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of Nuclear-Waste Ceramics

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MICROSTRUCTURAL CHARACTERIZATION OF NUCLEAR-WASTE CERAMICS*

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ABSTRACT

Characterization of nuclear waste ceramics requires techniques possessing high spatial and x-ray resolution. XRD, SEM, EMPA, TEM and AEM techniques are applied to ceramic formulations designed to immobilize both commercial and defense-related reactor wastes. These materials are used to address the strengths and limitations of the techniques above. An iterative approach combining all these techniques is suggested.

INTRODUCTION

The continuing development and improvement of scanning electron microscopy (SEM), electron probe microanalysis (EMPA), transmission electron microscopy (TEM) and analytical electron microscopy (AEM) have fostered dramatic improvements in chemical analysis and microstructural characterization [1]. The importance of microstructural characterization to better understanding polyphase crystalline materials has now been demonstrated for a number of materials. Principal concerns of such investigations include the presence, distribution and composition of intergranular amorphous films, chemical inhomogeneities within individual phases, and chemical segregation due to the formation of discrete precipitates or crystallographically coherent exsolution lamellae.

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In many ceramic materials the formation of a high temperature liquid phase is required in order to aid densification. This is prevalent in the fabrication of covalent solids such as nitrogen or carbide ceramics. After densification, these high temperature liquids may remain within the material as a combination of intergranular glass and crystals. These secondary phases exhibit a major effect upon the properties of the final material. Typical examples of such properties include the high-temperature mechanical properties of Mg, Y, Al, and Sc-fluxed Si_3N_4 alloys [2-7] and the anomalously high dielectric constants of NaNbO_3 fluxed BaTiO_3 ceramics [8]. In some instances the intergranular phases reflect the chemistry of impurities in starting materials as well as that of additives. A case in point is the presence of chlorine within the intergranular glass in Si_3N_4 alloys [6,7].

In geologic material, the presence of molten intergranular phases has been postulated as the cause of anomalously high electrical conductivity and seismic attenuation within regions of the earth's mantle [9]. A number of experiments have been designed to test these hypotheses. Samples quenched from high temperatures (greater than 1200°C) and pressure (greater than 20kb) are characterized by TEM analysis in order to determine the presence or absence of resulting intergranular glass phases [10,11]. In another application, TEM analysis is employed to determine the coarsening of exsolution lamellae in important rock-forming minerals, i.e., pyroxenes and feldspars [12]. Time-temperature histories for samples containing these phases can be elucidated on the basis of such data.

The characterization of ceramic materials for the long-term immobilization of high-level nuclear waste presents a number of special problems. Firstly, nuclear waste from both commercial reactors and as by-products of nuclear weapons production are chemically complex, representing a large portion of the naturally occurring elements as well as the actinides. The utilization of ceramics for immobilization of these wastes is predicated upon the incorporation of radionuclides as essential structural constituents within a limited number of crystalline phases. Formation of the desired assemblages is accomplished by blending of a specified suite of additive components with the waste stream. This allows the waste composition to be altered such that it enters the desired phase volume. Armed with the necessary data regarding radionuclide substitution mechanisms and desired waste loading, simple algorithms can be constructed for the formulation of optimum additive proportions [13].

In characterizing the densified product, the initial concern is simply that of establishing whether or not the proposed assemblage was indeed produced. In large part, powder x-ray diffraction can answer this question. However, a number of major concerns cannot be satisfied by this method alone. These include determinations of the following.

1. Quantitative chemical analysis of the phases formed, and distribution of radionuclides among them.
2. Presence of radionuclide-rich phases in amounts below detectability by XRD or hidden below reflections of major phases.
3. Presence, composition and distribution of intergranular glass,
4. Overall textural and compositional homogeneity.

These features are crucial to satisfying the intended performance criteria of these materials, namely, long-term stability in a geologic repository. Hence, microstructural characterization and chemical analyses of individual phases is required. As these materials are typically fine-grained (less than $1\mu\text{M}$), techniques with high spatial resolution are required.

