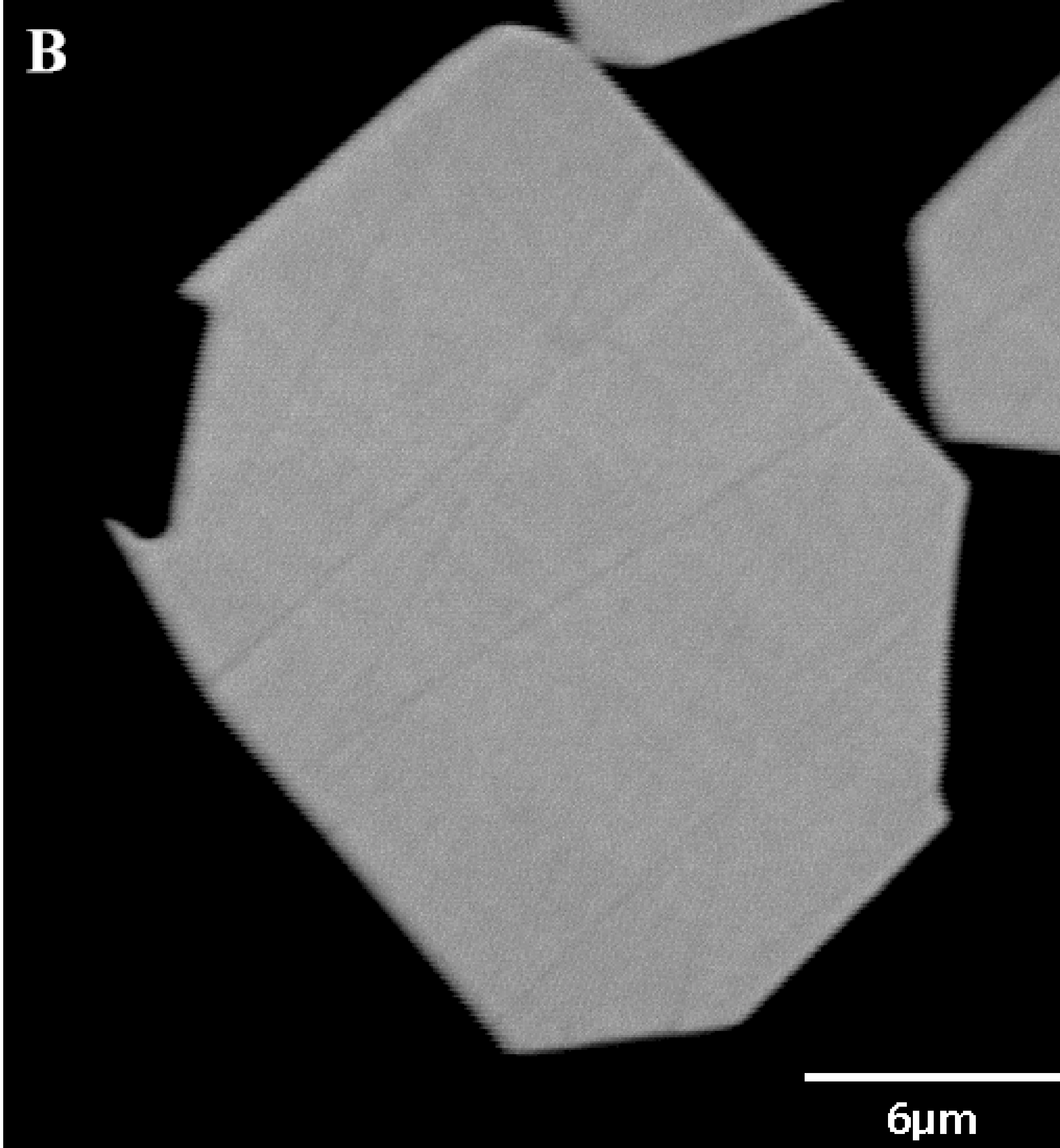
Gd-bearing glasses.

- Most Gd-bearing samples are crystal-free
- Samples B15Gd48 contained crystals: elongate, acicular, prismatic or dendritic with hexagonal cross-sections (Figure 1A)
- The darker area of the BSE image is enriched in Si, Al and Na, whereas the brighter area is enriched in Gd.

