

**GADOLINIUM BOROSILICATE GLASS-BONDED
Gd-SILICATE APATITE: A GLASS-CERAMIC
NUCLEAR WASTE FORM FOR ACTINIDES**

Donggao Zhao*, Liyu Li, L.L. Davis**
W.J. Weber**, R.C. Ewing***

***Departments of Nuclear Engineering & Radiological
Sciences and Geological Sciences, University of Michigan
Ann Arbor, Michigan 48109-2104**

****Pacific Northwest National Laboratory
Richland, Washington 99352**



Abstract

A Gd-rich crystalline phase precipitated in a sodium gadolinium aluminoborosilicate glass during synthesis. The glass has a chemical composition of 45.4-31.1 wt % Gd_2O_3 , 28.8-34.0 wt % SiO_2 , 10.8-14.0 wt % Na_2O , 4.3-5.9 wt % Al_2O_3 , and 10.8-14.9 wt % B_2O_3 . Backscattered electron images revealed that the crystals are hexagonal, elongated, acicular, prismatic, skeletal or dendritic, tens of μm in size, some reaching 200 μm in length. Electron microprobe analysis confirmed that the crystals are chemically homogeneous and have a formula of $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ with minor B substitution for Si. The X-ray diffraction pattern of this phase is similar to that of lithium gadolinium silicate apatite. Thus, this hexagonal phase is a rare earth silicate with the apatite structure. We suggest that this Gd-silicate apatite in a Gd-borosilicate glass is a potential glass-ceramic nuclear waste form for actinide disposition. Am, Cm and other actinides can easily occupy the Gd-sites. The potential advantages of this glass-ceramic waste form include: 1) both the glass and apatite can be used to immobilize actinides, 2) silicate apatite is thermodynamically more stable than the glass, 3) borosilicate glass-bonded Gd-silicate apatite is easily fabricated, and 4) Gd is an effective neutron absorber.



Introduction

- Borosilicate glass is the most commonly proposed waste form for HLW. Glasses in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have been developed to determine the effects of changing compositions on the solubilities of the neutron absorber Gd.
- When Gd exceeds its solubility limit in the glass, a Gd-rich crystalline phase may precipitate. The initial purpose of the study was to synthesize a Gd-borosilicate glass and to incorporate as much Gd as possible into the glass. Thus, a Gd-rich crystalline phase in glass was considered undesirable.
- However, the Gd-rich crystalline phase, Gd-silicate apatite may immobilize actinides.



Sample Synthesis

- The baseline glass $15\text{B}_2\text{O}_3 \cdot 20\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 \cdot 60\text{SiO}_2$ (mole %) was synthesized between 1110°C and 1400°C from powders of SiO_2 , Al_2O_3 , H_3BO_3 and Na_2CO_3 .
- The glasses were melted again at 1450°C after adding Gd_2O_3 . The glass melts were quenched by immersion of the base of the crucible in water.
- The resulting products are transparent, colorless sodium gadolinium borosilicate glasses; one of these glasses (B15Gd48) contained an crystalline phase.



Analytical Techniques

- Electron microbeam and X-ray techniques: electron microprobe analysis (EMPA), backscattered electron (BSE) imaging, energy dispersive X-ray spectroscopy (EDS), and X-ray powder diffraction (XRD).
- EMPA procedures: The accelerating voltage was 20 kV; the beam current was 15 nA; and the peak and background counting times were 30 and 15 seconds, respectively. Large beam sizes, lower beam current, and a shorter counting time were used to avoid possible Na migration.
- Standards were SiO_2 for Si, andalusite (Al_2SiO_5) for Al, albite ($\text{NaAlSi}_3\text{O}_8$) or jadeite ($\text{NaAlSi}_2\text{O}_6$) for Na, Gd phosphate (GdPO_4) for Gd, and metallic Hf for Hf. Glass standards were not used due to alkali loss.



Gadolinium Borosilicate Glass - Chemical Heterogeneity

- Two compositional domains (Figs. 1 and 2): 1) darker upper left area enriched in Si, Al and Na and depleted in Gd; 2) brighter region is enriched in Gd.
- Heterogeneous glass compositions: 45.39-31.13 wt % Gd_2O_3 , 28.80-34.04 wt % SiO_2 , 10.75-14.02 wt % Na_2O , 4.30-5.89 wt % Al_2O_3 , and 10.75-14.91 wt % B_2O_3 (Table 1).
- The heterogeneity of the glass may be a result of crystallization that removes Gd from the glass matrix.



