Gd-apatite Precipitates in a Sodium Gadolinium Alumino-borosilicate Glass

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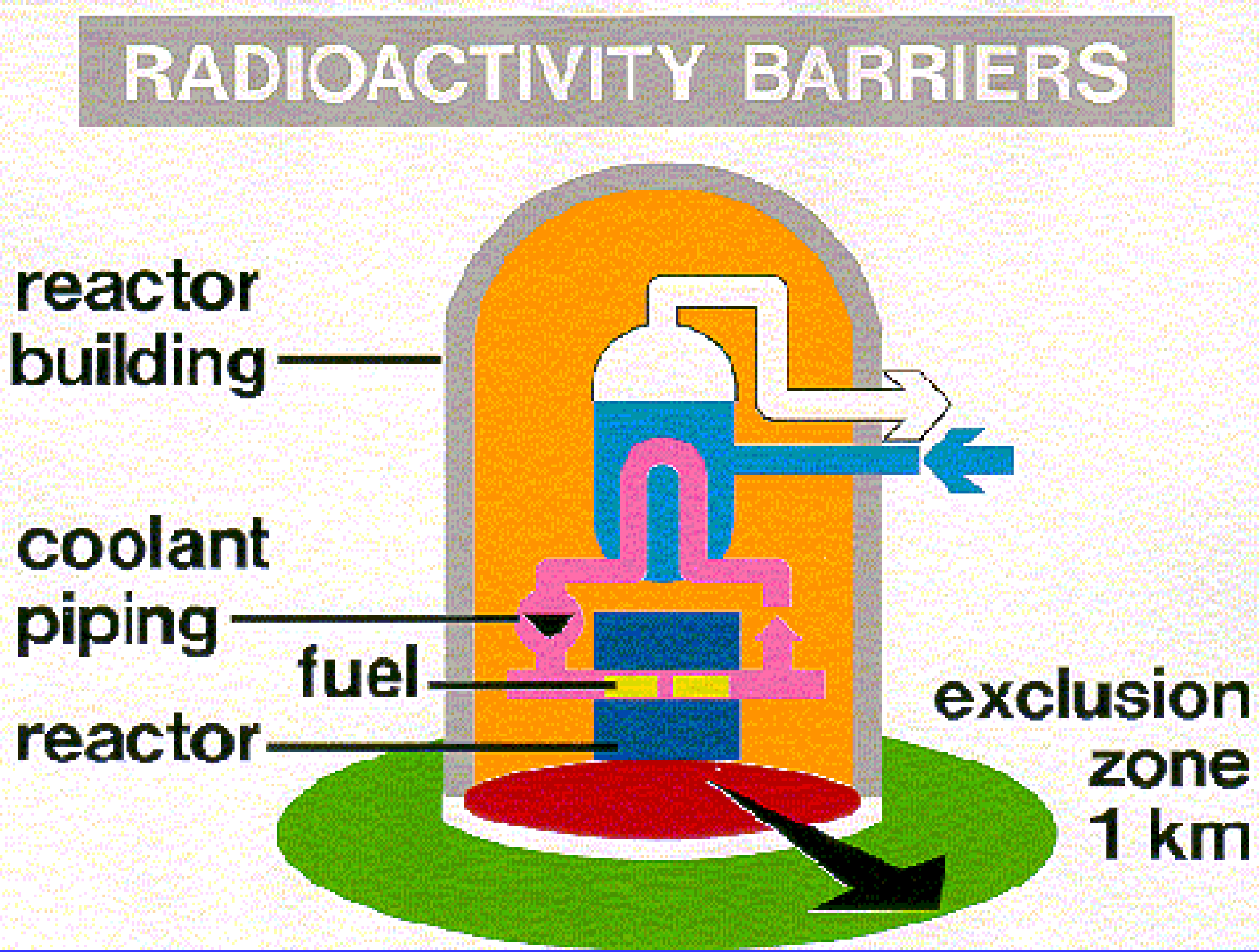
Objectives

- This work is part of a project which determines:
- Distributions and solubility of radionuclides and neutron absorbers in borosilicate glass waste
- Local atomic structure of radionuclides and neutron absorbers in phases;
- Partitioning of key elements, such as Gd;
- Release of radionuclides and neutron absorbers from waste forms

Background: nuclear waste

- Sources of nuclear wastes: mining of uranium, nuclear reactors, nuclear weapons
- In 50 years of producing power and weapons from nuclear fuel, US has accumulated millions of cubic meters and tens of billions of curies of radioactive wastes
- For cleanup of the US weapons complex, the remediation and restoration activities will cost roughly $189 to $265 billions.

Nuclear reactor



Background: borosilicate glass

- Borosilicate glass is waste form for the immobilization of high-level nuclear waste
- Borosilicate glass compositions with neutron absorbers, such as Gd, being developed for the immobilization of actinides, e.g., excess weapons plutonium.
- Gd crystalline precipitates studied comes from such borosilicate glass

Background: silicate apatites

- Durable geologically
- Actinide waste form
- $A_{4-x}REE_{6+x}(SiO_4)_{6-y}(PO_4)_y(F,OH,O)_2$
- where A = Li, Na, Mg, Ca, Sr, Ba, Pb and Cd, and
- REE = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd

