TRANSFORMATION OF CALCINE TO A DURABLE WASTE FORM

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WASTE FORM TYPES : GLASS, GLASS-CERAMIC, SYNROC

CALCINE CHARACTERISTICS: CHEMISTRY AND MICROSTRUCTURE

WASTE FORM DEVELOPMENT: FORMULATION
PREPARATION OF GLASS BY MELTING
PREPARATION OF GLASS-CERAMIC BY HOT ISOSTATIC PRESSING (HIP)

WASTE FORM CHARACTERIZATION: MICROSTRUCTURE
PHASE COMPOSITION
CHEMICAL DURABILITY
MECHANICAL STRENGTH

slide 1

I will here present a short discussion on how we are trying to transform the high level waste calcine at ICPP into a durable body or an inorganic material.

My cosscientists on this task are Krishna Vinjamuri and Bruce Staples. The project is supervised by Dr. Dieter Knecht.

Waste form is a solid body containing the waste. and in high level waste technology we recognize three such solids called glass, glass-ceramic and synthetic rock. Typically we will call the waste form as glass when it is devoid of abundant crystalline matter, a glass-ceramic when it contains both amorphous and crystalline matter, and synthetic rock, when the compositions of the amorphous and crystalline matter are analogous to natural rocks. At ICPP our efforts mainly concentrate$ on the development of glass-ceramic, with supporting experiments on glass as well as synthetic rock.

We will look at calcine characteristics, in the form of its chemistry and microstructure- the calcines that we are currently working with are simulated analogs of the actual hot calcine.

To transform the calcine into a solid inorganic material, chemical components are added, and this is what we call formulation.

The chemical mixture is then melted in a crucible and quenched to form glass, or is subjected to high temperature under pressure to form glass-ceramic.

We have been using X-ray powder diffraction, Polarized light microscopy, electron microscopy and electron microprobe to determine the interrelations among glass and crystals, and their chemical composition. The waste forms are tested for durability in deionized water at 90oC- the test is called MCC-1 test.
The mechnical strength is also of interest here, we hope to address this issue in the near future. Currently, we carry out creep experiments, because creep is often an indicator of diffusion mechanism.

slide-2

The composition of the calcine is quite diverse. B_2O_3 and Al_2O_3 may play dual role as glass formers and modifiers, there are several typical glass modifiers- like CaO, CdO, K_2O and Na_2O. But in addition there are large concentrations of refractory components like CaF_2, ZrO_2 and Cr_2O_3 that have a very low solubility in a common borosilicate glass.

slide-3

The calcine fragments are in the order of 200 microns., have a high porosity and have concentric nodular pattern.

slide-4

The chemical species are also concentrically distributed. This distribution is particularly evident in the major elements of the calcine namely, Al, Na, Ca, Zr, B, Cr and Cd, while the minor elements like S and Ce occur scattered, suggesting that there is no preferred chemical segregation.

slide-5

In order to transform the calcine into glass or glass-ceramic it is necessary to add silica. In addition other components to tailor the formation of specific phases. Here are two formulations that are currently being investigated for forming glass-ceramic bodies. In formulation -I the calcine loading is maintained at 70%, silica at 25% and the components of B_2O_3, Ti and Al metals are varied as shown in this diagram to form calcium titanium silicate called sphene, titanates and boron containing aluminosilicate glasses.

In formulation-II the calcine loading is maintained at 80%, silica at 10%, and the components of P_2O_5, metallic Si and Al are varied as shown in the diagram to form phosphate bearing phases.

Sphene is a principal component in the glass-ceramic being developed by the Canadian Nuclear Fuel Waste Management Program as an alternative to nuclear waste from borosilicate glass. Here sphene and titanates are actinide bearing phases in nuclear waste forms.

In formulation -II apatite and phosphates are the actinide bearing phases.

slide-6

The frit so formulated is mechanically mixed with calcine , cold pressed in a stainless steel container and vacuum sealed.

The waste form is developed in the hot isostatic press. The pressure is initially raised to about 15000 PSI. This is followed by a rise in temperature and pressure to 1000 C and 20,000 PSI. At maximum P-T the waste form is maintained for two hours or so and then cooled. Since the waste forms contain glass, the microstructure is further stabilized by annealing in the neighborhood of glass transition region.