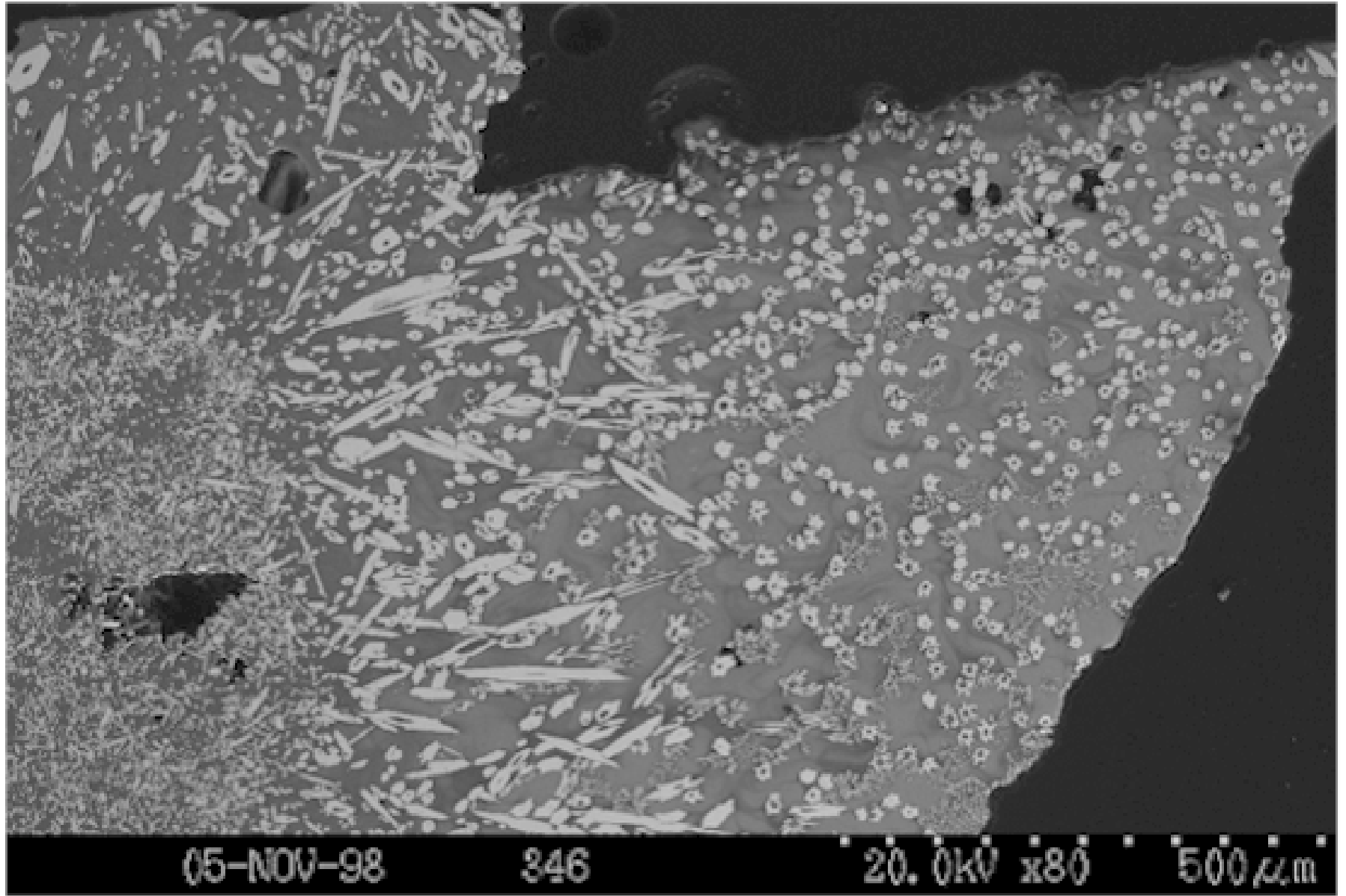


Fig. 1. Backscattered electron images of glass sample B15Gd48 containing the precipitated crystals. Glass matrix in the upper left area slightly darker than the central and lower right areas, indicating chemical heterogeneity of the matrix.