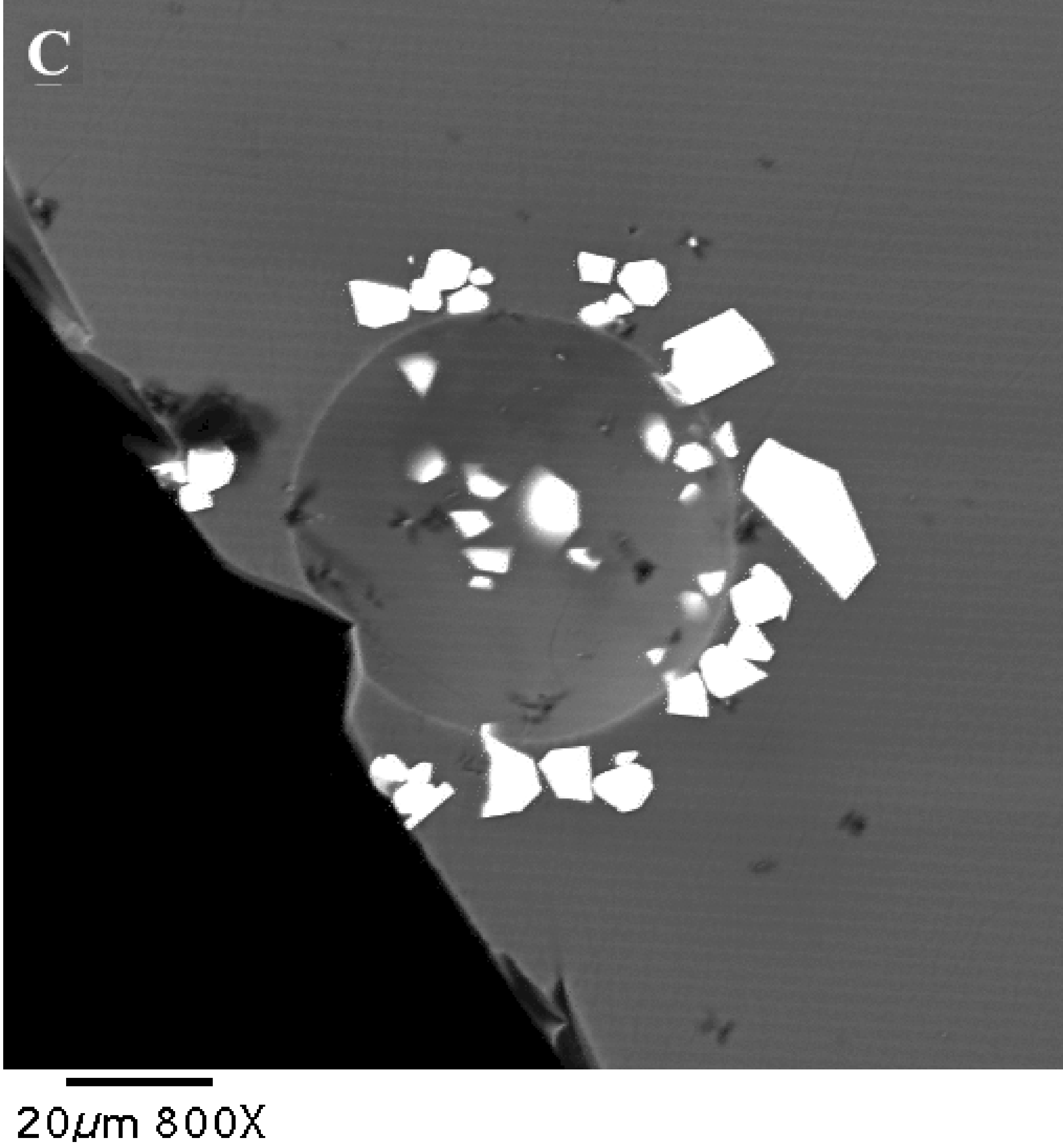
A) B15Gd48: elongated, acicular, prismatic or dendritic Gd silicate apatite crystals ($NaGd_9(Si_{5.25}B)O_{26}$) ; the upper left area darker than the central and lower right areas, indicating chemical heterogeneity of the matrix