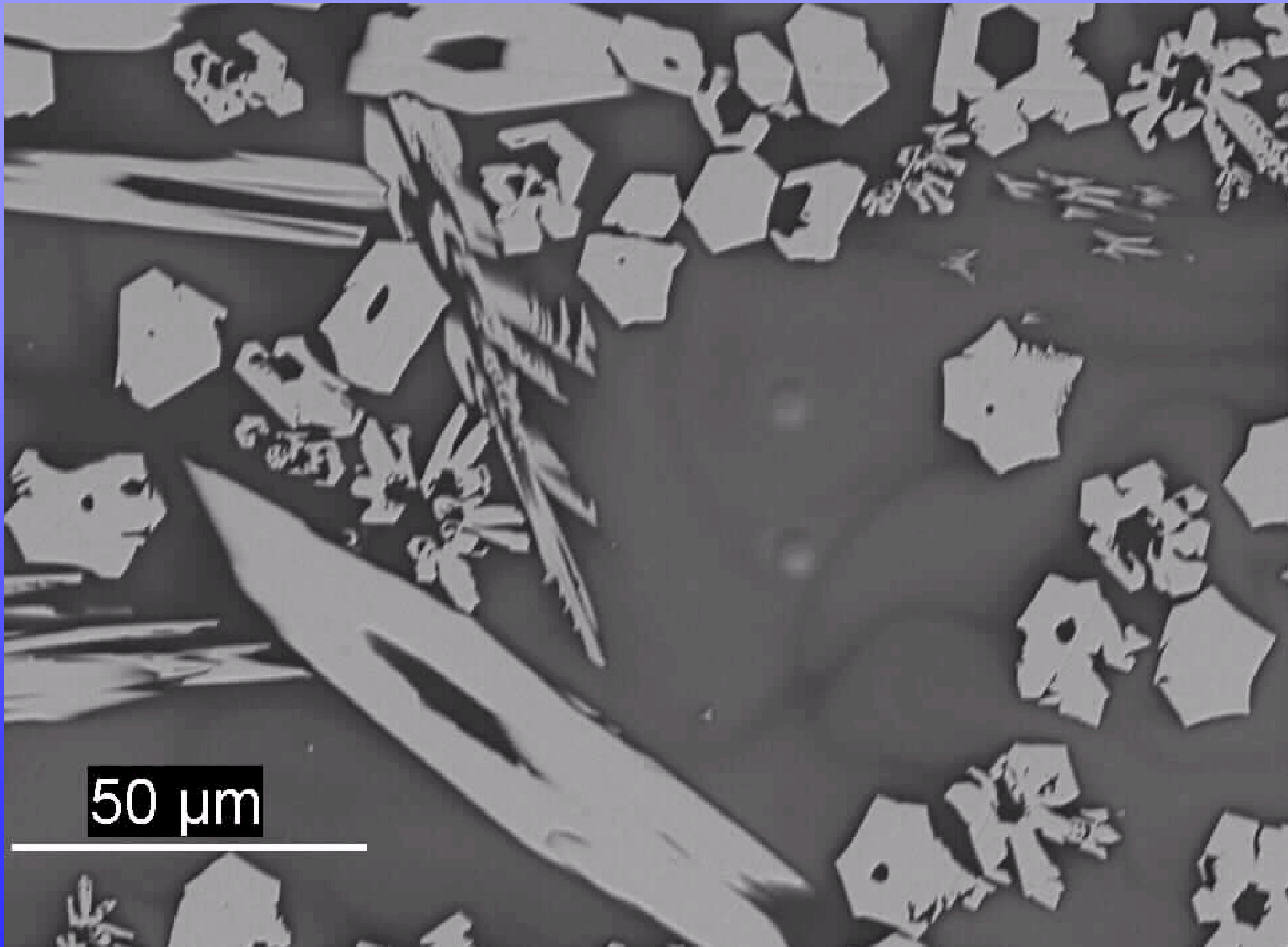
Sample

- Baseline glasses $15B_2O_3$-$20Na_2O$-$5Al_2O_3$-$60SiO_2$ synthesized from SiO_2, Al_2O_3, H_3BO_3 and Na_2CO_3
- Glass compositions: 45.39-31.13 wt % Gd_2O_3, 28.80-34.04 wt % SiO_2, 10.75-14.02 wt % Na_2O, and 4.30-5.89 wt % Al_2O_3
- Crystals precipitated above the Gd solubility limit (11.3 mol %) in a gadolinium alumino-borosilicate glass

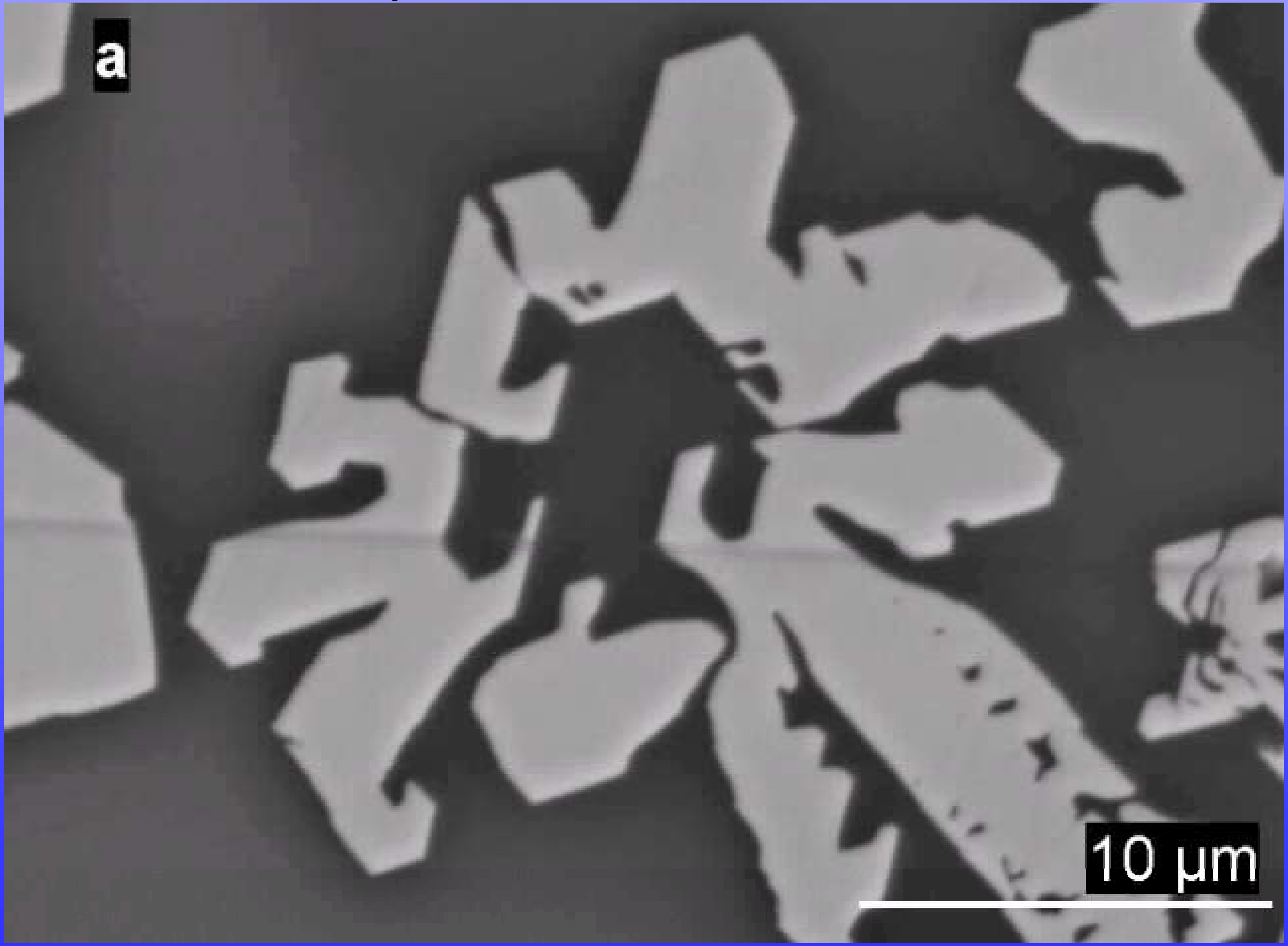
Crystal morphology

- Size: tens of μm, some 200 μm in length
- Shape: elongated, acicular, prismatic, skeletal or dendritic
- Hexagonal: with or without euhedral voids