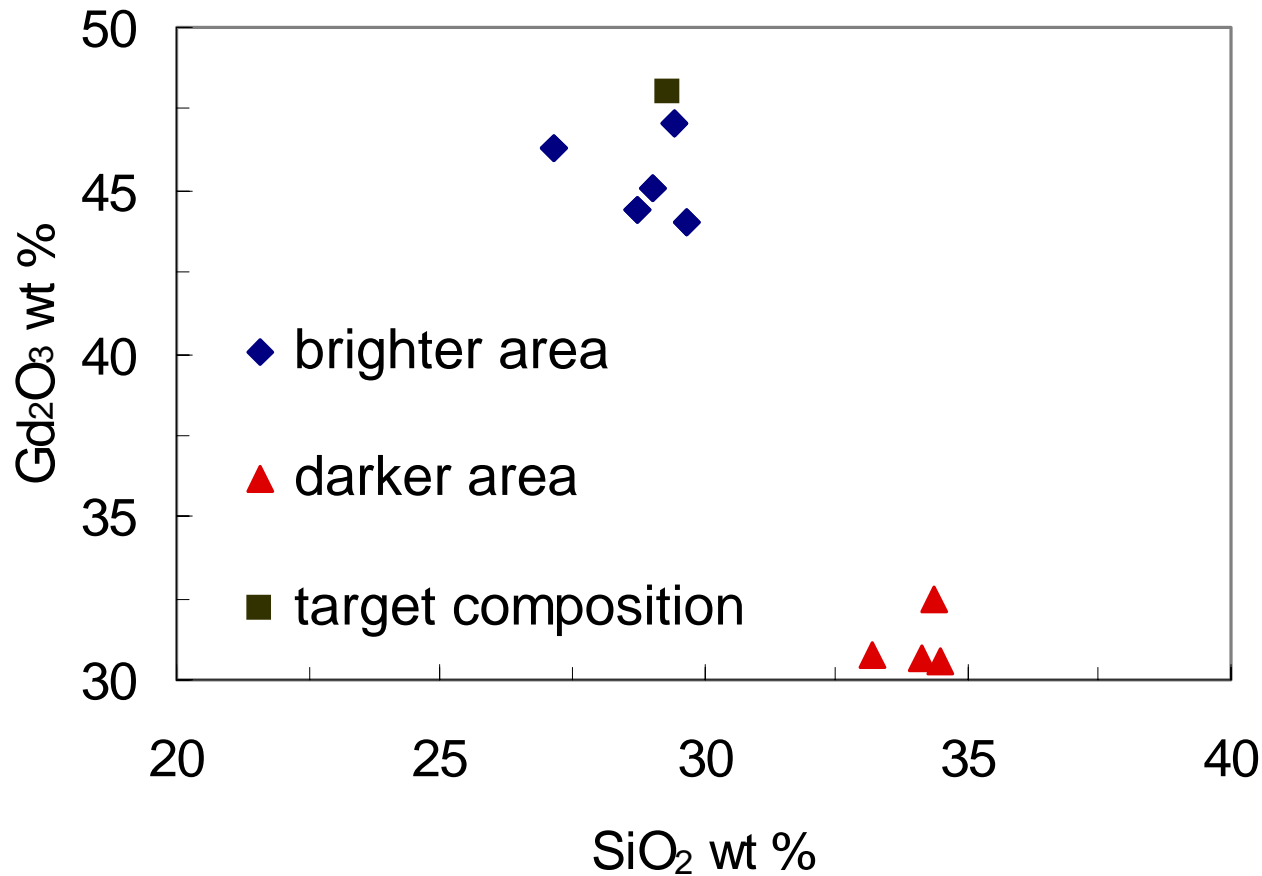


Fig. 2. Distributions of SiO₂ and Gd₂O₃ in the glass for the sample B15Gd48 containing crystals. Low Gd₂O₃ and high SiO₂ spots are from the darker area of the BSE image (the upper left corner of Fig. 1). High Gd₂O₃ and low SiO₂ spots are from the brighter area (the lower right area of Fig. 1)

Table 1. Target and measured compositions (wt %) of the glass host and measured composition of the precipitated Gd-silicate apatite in sample B15Gd48

	<i>target</i>	<i>bright glass domain</i>	<i>dark glass domain</i>	<i>crystal</i>
<i>Average</i>		5 analyses	4 analyses	22 analyses
<i>SiO₂</i>	29.30	28.8±0.3	34.0±0.3	15.7±0.2
<i>Al₂O₃</i>	4.14	4.3±0.1	5.9±0.1	0.0
<i>Na₂O</i>	10.07	10.8±0.2	14.0±0.3	1.4±0.1
<i>Gd₂O₃</i>	48.00	45.4±1.4	31.1±1.1	81.6±2.0
<i>B₂O₃</i>	8.49	10.8	14.9	1.7

Note: 1 σ analytical errors from counting statistics given for measured compositions; B₂O₃ by difference.

Gadolinium Borosilicate Glass

- Differences from the Target Composition

- Differences between the target and the measured compositions are significant.
- The glass matrix has 31.13 wt % Gd_2O_3 in the darker areas and 45.39 wt % Gd_2O_3 in the brighter areas, both different from the target composition of 48.00 wt % Gd_2O_3 .
- The composition of the brighter areas is closest to the target composition (Table 1).