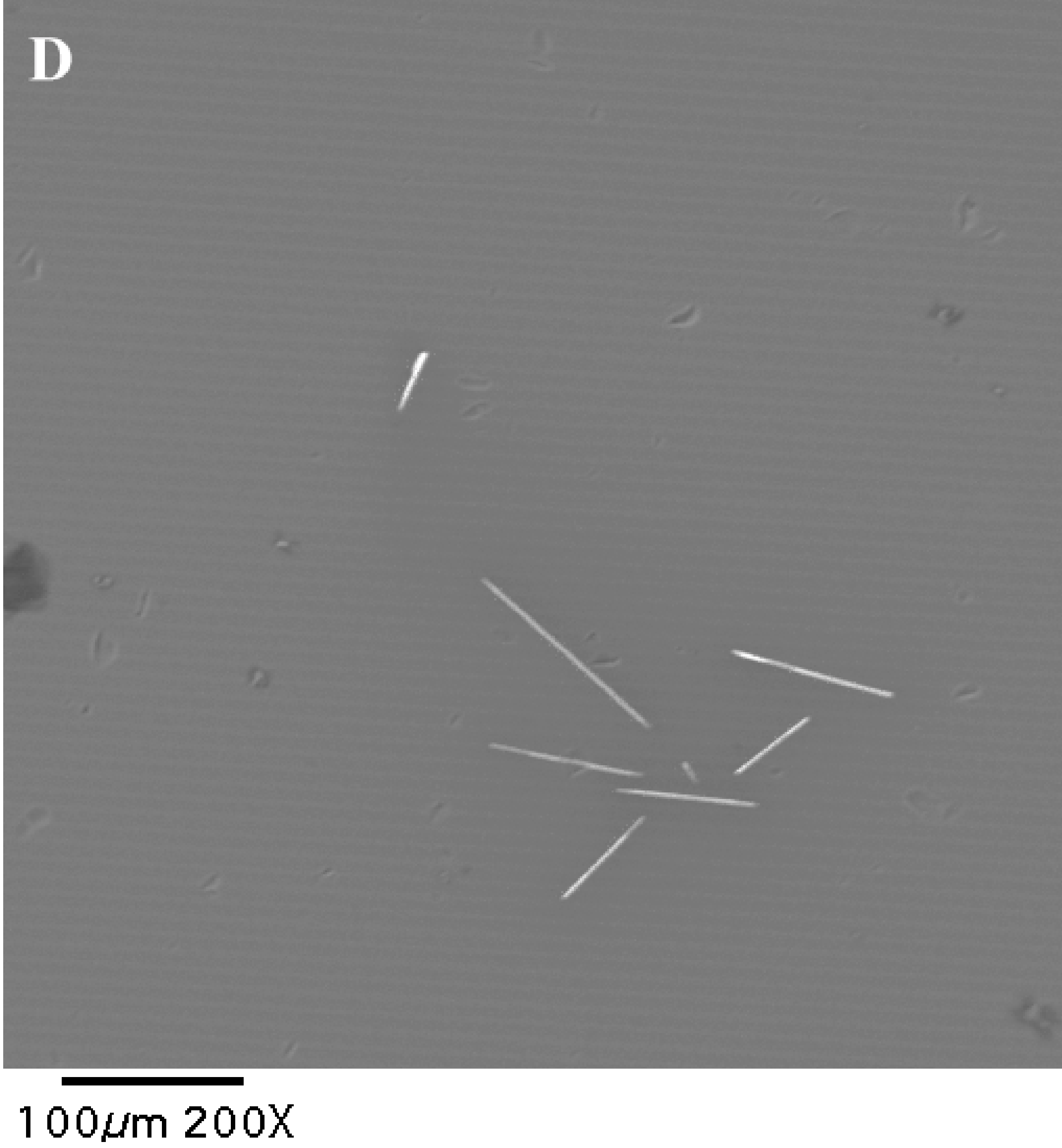
B) Na30Hf35b with euhedral HfO_2 crystals.