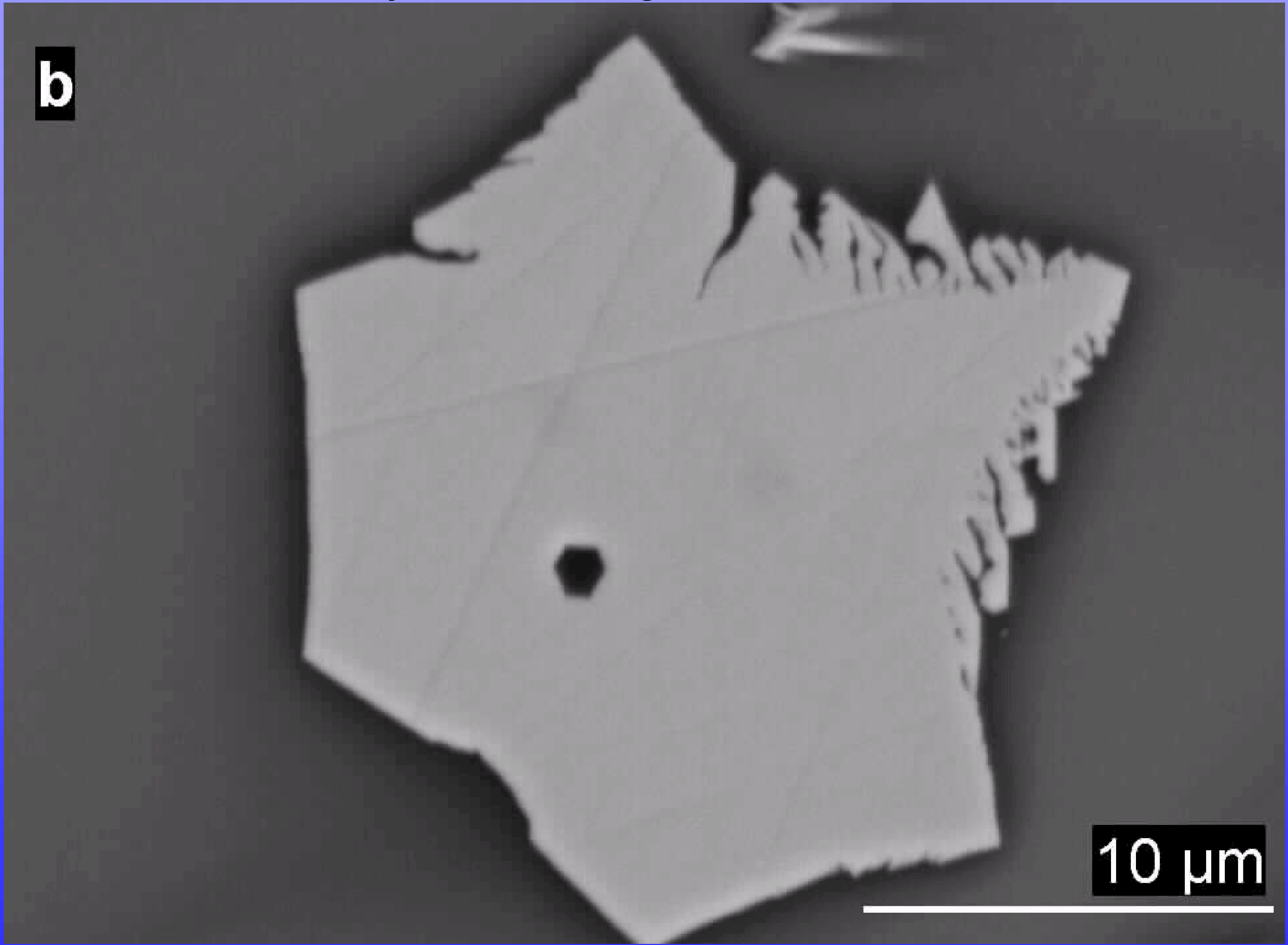
Precipitated crystals tens of μm, some 200 μm



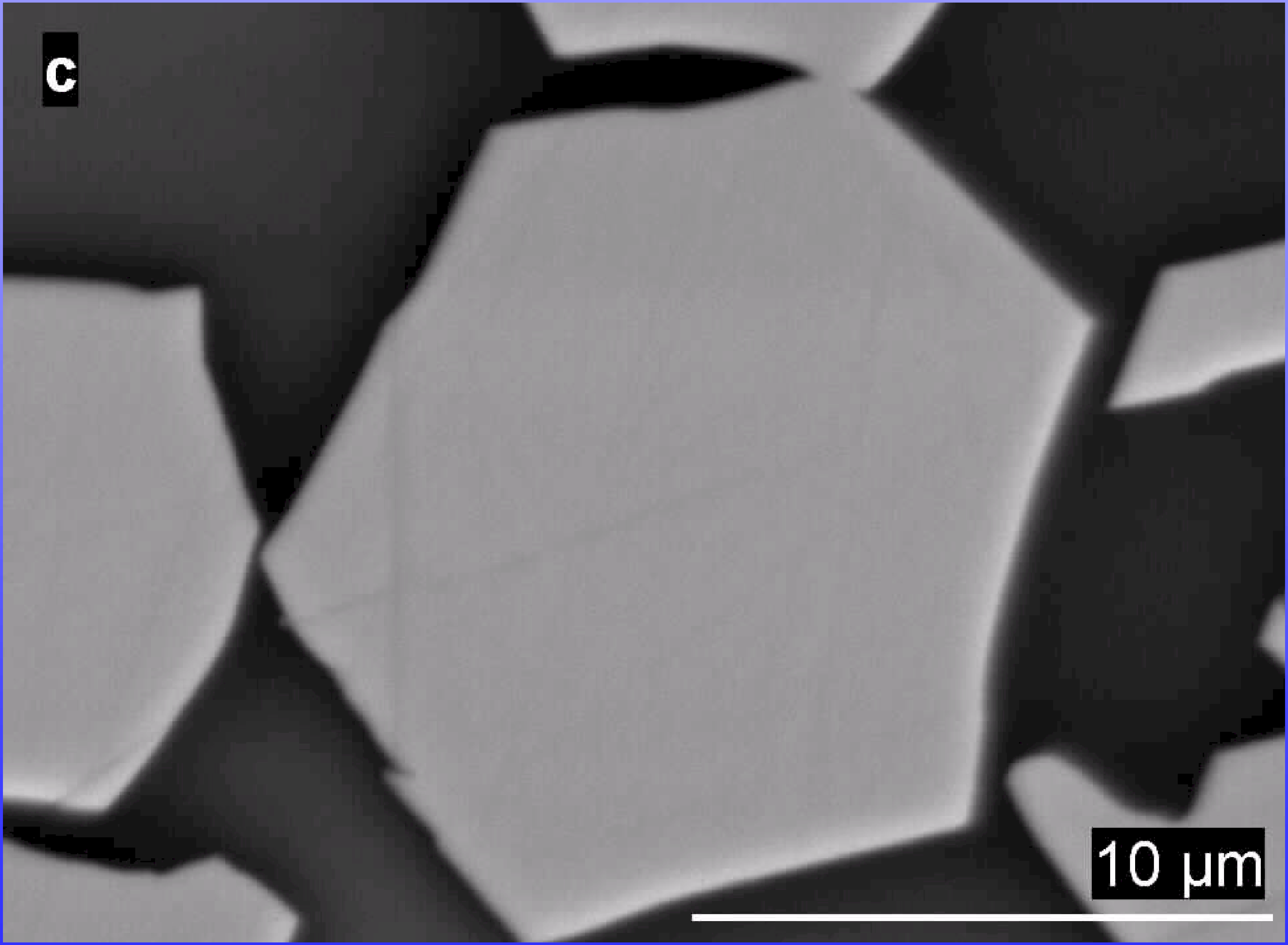
Precipitated crystals: dendritic or skeletal