In this paper, the characterization of two different types of titanate-based nuclear ceramics is described in light of the concerns expressed above.

The first material is designed to incorporate nuclear wastes produced as by-products of nuclear weapons production which are now in tank storage at the Savannah River Plant, Aiken, North Carolina [14]. The second material is designed to incorporate waste from commercial reactors. These are designated as DTC (defense titanate ceramic) and CTC (commercial titanate ceramic) [15]. These forms are contrasted to illustrate the implications of waste stream composition on additive formulations and sample microstructure.

TITANATE-BASED NUCLEAR WASTE CERAMICS

The use of titanate-based ceramics for nuclear waste disposal was introduced by Ringwood et.al. under the acronym, SYNROC (synthetic rock), and was originally intended for the immobilization of commercial reactor waste [16,17]. Perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$) and "hollandite" ($\text{BaAl}_2\text{Ti}_6\text{O}_{18}$) are the principal phases of interest. It is assumed that the distribution of radionuclides in this assem-

blage is as follows: alkalis enriched in hollandite, alkaline earth, lanthanides and trivalent actinides enriched in perovskite, and tetravalent actinides and uranium enriched in zirconolite. In practice, Mo, Ru, Re, and Pd are reduced to the metallic state and reside in a metallic alloy. It is interesting to note that Dosch and coworkers, working independently, produced assemblages containing some of the same phases [18]. CTC has a composition and phase assemblage closely resembling SYNROC-C.

In applying the perovskite-zirconolite-hollandite formulation to defense wastes, the high concentration of transition metals, alumina, sodium and silica as inert processing contaminants must be considered [14]. In such compositions hollandite proved to be unstable requiring the addition of a new cesium host phase. Since silica and sodium were present in the waste stream, the alkalis were recast as an alkali aluminosilicates, nepheline ($\text{NaAlSi}_3\text{O}_8$) and pollucite ($\text{CsAlSi}_2\text{O}_6$). The transition metals form spinels and metal alloys. DTC has been formulated on this basis [13].

It should be noted that a large portion of the transition metals require reduction to the form spinels. Hence, proper redox control must also be verified during sample characterization.

SAMPLE PREPARATION

Both DTC and CTC starting powders were produced by spray drying slurries of additive components and aqueous solutions of waste stream constituents. The powders were fired in air at 600°C to devolatilize the samples. This was followed by a reducing calcine. DTC powders were reduced in mixtures of CO/CO₂ mixed to approximate the Ni-NiO buffer at 800°C. Samples were then uniaxially hot pressed in graphite dies at 1100°C and 1250°C for DTC and CTC, respectively. XRD of the powders prior to pressing indicates that they are partially crystalline, usually containing minor perovskite, ZrO₂ and spinels.

ANALYTICAL TECHNIQUES

As mentioned previously, the goals of waste form characterization are to identify the phases within the form and to obtain qualitative and quantitative compositional data relating to the distribution of radionuclides. In order to meet these requirements, XRD, SEM, wavelength dispersive (WDS) EMPA, TEM and AEM techniques are employed. It is necessary to use a number of

analytical techniques in conjunction in order to adequately characterize these materials. No single technique has proven capable of meeting all these requirements. In some cases it has even been necessary to fabricate additional samples under a variety of conditions in order to resolve ambiguities in characterization. In this paper, DTC and CTC wasteforms are used to illustrate the strengths and limitations of the various techniques in addressing the problems above.