We are also carrying out a parallel basic study to determine the pressure-temperature stability of waste forms as a function of composition. Such a study would eventually be used for optimizing the process parameters. The diagram is largely based on concept of thermodynamics. We have at present two experimental data points, and additional experiments are currently in progress.

slide-7

The waste forms vary in their microstructure as a function of composition. This cross-polarized light micrograph of one of the waste forms made using formulation-1. The microstructure looks similar to a volcanic rock, where crystalline grains occur interlocked, with intergranular glass. This particular waste form is abundant in zircon. Zircon in nature is a resistant mineral, and often contains, Th in the Zr site of crystal structure.

slide-8

Fine CaF_2 grains of calcine grow into large sizes during Hipping, and are here observed embedded in the glass matrix. At a high magnification like 1500X dendrites of sphene are noted in the glass., sphene seems to be a host not only for actinides, as has been noted by Canadian Mines, but in our work it also seems to contain 5% Cd in the Ca site.

slide-9

We have also attempted to crystallize feldspars in the waste forms. The feldspars could be a possible host for Sr, where Sr would occupy the Ca site. In fact some of the feldspar rocks in nature are as old as 1.0 B.Y. The adirondack mountain is a classic example, whose age was determined because of the occurrence of radioactive Sr isotopes in them. Feldspar compositions in the optical microscope are determined by the conoscopic optical image shown here.

slide-10

These are scanning electron micrographs that reveal the effect of additive composition on crystallization. The additive compositons are, like 5% B2O3 vs. 3% B2O3, 3% Ti vs. 6% Ti, and 1% Al vs. 3% Al. Although the additives are of different types, the absence and presence of zircon grains in glass islands is shared by all of them. The microstructures on either side are nearly similar. Possibly, the growth of these crystals is related to the vsicosity of the liquid, and hence the glass structure.

slide-11

the glass compositions of the two sets of micrographs, nearly have the same Al/Si ratio and are silica enriched, perhaps suggesting that tetrahedral substitution of Al for Si. The compositions however, differ in the Ca content. The higher Ca content may promote crystallization, by unbridging the network which may lead to decrease in viscosity. Possibly, Ca variations in the glass result from the fractionation of Ca in titanate and aluminosilicate phases in the solid state prior to formation of the liquid. For example, increases in Ti, and Al contents would lead to increased extraction of Ca prior to melting.

The glass analysis also shows that in pure glass, only about 3 to 5% CaF2 and ZrO2 are dissolved. This low solubility places a similar limitation on the solubility of calcine in glass.

slide-12

This waste form was made using formulation -2. Addition of phosphorous and water seems to promote a greater growth of CaF2, a more even distribution of grain boundary phases, and crystallization of apatite.

slide-13

we are also persuing our studies in the preparation of glass. Many glass formulations exist in the literature for accommodating high level nuclear waste. The general structure of glass is nearly similar, as a result despite variations in their chemistry, the mechanism of accommodation of nuclear waste is nearly the same. The exercise here was carried out to study what changes the ICPP calcine introduces to a typical glass. Batch composition B was chosen in the soda-slica-b2o3 system. The compostion is far removed from Na2O. The composition falls in the immiscible field. Possibly, the excess free energy leads to phase separation of the composition into pure silica and composition G. This is clearly evident in the microstructure of this glass.

slide-14

The bright patch here is of pure silica. Possibly, one can also make use of this excess free energy to promote solubility of calcine. When 30% calcine is introduced, the glass appears very heterogeneous, although, there are no relics of unmelted calcine in this glass. Complex phase separation is introduced, in the form of mottled structure and B2O3 containing bubbles in the soda aluminosilicate matrix.

slide-15

we are commencing to probe into the structure of glass, with calcine addition. The clear glass and the mottled structures were probed using laser Raman. This preliminary data indicates structural changes perhaps in the form bridging and non-bridging oxygens in the three dimensional vs. the two dimensional network. we plan to persue detailed studies to establish relations among glass structure, calcine loading and durabilility.