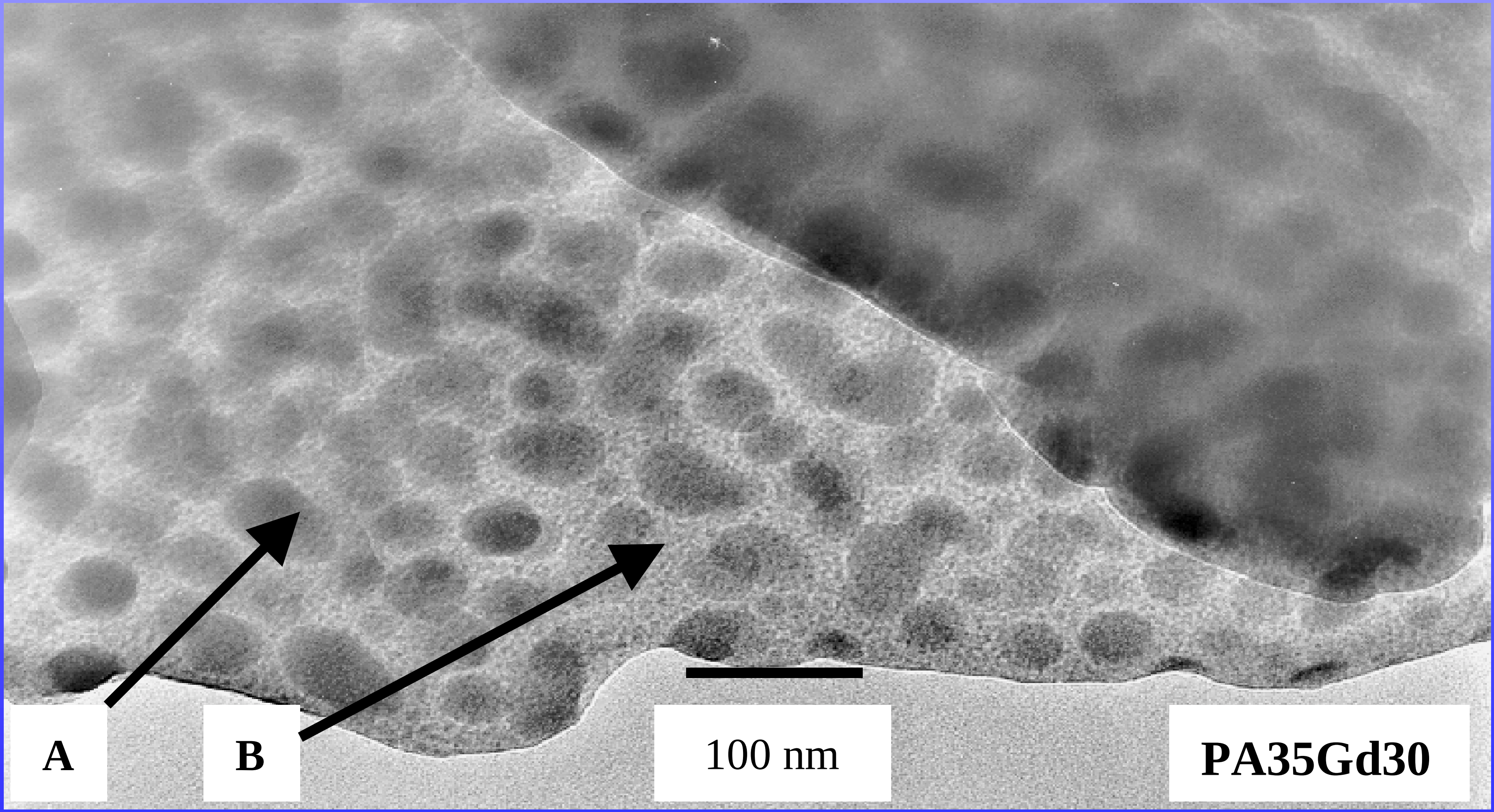
Precipitated crystals: hexagonal with euhedral void



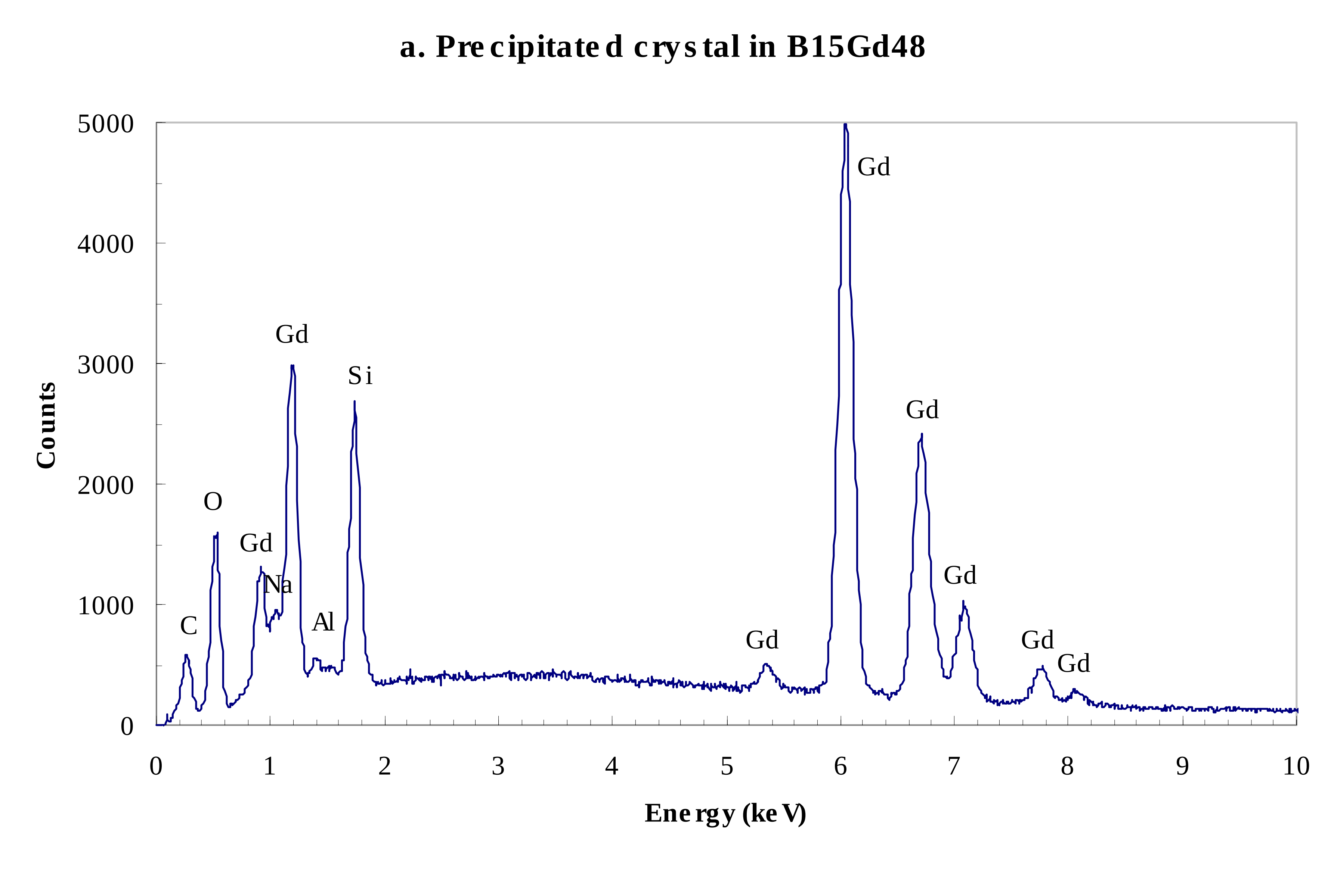
Precipitated crystals: hexagonal with no central void