Since the techniques used in this study are well known, they are not described here in detail. One exception, however, is the observation of intergranular amorphous phases by diffuse dark field imaging of electrons diffracted from these phases [19]. This method is illustrated schematically in Figure 1. Electrons diffracted from an amorphous phase give rise to a series of concentric rings of decreasing intensity. These rings correspond to the peaks on the radial distribution function of the amorphous phase. In the case of silicate glasses, the most intense peak is produced at $3.4 \text{ \AA}^{-1}$ corresponding to the Si-Si bond length [20]. Hence, silicate glasses may be imaged by placing the objective aperture at the corresponding distance in the back focal plane of the TEM. Discrete diffraction spots from adjacent crystalline material should, of course, be excluded. An example of this type of imaging from a "supercalcine ceramic" is illustrated in Figures 2 and 3 [21]. The diffuse

Figure 1. Schematic illustration of the positioning of the objective aperture in the back focal plane in order to obtain a diffuse dark field image of a noncrystalline phase.

Figure 2. Diffraction pattern recorded from an amorphous region in the "supercalcine" ceramic in Figure 3.

Figure 3. TEM images recorded from "supercalcine" ceramic (a) bright field image, (b) diffuse dark field image produced by imaging the diffraction ring in Figure 2.

ring in the diffraction pattern from an amorphous phase is imaged in dark field in order to "light up" the amorphous regions (Figure 3b). It should be noted that the contrast in bright field is not sufficient to distinguish the amorphous from crystalline phases simply on the basis of atomic number contrast (Figure 3a)

DEFENSE TITANATE CERAMIC

DTC can be used to illustrate the difficulty in obtaining quantitative chemical analyses in chemically complex, fine-grained (1μm) polyphase ceramics. Samples fabricated at 1100°C typically have an average grain size of 1μm with some grains as large as 3μm (Figure 4). XRD establishes the presence of the predicted major phases, zirconolite, perovskite, nepheline, an ulvöspinel and a hercynitic spinel (Figure 5a), but does not allow chemical analysis of the observation of amorphous phases. Hence, microstructural techniques are required.

A backscattered electron image from a 1100°C run obtained with an accelerating voltage of 15 KV is capable of resolving individual phases (Figure 4). The corresponding K-alpha line x-ray images for Si, Fe, and Ca, obtained at the same accelerating voltage, also resolve the chemical segregation within the sample (Figure 4). However, throughout most of the sample, it is difficult to correlate regions of high iron concentration

with those of low calcium concentration, for instance. This correlation is expected based upon the mineralogy observed in XRD, and its absence indicates the near equality of x-ray excitation volume and grain size. The correlation can be observed in a single $2\ \mu\text{M}$ region, "A", in Figure 4. However, an EDS spectra obtained from this region indicates the presence of Ca in this region (Figure 6). Since calcium is not known to be incorporated in spinel structures, the calcium signal must be generated from adjacent grains. Hence, grains of $2\ \mu\text{M}$ or less in diameter cannot be analyzed by EMPA techniques at 15 KV. Lower accelerating voltages would increase the spatial resolution, but also increase the detectability limits, or totally preclude analysis, of some important radionuclides, i.e. the lanthanides. Obviously, either the grain size of the sample, or the spatial resolution of the analytical technique must be increased.

Figure 4. Backscattered electron and Fe_K , Ca_K , and Si_K x-ray images from DTC pressed at 1100°C .

In an attempt to increase grain size, a sample of the identical composition was pressed at 1200°C . This produced a sample with grains as large as $10\ \mu\text{M}$ in diameter (Figure 7). X-ray images for a number of elements can now be used to discriminate the phases chemically. The lanthanides and strontium images correlate with calcium, while uranium correlates with zirconium. This indicates the immobilization of strontium and the lanthanides in perovskite and uranium in zirconolite. Phases of this grain size are also suitable for quantitative analyses by EMPA. Typical analyses of major phases are given in Table I.

Figure 5 X-ray diffraction patterns. (a) DTC (LLLS04HP4A) and (b) CTC (S08HIP2A) (courtesy of P.H.P. Morgan)

Figure 6. EDS of a high-Fe, low-Ca region (area "A"), Fig. 4.