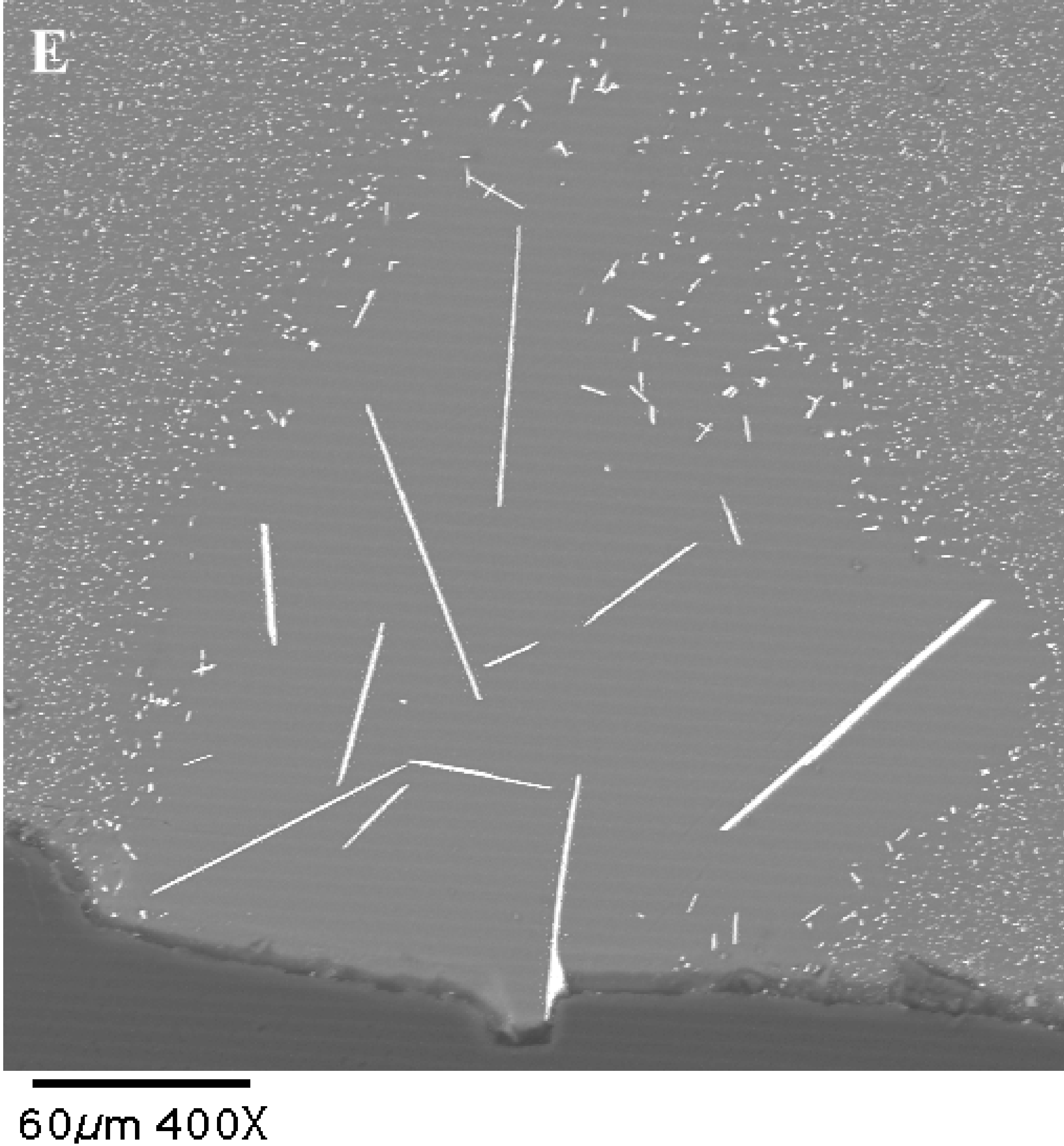
C) Na30Hf35b with HfO_2 crystals surrounding a bubble in the glass.