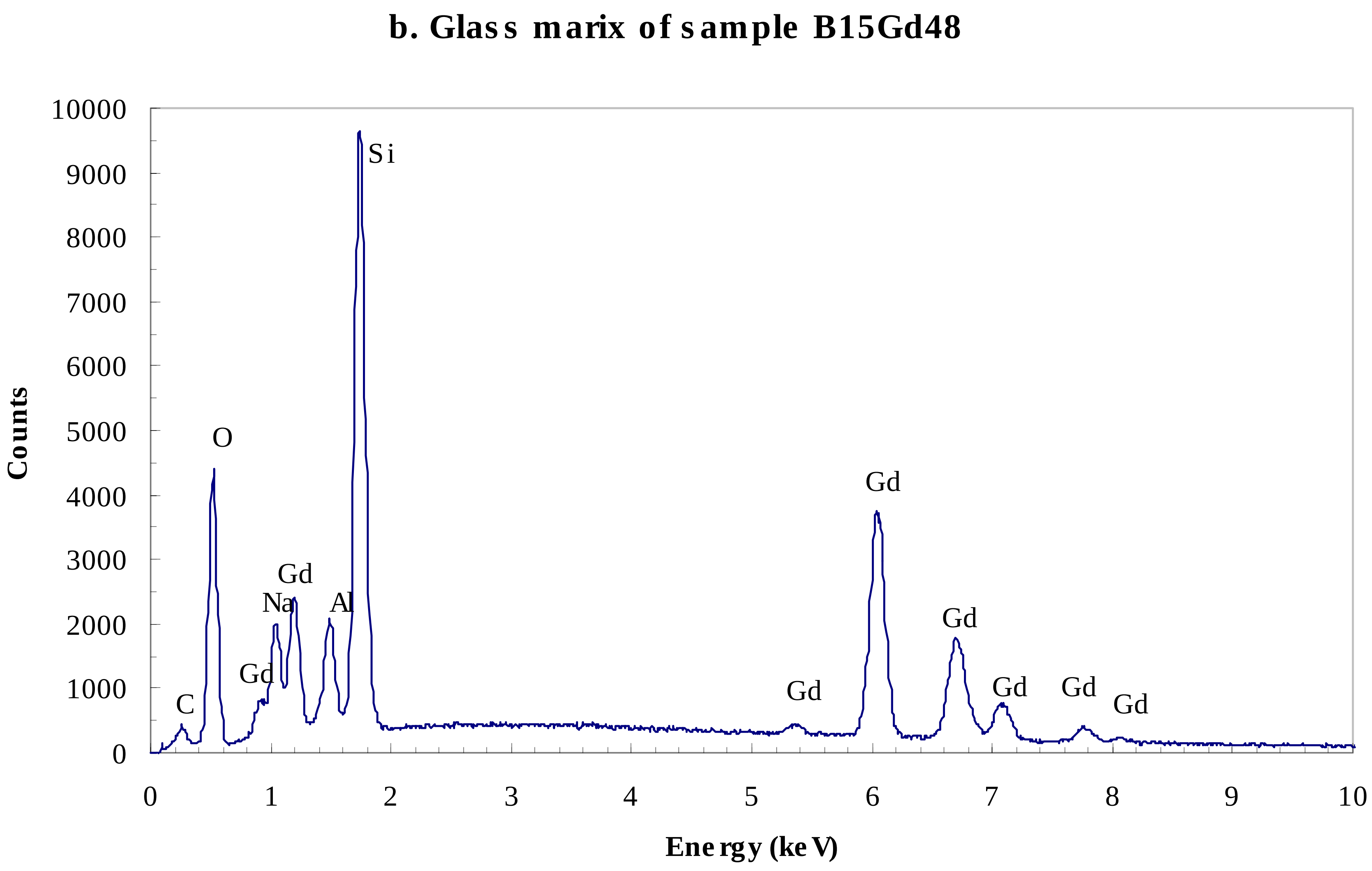
Precipitated phase: TEM



Precipitated crystals: EDS



Glass matrix: EDS



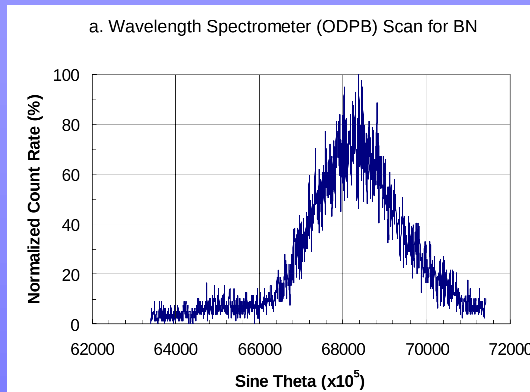
Crystal composition

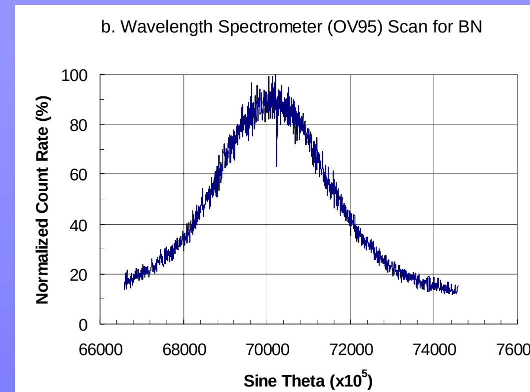
- Boron analysis: Correlation between B-contents and the peak counts (WDS)
- Sodium analysis : same using different electron beam sizes and beam currents
- EMPA: procedures (Table 1), compositions (Table 3)
- Homogeneous: $NaGd_9(Si_{5.25}B)O_{26}$ or $NaGd_9(Si_{6-0.75x}B_x)O_{26})$ when x = 1
- In apatite formula: $NaGd_9(Si_{0.875}B_{0.167}O_4)_6O_2$
- Relative to the glass: enriched in Gd_2O_3 81.25 wt %, depleted in SiO_2 15.66 wt % and Na_2O 1.38 wt %