TABLE I. Microprobe Analyses (wt%) of DTC Phases					
	PER	ZIR	SP 1	SP 2	GLASS
SiO ₂	0.13	1.44	--	--	34.49
Al ₂ O ₃	0.72	3.19	11.81	51.42	30.43
TiO ₂	49.77	23.43	25.27	4.21	5.82
ZrO ₂	0.92	30.33	--	--	1.58
Na ₂ O	2.11	0.66	--	--	9.51
CaO	26.05	7.88	--	--	6.96
SrO	0.60	0.25	--	--	0.04
MnO	0.86	2.22	12.42	8.13	1.90
FeO	1.70	11.52	47.53	35.97	5.21
NiO	0.19	5.10	0.03	0.58	0.00
Ce ₂ O ₃	5.14	0.66	--	--	0.04
Nd ₂ O ₃	4.63	0.97	--	--	0.00
UO ₂	5.96	11.92	--	--	0.00
Total	98.77	99.57	97.06	100.31	96.38

Figure 7 Backscattered electron and x-ray images for Ca_K , Al_K , Zr_L , Ce_L , Nd_L , Sr_L , and I_M lines for DTC pressed at 1200°C .

Quantitative chemical analyses are extremely important for a number of applications. Of particular importance is their application to quantitative modeling of wasteform leaching. Ceramic wasteforms dissolve incongruently, certain phases (i.e. silicates) dissolving more readily than others. Hence, in order to predict elemental leach rates it is necessary to obtain quantitative analyses of these phases [22].

Quantitative analyses coupled with crystalline phases stoichiometries can also be used to determine the redox states of multivalent cations. For instance, DTC contains a high concentration of iron which may occur as either Fe^{+2} or Fe^{+3} , and resides almost totally in spinels. Hence, the redox state of iron in spinels is indicative of that in the entire sample [23]. The cation to oxygen ratio in spinel is 3 to 4, so that the microprobe analyses (all iron as FeO) can be recast on this basis to determine $\text{Fe}^{+2}/\text{Fe}^{+3}$. This amounts to assigning the cations to ulvöspinel (M_2TiO_4), hercynite (MAl_2O_4) and magnetite (Fe_3O_4) end members ($\text{M} = \text{a divalent cation, Mn, Ni, Fe}^{+2}$). Magnetite is the only endmember containing Fe^{+3} ($\text{FeO} + 2\text{Fe}_2\text{O}_3$). The results of this type of recalculation are shown for a number of DTC samples in Figure 8.

The chemistry of large grains produced at high temperatures must be qualitatively verified for the lower temperature experiments by TEM and AEM analysis. Energy dispersive analyses obtained in the AEM for perovskite and zirconolite in 1100°C DTC samples confirm the major element and radionuclide distribution in these phases (Figure 9). Uranium is found in both phases while Na can be distinguished in perovskite. Cerium, the other

Figure 8. Microprobe analyses of spinels from DTC recast on mole% M_2TiO_4 (ulvöspinel), MAl_2O_4 (hercynite) and Fe_3O_4 (magnetite) endmembers.

Figure 9. EDS results obtained from DTC in the AEM, (a) perovskite, (b) zirconolite

abundant lanthanide in these samples, is also present in perovskite, but its L-lines are convoluted with the Ti K-lines. The Ce K-lines can be distinguished at higher voltages ($\alpha=34.57$ KV). Lower count rates are exhibited for lanthanide K-lines, however. In general, AEM allows sufficient overvoltage to excite all the necessary x-ray transitions. Hence, unconvoluted lines may be distinguished for most radionuclides. However, low count rates for some lines, coupled with small sample areas may yield unacceptably high detection limits.

The higher spatial resolution of TEM and AEM analyses allow better characterization of glassy and minor phases in DTC samples. $UO_2 \cdot x$ was found included as small ($\sim 500\text{\AA}$) grains in a glassy matrix (Figure 10). The glass was distinguished by diffuse dark field imaging and undergoes radiation damage under the 100 KV electron beam. This radiation damage is accompanied by alkali loss during analysis. This is particularly troublesome with regard to cesium analysis in the glass phase. Cesium K-lines ($\alpha=30.54$ KV) must be used for analysis due to the convolution of its L-lines with the Ti K-lines. The reduced count rates of the K-lines relative to the L-lines, accompanied by the volatilization of alkalis can make even qualitative analysis of cesium distribution difficult. This glassy phase appears not only at triple junctions, but also along grain boundaries (Figure 10b). This most surely indicates a continuous glassy phase throughout the sample. Since silicate glasses in these samples are particularly susceptible to dissolution, data regarding its distribution is critical to understanding the sample's leaching behavior [22,23].