Gd-silicate Apatite - Morphology

- The Gd-silicate crystals: elongated, acicular, skeletal, prismatic or dendritic .
- Most crystals are tens of μm in size, but some up to $200 \mu\text{m}$ in length (Fig. 3) .
- Cross-sections of the crystals are often hexagonal, sometimes skeletal with hexagonal euhedral voids at their centers.





Fig. 3. Enlarged image of the central area in Fig. 1. The Gd-silicate apatite crystals are elongated, acicular, prismatic or dendritic; cross-sections are often hexagonal. The average size is tens of μm , but some crystals are up to 200 μm in length.

Gd-silicate Apatite - Composition

- EMPA from three analytical sessions were the same; Na₂O contents of the crystals were the same when using different electron beam sizes (from a point beam to a 15 × 15 μm rastered beam), indicating that alkali, i.e., sodium, loss is not significant.
- The mean and standard deviations of 22 analyses are: SiO₂ 15.66 ± 0.30 wt %, Gd₂O₃ 81.25 ± 0.81 wt %, and Na₂O 1.38 ± 0.06 wt %.
- The crystals of different shapes have the same composition, and each crystal is chemically homogeneous.



Gd-silicate Apatite - Structure

- The powder X-ray diffraction pattern of the precipitated crystals can be indexed in the hexagonal system and is similar to that of lithium gadolinium silicate $\text{LiGd}_9\text{Si}_6\text{O}_{26}$, a rare earth silicate apatite.
- The $\text{LiGd}_9\text{Si}_6\text{O}_{26}$ has space group $P6_3/m$ or $P6_3$, and cell parameters $a = 0.9407$ nm and $c = 0.6842$ nm based on powder and single-crystal X-ray examination.
- The chemical and structural examinations demonstrate that the precipitated crystalline phase is a rare earth silicate apatite, belonging to the mixed-cation oxyapatite group.



Gd-silicate Apatite - Formula

- The chemical formula of this phase based on EMPA is approximately $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ or $\text{NaGd}_9\text{Si}_6\text{O}_{26}$, which has the same idea formula as $\text{LiGd}_9\text{Si}_6\text{O}_{26}$. Some minor B may substitute for Si in the structure.
- If Si substitutes P in apatite, the Ca apatite $\text{Ca}_4\text{Ca}_6(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2$ can be given as $\text{A}_{4-x}(\text{REE})_{6+x}(\text{SiO}_4)_{6-y}(\text{PO}_4)_y(\text{F},\text{OH},\text{O})_2$, where A (4f site), which can be Li, Na, Mg, Ca, Sr, Ba, Pb or Cd, is coordinated by nine silicate oxygens, and REE (three 4f and six 6h sites) are 4f transition lanthanides in nine-fold (4f site) or seven-fold (6h site) coordination.
- If Si substitutes for all of the P in apatite, the formula can be rewritten as $\text{A}(\text{REE})_9(\text{SiO}_4)_6\text{O}_2$.



Radiation Stability of Silicate Apatite -Significance

- One of the primary concerns with crystalline Gd-silicate apatite as an actinide waste form is radiation stability, i.e., its susceptibility to radiation-induced amorphization caused by α -decay of actinides.
- Radiation damage of nuclear waste forms can result in significant changes in volume, leach rate, stored energy, structure and mechanical properties.



Radiation Stability of Silicate Apatite - Previous Studies

- Weber et al. (1979) have demonstrated that self-radiation damage of ^{244}Cm -bearing $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$ from the decay of the ^{244}Cm resulted in the transformation to the amorphous state, which further resulted in microcracking of the glass due to volume expansion of the damaged crystals.
- Radiation instability of $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$ and other silicate apatites suggests that $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ will also be sensitive to radiation-induced amorphization although radiation damage of this specific silicate apatite has not yet been studied.



Radiation Stability of Silicate Apatite - Further Study

- While the crystalline phase $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ is probably sensitive to radiation-induced amorphization, further work is required to characterize the temperature dependence (kinetics) of radiation damage for this composition, because the kinetics of the radiation damage and annealing processes are known to be composition dependent.
- Weber et al. (1997) showed that amorphization may not occur under repository conditions for some apatite compositions because the recovery kinetics are sufficiently rapid at room temperature. If this can be shown to be the case for $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$, then self-radiation damage should not be an important issue.