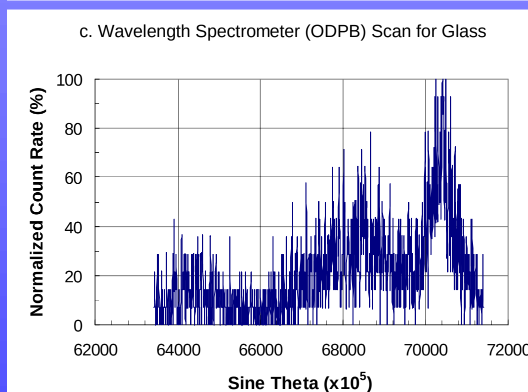
WDS spectra

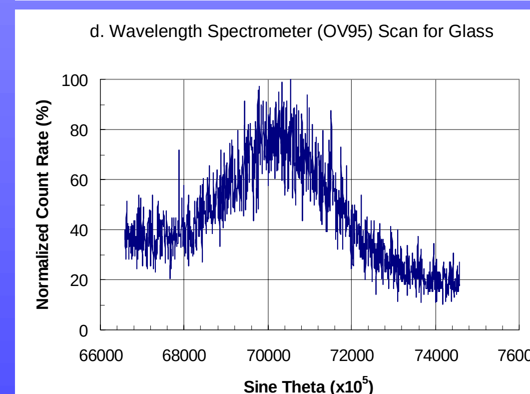
ODPB

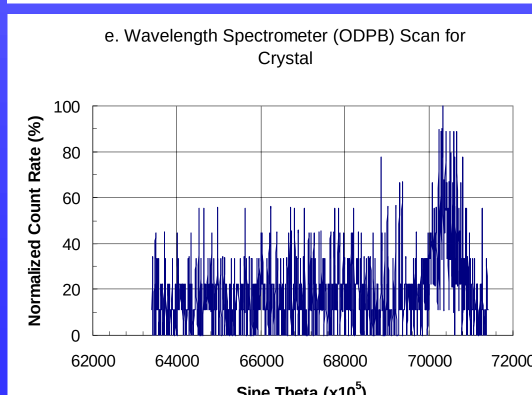
OV95

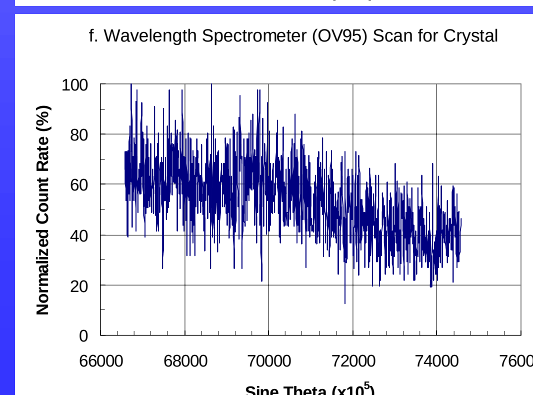




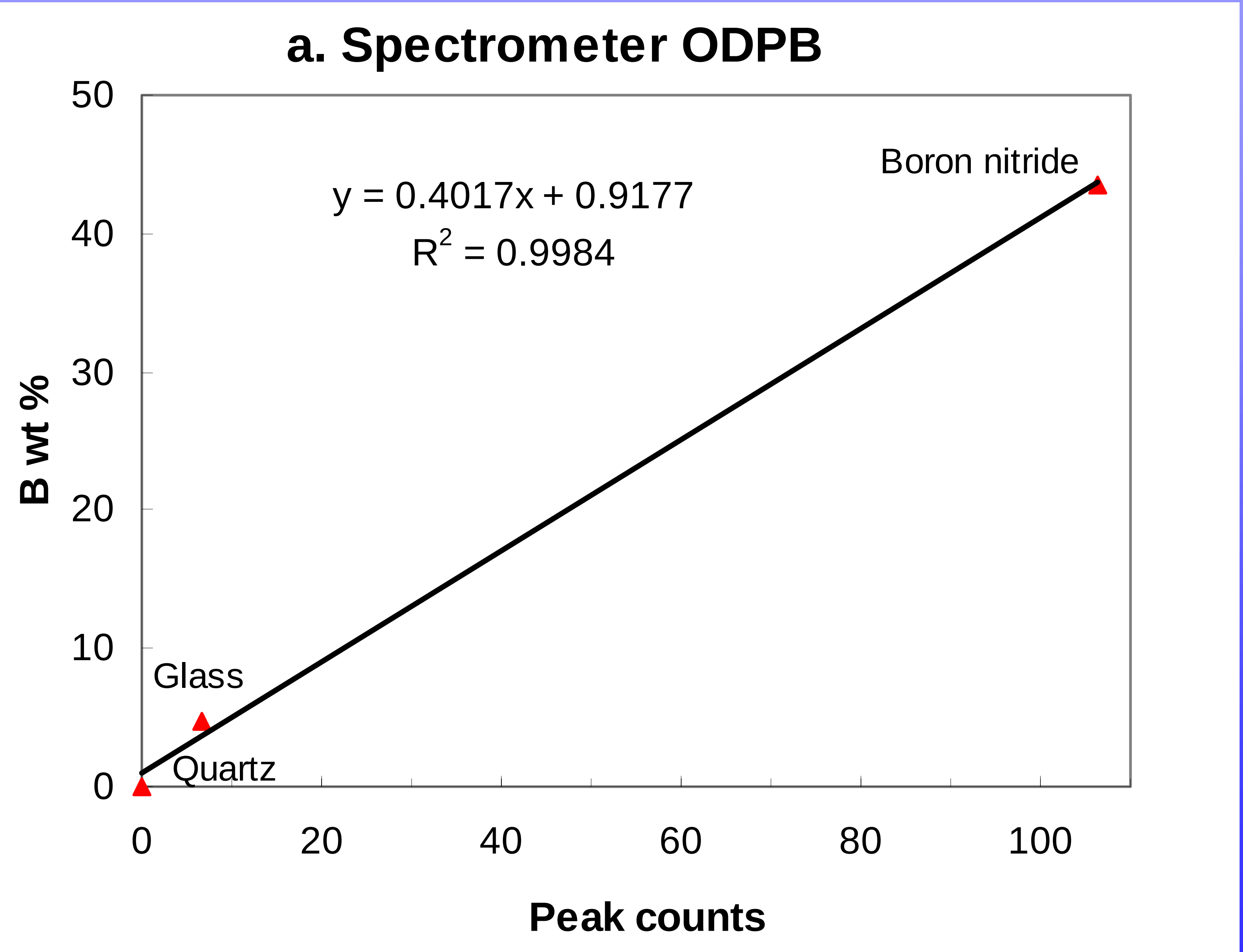




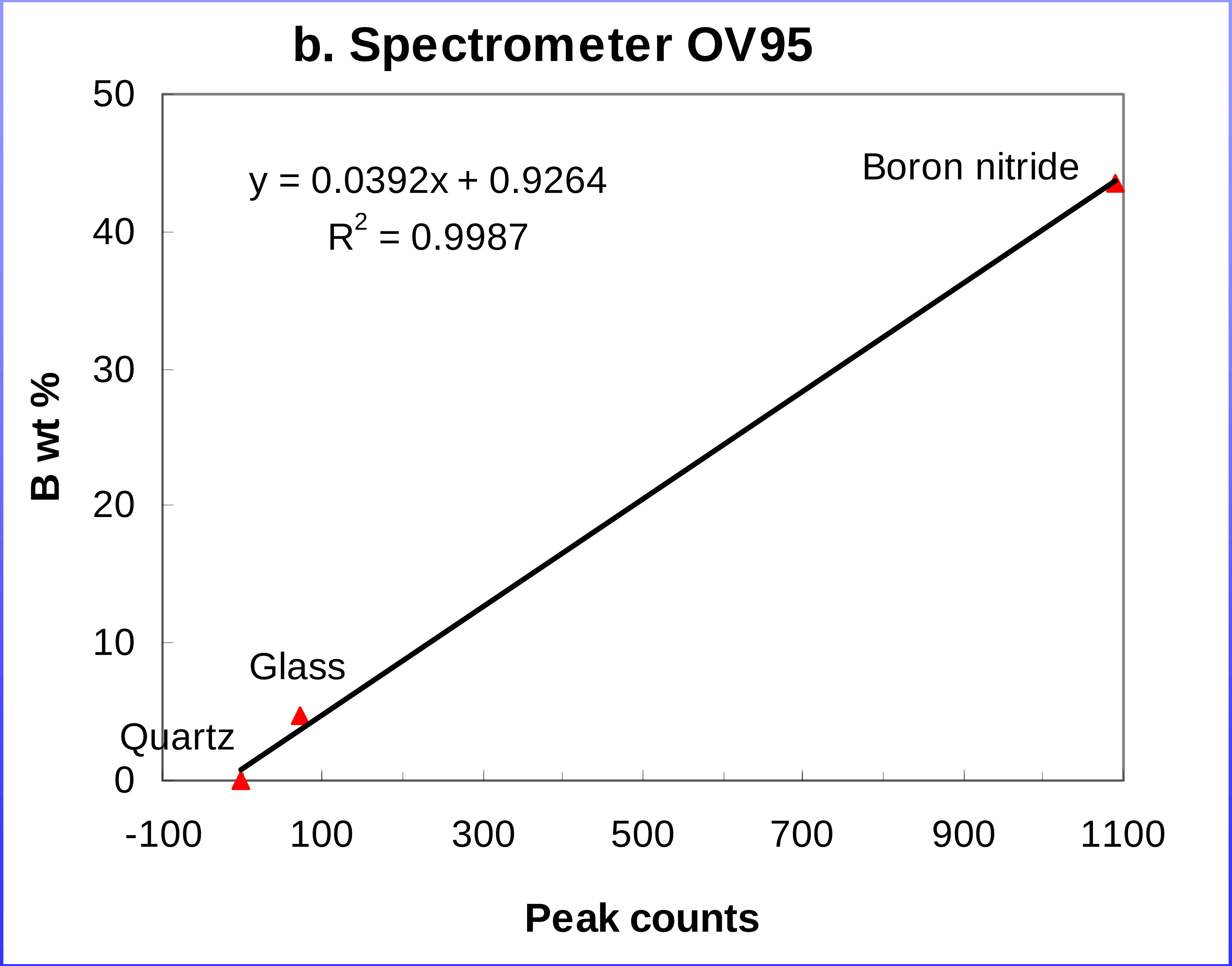




B-contents vs. peak counts



B-contents vs. peak counts



EMPA procedures

Table 1. Electron microprobe analysis procedures for the precipitated sodium gadolinium silicate crystals in a sodium gadolinium alumino-borosilicate glass

Procedure	1a	1b	2a	2b
Accelerating voltage	20.0 kV	20.0 kV	15.0 kV	15.0 kV
Electron beam current	15 nA	15 nA	6 nA	6 nA
Electron beam size	Point mode	3×3 μm	6×6 μm	15×15 μm
Peak counting time	30 seconds	30 seconds	10 seconds	10 seconds
Standard for Si Kα	SiO_2	SiO_2	SiO_2	SiO_2
Standard for Al Kα	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5
Standard for Na Kα	$NaAlSi_2O_6$	$NaAlSi_2O_6$	$NaAlSi_2O_6$	$NaAlSi_2O_6$
Standard for Gd Lα	$GdPO_4$	$GdPO_4$	$GdPO_4$	$GdPO_4$
Standard for O Kα	SiO_2	SiO_2	O not measured	O not measured

EMPA standards

Formula	Detailed composition (weight fraction)
SiO_2	O 0.5330, Si 0.4670
Al_2SiO_5	Al 0.3331, Si 0.1734, O 0.4935
$NaAlSi_2O_6$	Na 0.1128, Al 0.1299, Fe 0.0019, Mn 0.0002, Mg 0.0018, Ca 0.0018, Si 0.2750, K 0.0004, O 0.4707, Ti 0.0001