Figure 10. Bright field images of DTC thin foil. (a) U_M line profile indicating UO_{2+x} in the glassy matrix (courtesy of C. Echer), (b) glass at grain boundaries and triple junctions.

COMMERCIAL TITANATE CERAMICS (CTC)

Critical to the microstructural development of DTC was the presence of a glassy intergranular silicate phase. CTC contains no silica and, hence, should not include a continuous glassy network. Grain boundaries in CTC are devoid of glass as expected, but inspection of triple junctions by diffuse dark field imaging and convergent beam diffraction indicates the presence of a glassy phase (Figure 11). The glass phase is readily damaged under the electron beam, and EDS analysis indicates a phosphate rather than silicate chemistry (Figure 12). The glass is approximately 30wt% P_2O_5 (EMPA semiquantitative analysis), and the entire sample contains 0.15wt% P_2O_5 . Assuming that the glass density is 50% that of the coexisting titanate crystals, the volume percentage of glass should be less than a percent of the entire sample. Hence, it appears likely that the glass is not continuous throughout the wasteform, but instead, isolated at triple junctions. Further microstructural analysis coupled with quantitative leaching models are necessary to resolve this question.

The presence of five major phases are observed in backscattered electron and x-ray images of CTC (Figure 13). As predicted, perovskite, zirconolite and hollandite coexist with an alloy and magnetoplumbite (nominally $CaAl_{12}O_{19}$). Compositions determined by EMPA are given in Table II. It should be noted that only the 3 major phases were positively identified in XRD (Figure 5). Uranium is again distributed between perovskite and zirconolite; perovskite is the major host phase for the lanthanides. Cesium is incorporated in hollandite, and strontium is distributed between the magnetoplumbite and perovskite.

Figure 11. Bright field images of CTC thin foil. (a) Glass-free perovskite (twinned phase)-hollandite grain boundary, (b) phosphate glass at triple junction displaying radiation damage.

Hollandite chemistry can be used in much the same manner as that of the spinels i. DTC in determine the redox state of Ti. The cation to oxygen ratio in hollandite is 9 to 16, requiring that the number of trivalent cations be equal to $2Ba + Cs$. Hence, hollandite compositions can be resolved into the components $(Ba,Cs)Al_2O_4$, $(Ba,Cs)Ti_2O_4$ (trivalent Ti) and TiO_2 (tetravalent Ti). The resulting ternary can be contoured for $Ti^{3+}/Ti^{3+}+Ti^{4+}$, which increases for samples pressed in graphite compared to those sintered in air (Figure 14).

The analysis of hollandite also indicates the necessity of WDS analysis capabilities for these materials. The energy dispersive spectra obtained from hollandites by AEM are characterized by convoluted Ti_K , Ba_L , and Cs_L x-rays (Figure 15). Hence, quantitative analysis is dependent upon the accuracy of deconvolution algorithms. In WDS analysis the peaks are fully resolved, however.

The metallic grains in CTC are typically less than an micron in diameter requiring AEM analysis. EDS of these grains indicates that the noble metals are reduced to the metallic state and are immobilized in these grains. The reduction of Mo to the metallic state is of particular importance, as unreduced Mo may cause the formation of a water soluble cesium molybdate.