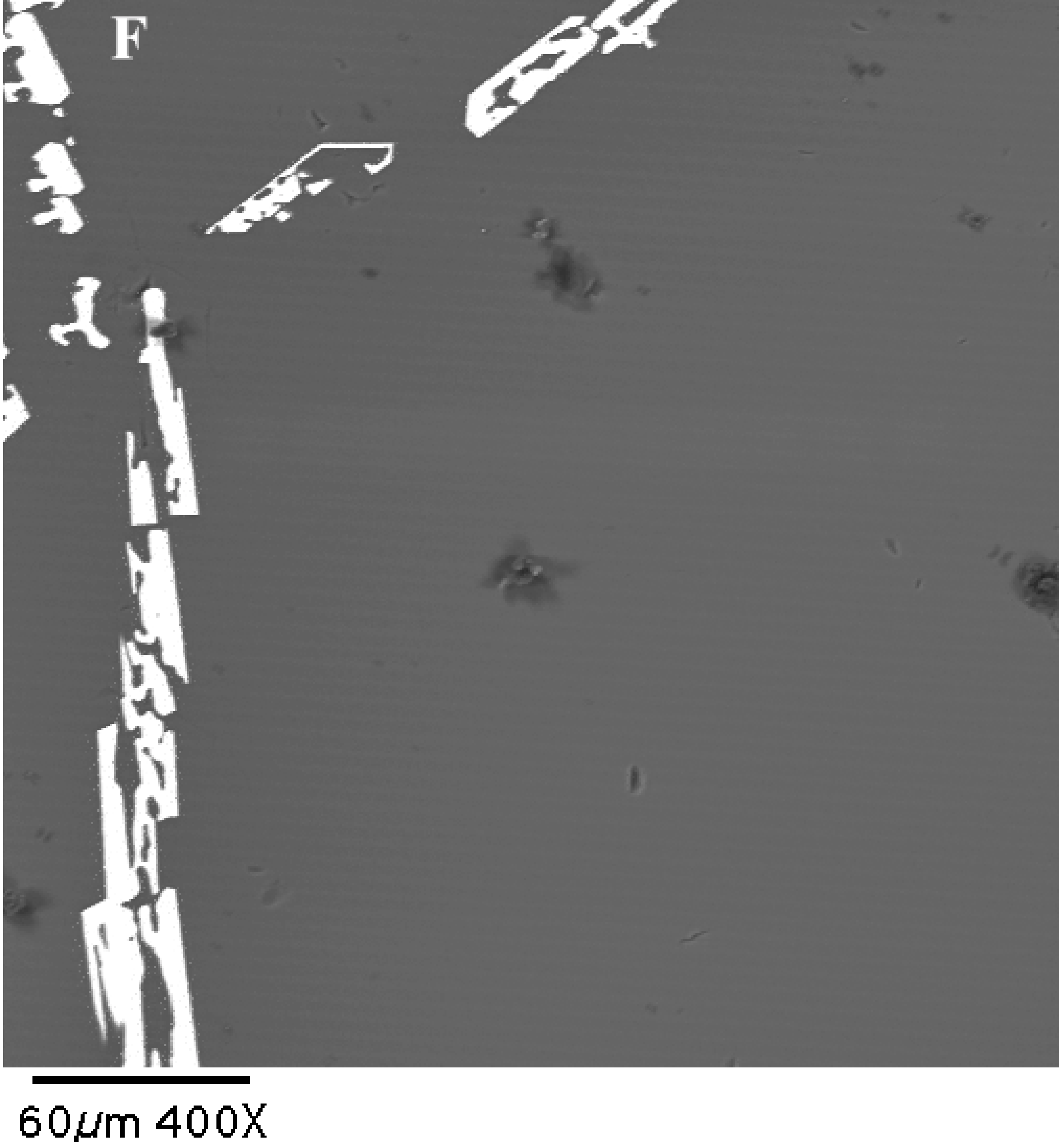
D) PL0.35Hf8a showing the edges of platy HfO_2 crystals (not common).



E) PL0.35Hf8b showing smaller micron-sized, undissolved HfO_2 with overgrowths and edges of larger platy HfO_2 crystals.



F) PL0.85Hf32 with bladed HfO_2 crystals.



Hf-bearing glasses.

- Crystal-free samples (B15Hf30, B15Hf31, Na30Hf30, Na30Hf34 and Na30Hf35a): homogeneous in composition.
- Precipitated crystals: composed of Hf and O; not homogeneously distributed (Na30Hf35); 20 µm (Figure 1B); surrounding a bubble (Figure 1C); elongated, representing the end-on sections of the platy crystals; micron-sized, undissolved HfO_2 with overgrowths (Figure 1E); bladed and large crystals in (Figure 1F).

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Compositions of glass matrix

Homogeneity of glass matrix

- Crystal-free glasses are homogeneous in composition.
- Two domains in B15Gd48: darker upper left area is enriched in Si, Al and Na; the brighter area is rich in Gd (Table II; Figure 2).
- Distributions of Hf across the glass grains showed variations (Figure 3)

Figure 2. Distributions of SiO2 and Gd2O3 in the glass matrix for B15Gd48 that contains precipitated crystals. Low Gd2O3 (31.13 wt %) and high SiO2 (34.04 wt %) spots are in the darker area of the BSE image (the upper left corner of Figure 1A). High Gd2O3 (45.39 wt %) and low SiO2 (28.80 wt %) spots are in the brighter area (the lower right area of Figure 1A)