slide-16

The table here shows the leach rates of waste forms, for some of the important elements. Most of the leach rates are well below the lower limit of 1 gram/m2-day set by MCC test. But greater decreases in leach rates seem to occur with the formation of crystalline phases, and perhaps suggests that crystalline phases are more durable than glass. For example, when the crystalline phase NaAlSi3O8 is present in the waste form the leach rate of Na is the lowest. The leach rates are also likely to be affected by the glass structure. Glasses with lower viscosity and more open structure, seem to increase the leach rate, thus this particular waste form shows a very laerge leach rate of 9.81 g/m2-day for Na.

slide-17

The components of calcine are partitioned into both glass and crystalline phases. The incompatible elements are preferentially accommodated in the glass, and the refractory components are contained in crystalline forms. Hence, it is possible to increase the calcine loading to 70 to 80 % by forming a glass-ceramic body. In contrast to 5% loading in homogeneous glass or 30% loading in heterogeneous glass.

the natural phases like sphene, zircon, apatite, feldspars are hosts for actinides and lanthanides, and are also far more resistent than glass. It has been possible to synthesize these crystalline phases in the waste forms and enhance its durability.

No additional wastes are produced in the glass-ceramic process. This is because both glass soluble and insoluble components are accommodated by glass-ceramic. However, in pure glass melting additional waste in the form of glass-melter waste is produced.

In hot isostatic pressing, the volatile phase is contained in the waste form, and dissolved in both crystalline phases. As a result high temperature glasses as well as crystalline phases are formed at relatively lower temperarutres. This may lead energy savings.

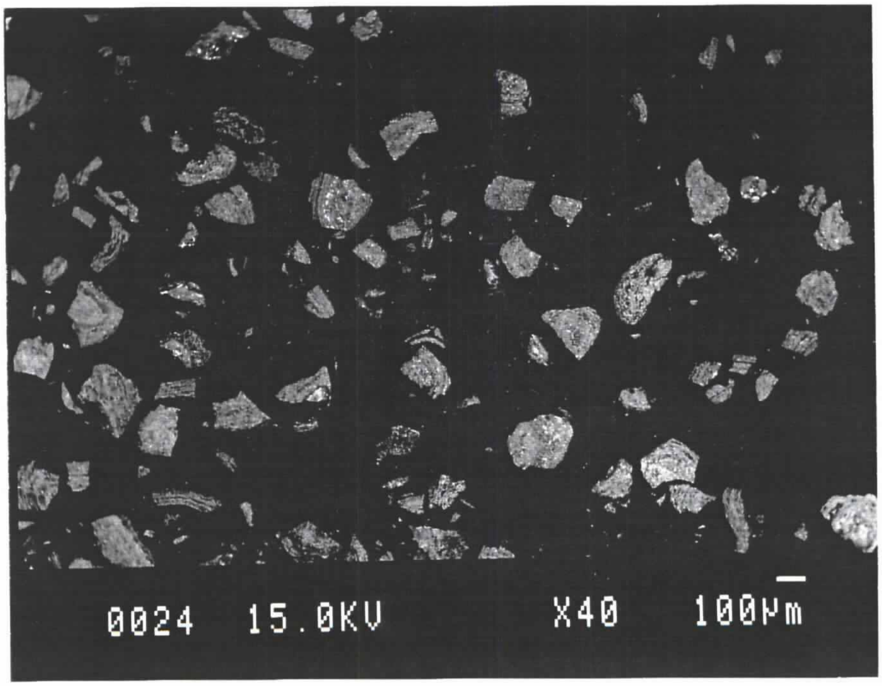
Future development efforts will concentrate on engineering grain boundaries, formulations, processing parameters, by concentrarting on issues of basic science as well as development. Because the present waste forms have several defects.