TABLE II. Microprobe Analysis (wt%) of CTC Phases

	Ho	Per	Zir	Mpb
TiO ₂	68.08	57.32	45.92	10.12
ZrO ₂	-	0.46	34.43	-
Al ₂ O ₃	9.45	0.21	2.27	76.80
CaO	0.74	30.29	13.39	5.15
BaO	18.10	0.48	0.17	0.74
NiO	0.45	0.00	0.00	0.76
FeO	0.03	0.02	0.19	2.47
MnO	0.03	0.10	0.09	0.00
SrO	0.22	0.63	0.00	0.37
Ce ₂ O ₃	-	3.22	0.35	0.13
Nd ₂ O ₃	-	2.30	0.37	0.00
Eu ₂ O ₃	-	0.10	0.07	0.00
Gd ₂ O ₃	-	0.35	0.08	0.00
Na ₂ O	0.00	2.02	0.47	1.37
Cs ₂ O	1.12	0.06	0.06	0.00
UO ₂	-	1.35	0.75	0.00
P ₂ O ₅	-	0.00	0.00	0.00
Total	98.22	98.91	98.61	97.91

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Figure 12. EDS analysis of phosphate glass in CTC (Figure 11b).

Figure 14. Hollandite analyses (EMPA) from CTC recast as fictive endmember components and contoured for $Ti^{3+}/Ti^{3+}+Ti^{4+}$ (see text).

Figure 13. Backscattered electron image and x-ray images from CTC.

Figure 15. EDS of hollandite from CTC obtained by AEM. Cs_L , Ba_L and Ti_K lines are convoluted.

Figure 16. EDS of metal grains in CTC obtained by AEM indicating immobilization and reduction of noble metals.

DISCUSSION

The characterization of nuclear waste ceramics imposes a number of stringent requirements upon the investigator. These are due to both the nature of the problem and the material itself. Solutions to the problem require,

1. quantitative analyses of all phases
2. identification of intergranular phases
3. identification of phases present in amounts less than 1%
4. the microstructural distribution of phases with poor leach resistance.

The nature of the materials provide difficulties due to their,

1. chemical complexity
2. fine-grained nature

Limitations in the various analytical techniques prevent any single technique from completely fulfilling our characterization needs. Hence, a number of techniques must be employed in an iterative approach.

XRD provides a rapid method of determining the phase assemblage. However, no data is obtained for phase chemistry and microstructural phase distribution. Minor phases can also be missed due to detection limits and/or overlapping reflections from major phases. EMPA and SEM techniques complement XRD by providing chemical and microstructural data. WDS analysis is particularly useful in complex chemical systems due to its excellent x-ray resolution (compared to EDS). However, the spatial resolution is not always sufficient in these techniques. As such, they must be complemented by TEM and AEM analysis with their superior spatial resolution. Unfortunately, quantitative AEM analysis is still in the developmental stage, and, should EDS techniques be employed, x-ray resolution is again a limitation. Another feature which must be addressed is the effect of radiation damage and volatile loss upon AEM results.

Characterization of nuclear waste ceramics requires the application of a number of techniques possessing both high spatial and x-ray resolution. Characterization at the "100% confidence level" is most likely impossible due to the inability of any single technique to meet all the analytical constraints. However, we propose that the iterative approaches outlined above provide credible solutions to a majority of the problems.

REFERENCES

1. A. H. Heuer and N. J. Tighe (ed.), Application of Electron Microscopy to Engineering Practice in Ceramics, J. Am. Ceram. Soc. **62**: 225-305 (1979).
2. F. F. Lange, Silicon Nitride Polyphase Systems: Fabrication, Microstructure, and Properties, International Metals, Rev. 247 (1980).
3. D. R. Clarke, Densification of Silicon Nitride Alloys Using a Eutectic Liquid: An Experimental Test, in "Sintering - Processes," G. C. Kuczynski, ed., Plenum Press, New York, N.Y. (1980).
4. G. R. Terwilliger and F. F. Lange, Hot-Pressing Behavior of Si_3N_4 , J. Am. Ceram. Soc. **57**:25 (1974).
5. L. K. V. Lou, T. E. Mitchell, and A. H. Heuer, "Impurity Phases in Hot Pressed Si_3N_4 ", J. Am. Ceram. Soc., **61**:392 (1978).
6. D. R. Clarke, N. J. Zaluzec, and R. W. Carpenter, The Intergranular Phase in Hot-Pressed Silicon Nitride: I. Elemental Composition, J. Am. Ceram. Soc. **64**:601-607 (1981).
7. D. R. Clarke, N. J. Zaluzec, and R. W. Carpenter, The Intergranular Phase in Hot-Pressed Silicon Nitride: II. Evidence for Phase Separation and Crystallization, J. Am. Ceram. Soc. **64**:608-611 (1981).