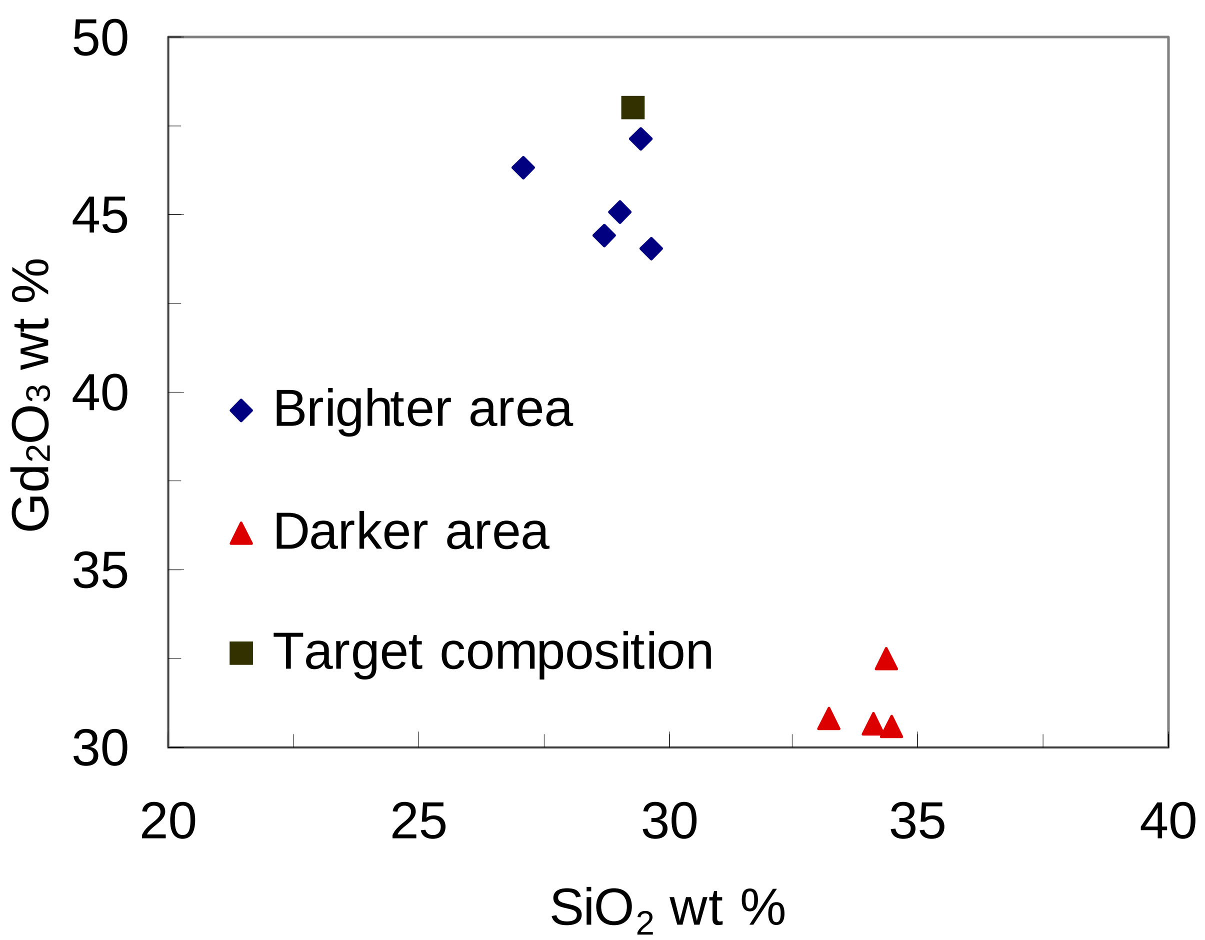

Figure 3. Oxide variations in Hf glass B15Hf31. HfO_2 varies significantly while other oxides remain constant. The profile steps are 20 µm.