$GdPO_4$	Gd 0.6234, P 0.1228, O 0.2538

Chemical Composition

	Procedure 1a*												Procedure 1b*		
Point	1	3	4	5	6	7	8	9	10	11	12	Ave.	1	2	Ave.
SiO_2	15.89	15.45	15.62	15.47	15.55	15.62	15.49	15.51	15.57	16.26	15.66	15.64	15.67	15.60	15.63
Al_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.17	0.00	0.02	0.00	0.00	0.00
Na_2O	1.47	1.42	1.40	1.39	1.33	1.36	1.32	1.36	1.33	1.52	1.42	1.39	1.33	1.37	1.35
Gd_2O_3	81.71	80.87	81.13	81.77	81.66	81.09	81.36	81.87	81.95	79.91	81.43	81.34	81.38	81.39	81.38
B_2O_3**	0.93	2.27	1.85	1.38	1.45	1.94	1.83	1.24	1.14	2.14	1.49	1.60	1.63	1.64	1.63
	Normal to 26 O														
Si	5.420	5.125	5.224	5.256	5.268	5.213	5.200	5.286	5.318	5.313	5.284	5.264	5.269	5.252	5.260
Al	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.065	0.000	0.007	0.000	0.000	0.000
Na	0.971	0.911	0.909	0.915	0.876	0.881	0.860	0.900	0.883	0.965	0.926	0.909	0.867	0.893	0.880
Gd	9.237	8.895	8.997	9.212	9.169	8.973	9.055	9.249	9.276	8.657	9.109	9.073	9.074	9.080	9.077
B	0.546	1.301	1.068	0.808	0.848	1.115	1.059	0.729	0.672	1.206	0.870	0.932	0.945	0.954	0.950
Σcation	16.174	16.232	16.198	16.191	16.162	16.183	16.173	16.171	16.150	16.206	16.189	16.185	16.155	16.178	16.166
ΣO	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000