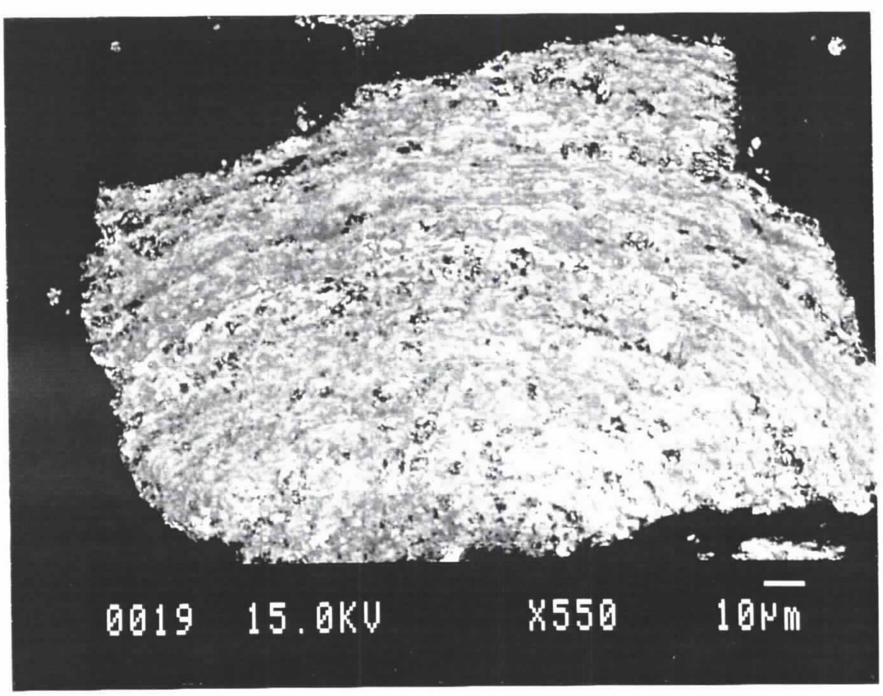
TABLE 1

CHEMICAL COMPOSITION OF SIMULATED CALCINE (WT%)

Component	Simulated Calcine (wt%)*
Al_2O_3	8.3
B_2O_3	4.4
CaO	11.5
CaF_2	35.1
CdO	3.9
CeO_2	1.1
Cl^{1-}	0.2
Cr_2O_3	1.2
Cs_2O	0.1
Fe_2O_3	0.3
K_2O	1.7
Na_2O	5.3
SrO	0.6
SeO	0.2
ZrO_2	16.9
PO_4^{3-}	0.2
Misc.	9.0
Total	100.00