Gd-silicate Apatite

- Substitution Mechanism

- The apatite structure is known to be tolerant of charge-coupled cation and anion substitutions (Fleet and Pan, 1995), as well as to cation, and probably, also anion deficiencies.
- Incorporation of Pu and other actinides into the apatite structure is feasible.
- Am^{3+} , Cm^{3+} , and Pu^{3+} readily enter the sites occupied by Gd because they have the same valence as Gd; thus these actinides could be highly concentrated in the REE silicate apatite.



Gd-silicate Apatite

- Substitution Mechanism

- Actinides with 4+ valence (Th^{4+} , U^{4+} and Pu^{4+}) could also enter the apatite structure by coupled substitution mechanisms:
$$2 \text{ REE}^{3+} = (\text{Th}, \text{U}, \text{Pu})^{4+} + \text{Ca}^{2+} \text{ (Forster, 1998) or}$$
$$3 \text{ REE}^{3+} = \text{Na}^{+} + 2 \text{ Pu}^{4+}.$$
- However, Pu^{4+} in a glass does not readily substitute for Gd during the crystallization of Gd-silicate apatite (Weber et al., 1982). Only trace amount of Pu^{4+} are accommodated.
- Studies of partitioning and charge balance constraints are needed in order to determine for which conditions and glass compositions Pu^{4+} will be readily incorporated into apatite.



Gd-silicate Apatite

- Substitution Examples

- Bros et al. (1996) have demonstrated that Pu and fissionogenic REE occur in the hydrothermal apatites from a natural nuclear reactor at the Oklo uranium deposit, Gabon. ^{239}Pu , produced by ^{238}U epithermal neutron capture, was trapped in the apatite structure during the nuclear reactions or soon after the end of the reactions.
- The theoretical study of Meis et al. (2000) have shown that both Pu^{3+} and Pu^{4+} substitute for Nd. Therefore, the Gd-silicate apatite may be a potential actinide waste form.



Glass-Ceramic Waste Form - Types

- Glass-ceramics have been proposed as nuclear waste form.
- Glass-ceramic form waste: barium aluminosilicate glass-ceramics, barium titanium silicate glass-ceramics, calcium magnesium silicate glass-ceramics (Lutze et al., 1979), calcium titanium silicate glass-ceramics (Hayward, 1988), phosphate apatite-based glass-ceramics (Bart et al., 1997), and glass-bonded sodalite (Morss et al., 1999).



Glass-Ceramic Waste Form - Advantages

- All glasses are thermodynamically unstable with respect to crystalline phases.
- Glass-ceramic waste forms are designed to solve the potential problem of devitrification of glass by producing a ceramic phase in a glass matrix to act as durable host for radionuclide.
- Glass-ceramic waste forms offer a useful compromise between glasses and crystalline ceramics because they are easier and less expensive to prepare than conventional ceramics and have a higher durability than the glass.



Gd-Borosilicate Glass-Bonded Gd-Silicate Apatite - a Glass-Ceramic Waste Form for Actinides

- As a more stable phase than glass and with an ability to incorporate actinides, $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ may be a good actinide waste form.
- Phosphorus-free silicate apatite, $\text{A}(\text{REE})_9(\text{SiO}_4)_6\text{O}_2$, has not previously been considered as an actinide waste form, especially as a component of a borosilicate glass.
- We suggest that Gd-borosilicate glass-bonded Gd-silicate apatite is a potential glass-ceramic waste form for actinides.



Gd-Borosilicate Glass-Bonded Gd-Silicate Apatite - Advantages as a Glass-Ceramic Waste Form

- Both the glass matrix and crystalline apatite precipitates incorporate actinides.
- Gd-silicate apatite precipitates are generally more durable than the glass host, thus increasing the overall durability of the waste form.
- Gd-silicate apatite has higher thermal stability than the borosilicate glass.
- Glass-ceramic waste forms may be more tolerant of compositional variations during processing than are corresponding crystalline ceramics prepared by conventional routines.



Conclusions

- A Gd-rich crystalline silicate apatite phase, $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$, precipitates from a Gd-borosilicate glass when the Gd exceeds its solubility limit (11.3 mol %).
- Due to its thermodynamic stability, enrichment in Gd_2O_3 , and tolerance to cation and anion substitutions and deficiencies, $\text{NaGd}_9(\text{SiO}_4)_6\text{O}_2$ is a potential actinide waste form. Thus, Gd-silicate combined with Gd-borosilicate glass are a potential glass-ceramic waste form for actinides.
- Radiation effects in this apatite caused by α -decay of actinides have not yet been studied, and this composition may be sensitive to radiation-induced amorphization, based on studies of other silicate apatites. However, recovery kinetics may be such as to prevent amorphization under repository conditions.



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