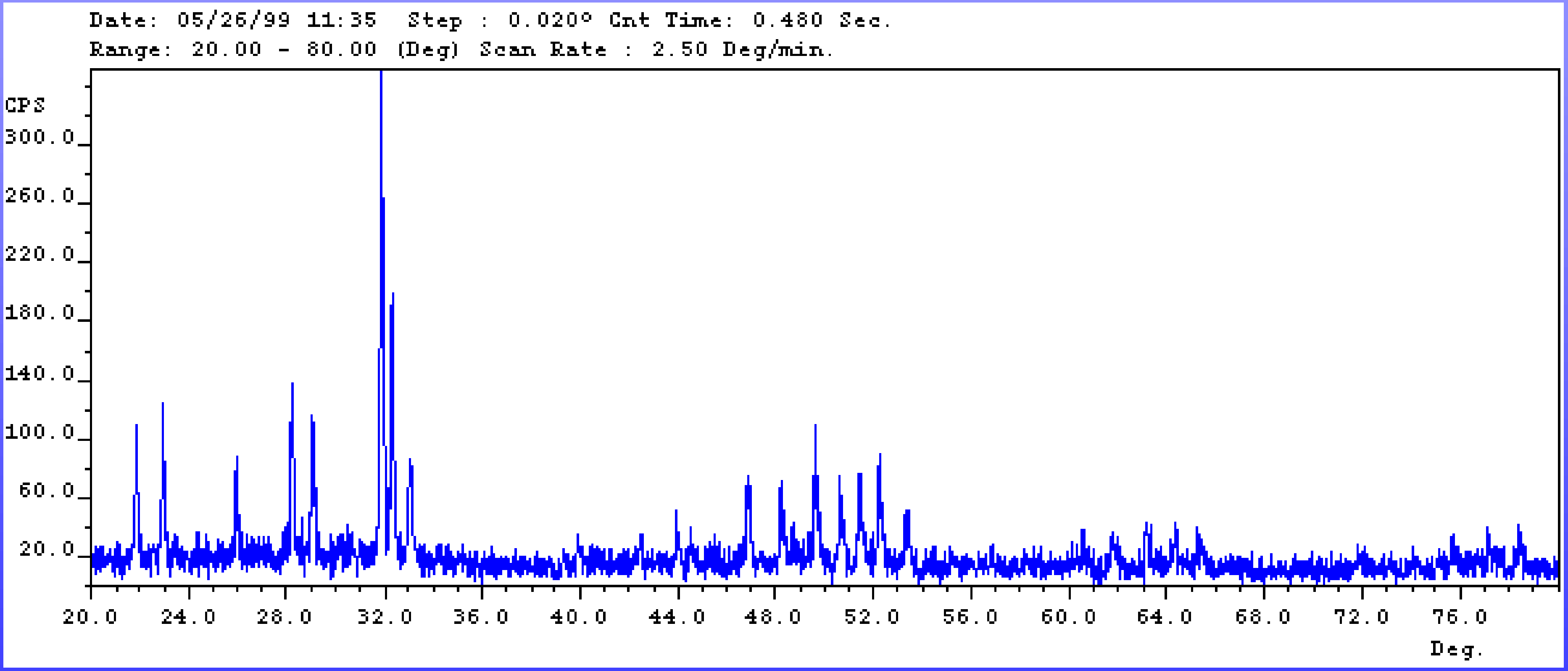
* See Table 2 for the details of each procedure. ** by difference.

	Procedure 2a*											Theoretical
Point	1	2	3	4	5	6	7	8	9	Ave.	Grand ave.	$NaGd_9(Si_{5.25}B)O_{26}$
SiO_2	16.06	16.46	15.79	15.12	15.71	15.39	15.65	15.65	15.27	15.68	15.66	15.67
Al_2O_3	0.03	0.10	0.01	0.01	0.16	0.00	0.05	0.03	0.00	0.04	0.03	0.00
Na_2O	1.37	1.46	1.38	1.25	1.38	1.45	1.45	1.30	1.36	1.38	1.38	1.54
Gd_2O_3	81.04	79.16	81.51	80.10	81.05	81.47	82.50	80.50	82.69	81.11	81.25	81.06
B_2O_3**	1.50	2.82	1.32	3.53	1.70	1.69	0.35	2.52	0.68	1.79	1.68	1.73
	Normal to 26 O											
Si	5.376	5.273	5.339	4.887	5.255	5.192	5.444	5.139	5.311	5.244	5.255	5.250
Al	0.010	0.036	0.002	0.003	0.063	0.000	0.022	0.013	0.001	0.017	0.010	0.000
Na	0.892	0.905	0.903	0.782	0.896	0.951	0.978	0.827	0.919	0.894	0.900	1.000
Gd	8.992	8.404	9.139	8.585	8.985	9.110	9.516	8.764	9.535	8.994	9.041	9.000
B	0.866	1.561	0.772	1.968	0.980	0.983	0.210	1.428	0.410	1.033	0.975	1.000
Σcation	16.136	16.179	16.155	16.225	16.179	16.236	16.170	16.171	16.176	16.181	16.182	16.250
ΣO	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000

Crystal structure

- XRD: similar to that of $LiGd_9Si_6O_{26}$ ($P6_3/m$, **a** = 0.9407 nm and **c** = 0.6842 nm)
- Hexagonal with the apatite structure

Precipitated crystals: XRD



XRD data

1		2	
d space	Intensity	d space	Intensity
4.063	30	4.070	35
3.871	27	3.876	30
3.427	25	3.420	20
3.160	39	3.153	35
3.072	33	3.078	40
2.805	100	2.809	100
2.768	57	2.767	45
2.707	25	2.715	30
2.620	8	2.620	2
2.550	**8**		
2.466	**8**		
2.406	**7**		
2.290	7	2.289	2
2.256	10	2.260	6
2.228	8	2.224	4
2.216	**8**		
2.139	8	2.146	1
2.129	10	2.127	4
2.061	**15**	**2.052**	**10**
2.034	**11**	**2.037**	**6**
1.994	10	1.990	1
1.936	21	1.938	20
1.886	21	1.886	12
1.869	12	1.869	5
1.836	31	1.833	25

1		2	
d space	Intensity	d space	Intensity
1.802	21	1.804	16
1.776	22	1.778	16
1.750	25	1.750	18
1.719	**14**	**1.711**	**8**
1.715	**15**		
		1.630	**4**
1.619	**8**		
1.576	8	1.577	2
1.538	8	1.540	4
1.528	11	1.529	6
1.502	11	1.495	5
1.471	12	1.471	8
1.448	12	1.447	7
1.430	11	1.431	3
1.427	10	1.426	5
1.314	**8**		
1.310	**8**		
1.293	**7**	**1.292**	**3**
1.280	**8**	**1.281**	**3**
		1.262	**2**
1.256	**10**		
		1.250	**4**
1.236	11	1.233	7
1.222	8	1.222	3
1.220	12	1.219	7

1. Sodium gadolinium silicate (B15Gd48); 2. Lithium gadolinium silicate (JCPDS-ICDD # 32-0557).

Conclusions

- Formula: $NaGd_9(Si_{5.25}B)O_{26}$
- Structure: hexagonal apatite structure
- Gd_2O_3–rich (81.25 wt %) phase with apatite structure can be formed from a borosilicate glass
- The precipitated crystals can serve as waste host for weapons Pu and other actinides