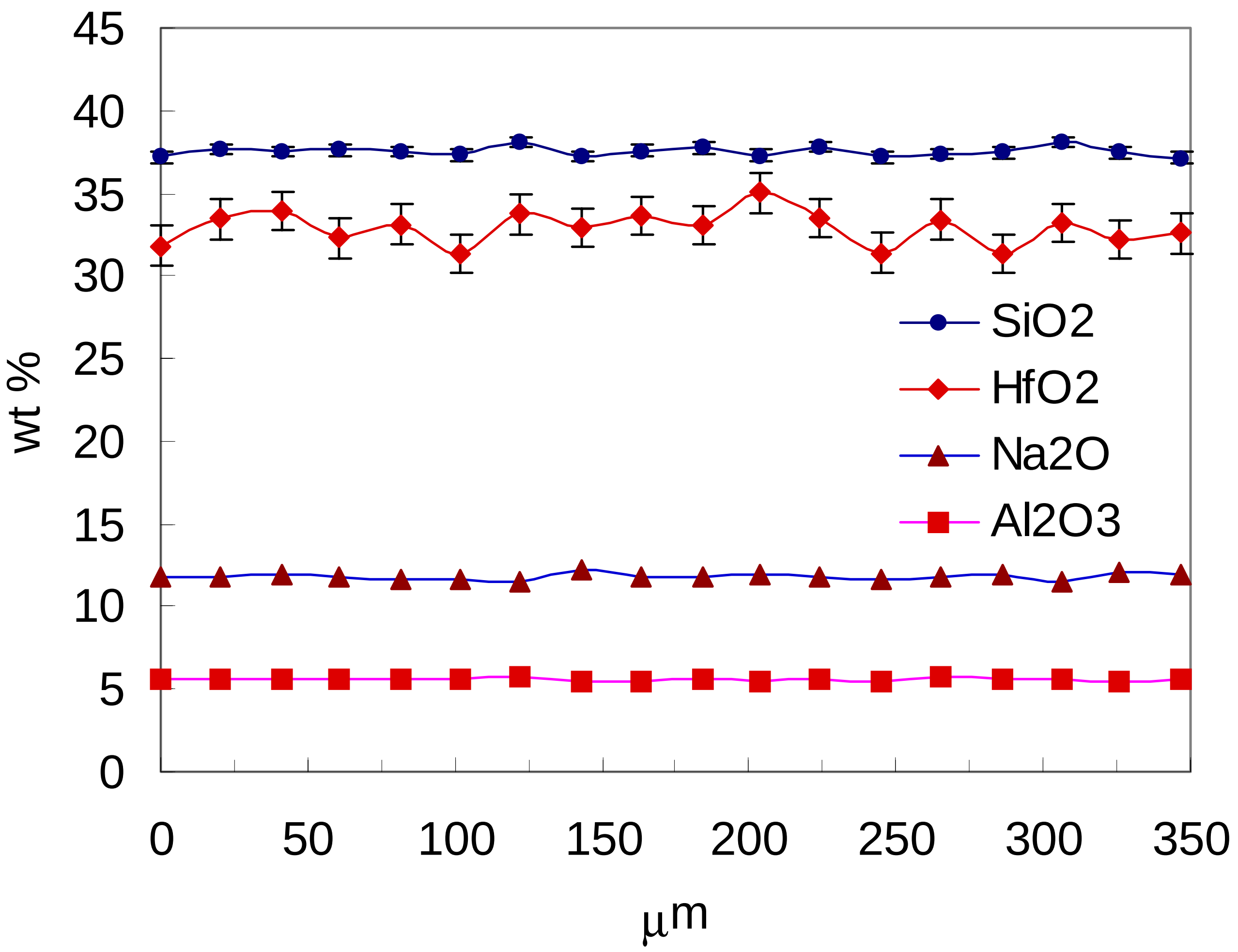

Table II. Electron microprobe analyses (wt %) of Gd and Hf alumino-borosilicate glasses.

Sample	Al15Gd18		B15Gd42		B15Gd48			Na10Gd20		B15Hf30	
Point	Ave (7)	Target	Ave (10)	Target	Ave (5)	Ave (4)	Target	Ave (8)	Target	Ave (33)	Target
SiO_2	38.10	39.84	30.94	32.68	28.80	34.04	29.30	47.72	49.90	37.03	39.44
Al_2O_3	16.31	16.91	4.43	4.62	4.30	5.89	4.14	6.86	7.06	5.54	5.58
Na_2O	12.72	13.70	10.90	11.23	10.75	14.02	10.07	7.49	8.58	12.15	13.56
Gd_2O_3	18.90	18.00	42.57	42.00	45.39	31.13	48.00	20.83	20.00	32.02*	30.00*
B_2O_3	13.97	11.55	11.16	9.47	10.75	14.91	8.49	17.10	14.46	13.26	11.42

* Content of HfO_2.

Table II. Electron microprobe analyses (wt %) of Gd and Hf alumino-borosilicate glasses (continued)

Sample	B15Hf31		Na30Hf30		Na30Hf34		Na30Hf35			PL0.35Hf8		PL0.85Hf32
Point	Ave (35)	Target	Ave (37)	Target	Ave (78)	Target	a Ave (22)	b Ave (41)	Target	a Ave (24)	b Ave (4)	Ave (11)
SiO_2	37.16	38.88	33.67	35.96	30.12	33.90	31.06	30.93	33.39	44.53	47.38	38.75
Al_2O_3	5.53	5.50	5.10	5.08	4.77	4.79	4.73	4.84	4.72	21.53	22.18	6.38
Na_2O	11.66	13.37	17.16	18.54	16.36	17.48	15.74	15.74	17.22	7.21	7.53	11.93
HfO_2	33.05	31.00	32.58	30.00	36.33	34.00	37.79	36.92	35.00	8.40	4.98	29.44
B_2O_3	12.61	11.25	11.49	10.42	12.42	9.83	10.67	11.57	9.67	18.33	17.93	13.50