8. L. E. Cross, and D. E. Payne, "The Role of Internal Boundaries upon the Dielectric Properties of Polycrystalline Ferroelectric Materials," to be published.
9. H. S. Waff, Theoretical Considerations of Electrical Conductivity in a Partially Molten Mantle and Implications for Geothermometry, Jour. Geophys. Res., 79: 4003-4010 (1974).
10. H. S. Waff and J. R. Balau, Equilibrium Fluid Distribution in a Ultramafic Partial Melt Under Hydrostatic Stress Conditions, Jour. Geophys. Res. 84:6109-6114 (1979).
11. J. R. Balau, H. S. Waff, and J. A. Tyburezy, Mechanical and Thermodynamic Constraints on Fluid Distribution in Partial Melts, Jour. Geophys. Res. 84:6102-6108 (1979).
12. R. A. Yund, A. C. McLaren, and B. E. Hobbs, Coarsening Kinetics of Exsolution Microstructure in Alkali Feldspar, Contrib. Mineral. and Petro. 48:45-55 (1974).
13. F. J. Ryerson, K. Burr, and R. B. Rozsa, "Formulation of SYNROC D Additives for Savannah River Plant High-Level Radioactive Waste," Lawrence Livermore National Laboratory, Livermore, CA Rept. UCRL-53237 (1981).
14. J. Campbell, C. Hoenig, F. Bazan, F. Ryerson, M. Guinan, R. Van Konynenberg, and R. Rozsa, "Properties of SYNROC D Nuclear Waste Form: A State-of-the-Art Review", Lawrence Livermore National Laboratory, Livermore, CA Rept. UCRL-53240 (1982).
15. F. J. Ryerson, C. L. Hoenig, and F. Bazan, SYNROC C: Preparation and Phase Equilibria, in: "High Temperature Materials Chemistry," (ed., D. D. Cubicciotti and D. L. Hildenbrand). The Electrochemical Society, 144-161 (1982).
16. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, "Immobilization of High-Level Nuclear Reactor Wastes in SYNROC," Nature, 278:219-223 (1979).
17. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization," Geochem. J., 13:141-165, (1979),
18. R. G. Dosch, A. W. Lynch, F. J. Headly, and P. F. Hlava, Titanate Waste Forms for High-Level Waste - An Evaluation of Materials and Process, in: "Scientific Basis for Nuclear Waste Management," J. G. Moore, ed., 3:123-130 (1981).
19. D. R. Clarke, Application of Electron Microscopy to the Processing of Ceramic Materials, Ultramicroscopy, 8:95-108 (1982).
20. M. Taylor, and G. E. Brown, Jr., Structure of Mineral Glass-I. The Feldspar Glasses $\text{NaAlSi}_3\text{O}_8$ KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$, Geochim. Cosmochim. Acta, 43:61-75 (1979).
21. G. J. McCarthy, and D. R. Clarke, Microstructural Characterization and Crystal Chemistry of the Synthetic Minerals in Current Supercalcine Ceramics, to be published.

22. F. J. Ryerson, F. Bazan, and J. H. Campbell, Dissolution of a Nuclear Waste Ceramic: An Experimental and Modelling Study, J. Am. Ceram. Soc. (submitted).
23. F. J. Ryerson, SYNROC-D: Phase Chemistry and Microstructural Characterization, J. Am. Ceram. Soc., (submitted).

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