Differences between target and measured compositions

- For the crystal-free Gd glasses, the measured and the target compositions are essentially the same (Table II).
- For the crystal-containing Gd glass, the differences are significant.
- For Hf glasses without or with a small amount of precipitated HfO2 crystals, the measured compositions are genrally close to the target compositions.
- However, if there are abundant precipitated crystals, the compositions of the glass matrix may vary significantly (Table II).

Compositions of precipitated crystals

- Precipitated crystals in Gd glasses (B15Gd48): a rare earth silicate with the apatite structure $A_{4-x}REE_{6+x}(SiO_4)_{6-y}(PO_4)_y(F,OH,O)_2$ (where A = Li, Na, Mg, Ca, Sr, Ba, Pb and Cd, and REE = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd), $NaGd_9(Si_{5.25}B)O_{26}$.
- For Hf-bearing glasses, the precipitated crystals are HfO_2.

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Conclusions

- Direct measurements of the glass compositions by EMPA demonstrate that glass matrices are homogeneous in chemical composition if there are no or few precipitated crystals. Our EMPA data also show that the measured glass compositions are in general the same as, or close to, the target compositions if there are no or few precipitated crystals.
- Glass samples with crystals that grew from the melt or abundant recrystallized HfO_2 powder are often heterogeneous in chemical composition; and their actual chemical compositions may be significantly different from the target compositions.

Conclusions

- The precipitated crystalline phase identified in a gadolinium alumino-borosilicate glass is a rare earth silicate apatite; and the precipitated crystals identified in hafnium alumino-borosilicate glasses are HfO_2.
- Therefore, electron microprobe data confirm that the solubilities of Gd and Hf in sodium alumino-borosilicate glasses based on the target glass compositions are valid if there are no or few precipitated crystals in glass matrices.

Acknowledgment

This study is supported by the Environmental Management Science Program, US Department of Energy through grant # DE-FG07-97-ER45672. The electron microprobe was acquired under Grant # EAR-82-12764 from the National Science Foundation. Liyu Li and Linda L. Davis are grateful to Associated Western Universities for facilitating their postdoctoral appointments at Pacific Northwest National Laboratory.

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References

1 H. Matzke, J. van Geel, In Disposal of Weapons Plutonium (eds. E.R. Merz and C.E. Walter), Kluwer Academic Publishers, 1996, 93-105.

2 R.C. Ewing, W.J. Weber, W. Lutze, In Disposal of Weapons Plutonium (eds. E.R. Merz and C.E. Walter), Kluwer Academic Publishers, 1996, 65-83.

3 Technical Summary Report for Surplus Weapons-Usable Plutonium Disposition, Report DOE/MD-0003, Office of Fissile Materials Disposition, U.S. Department of Energy, July 17, 1996.

4 L.W. Gray and T.H. Gould, Immobilization Technology Down-Selection Radiation Barrier Approach, Report UCRL-ID-127320, Lawrence Livermore National Laboratory, Livermore, CA, 1997.

5 X. Feng, H. Li, L.L. Davis, L. Li, J.G. Darab, M.J. Schweiger, J.D. Viena, and B.C. Bunker, Distribution and Solubility of Radionuclides in Waste Forms for Distribution of Pu and Spent Nuclear Fuels, Ceramic Transactions, 93, 409-419 (1999).

6 L. Li, D.M. Strachan, H. Li, L.L. Davis, M. Qian, Peraluminous and peralkaline effects on Gd_2O_3 and La_2O_3 solubilities in sodium-alumino-borosilicate glasses, Ceramic Transaction (in press).

7 L. Davis, L. Li, J.G. Darab, H. Li, D. Strachan, P.G. Allen, J.J. Bucher, I.M. Craig, N.M. Edelstein, D.K. Shuh, Scientific Basis for Nuclear Waste Management, XXII, Materials Research Society, Pittsburgh (in press).

8 Donggao Zhao, L.M. Wang, R.C. Ewing, Liyu Li, L.L. Davis, D.M. Strachan, Gd-Apatite Precipitates in a Sodium Gadolinium Alumino-Borosilicate Glass, Journal of Crystal Growth (submitted).