* - based on elemental analysis and oxide calculation of mixed ground calcine


0024 15.0KV X40 100µm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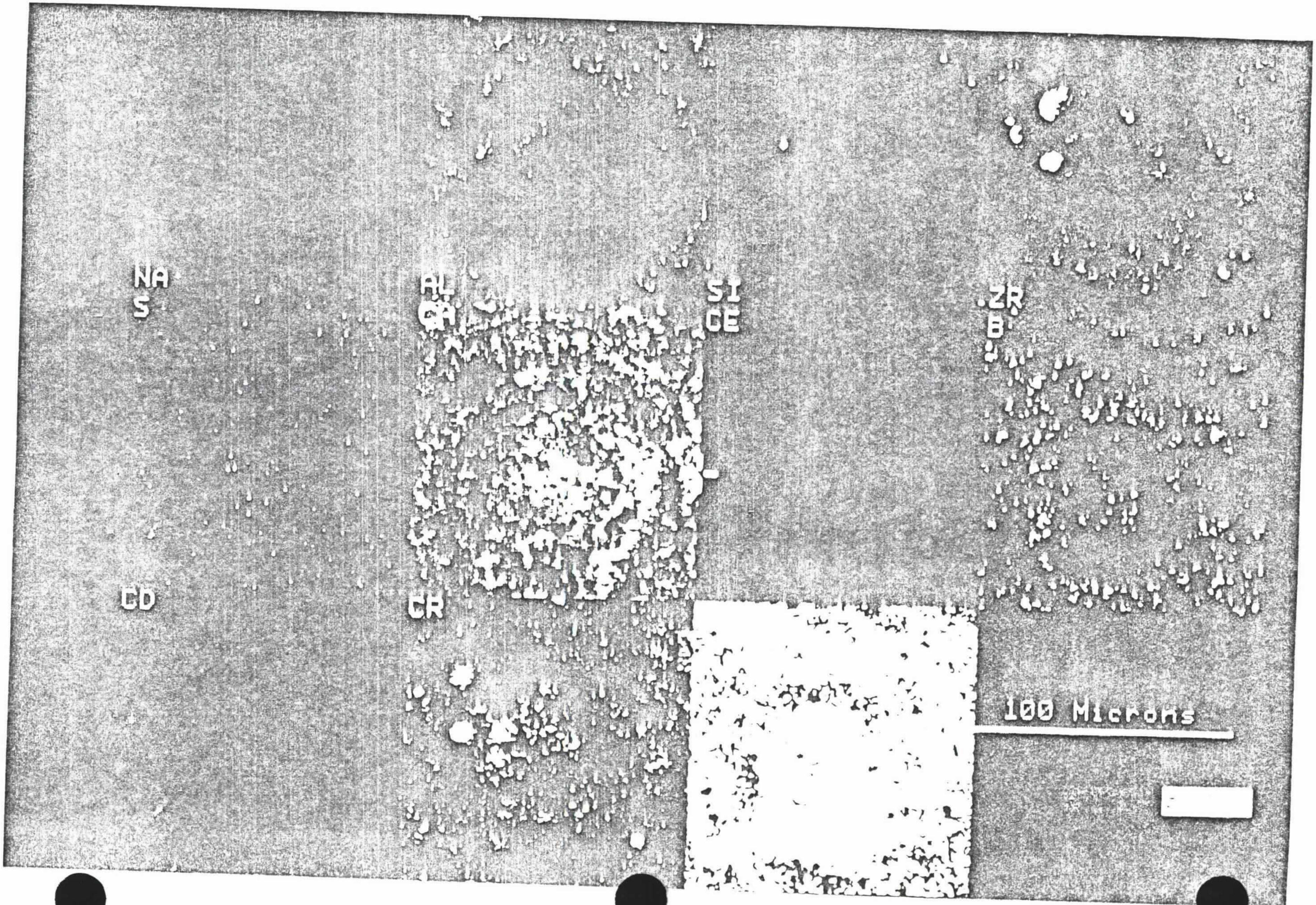
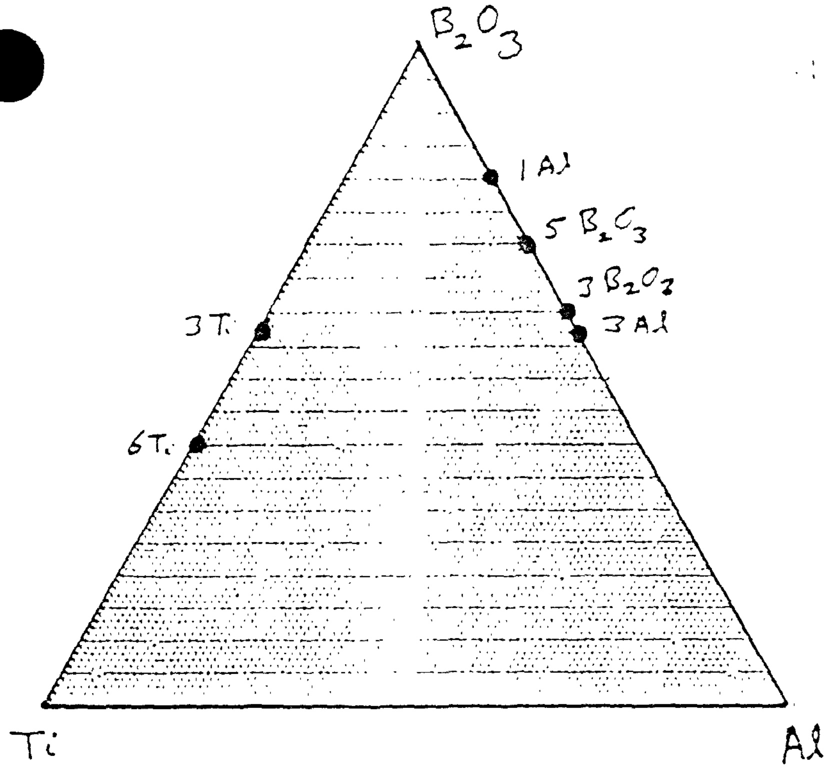


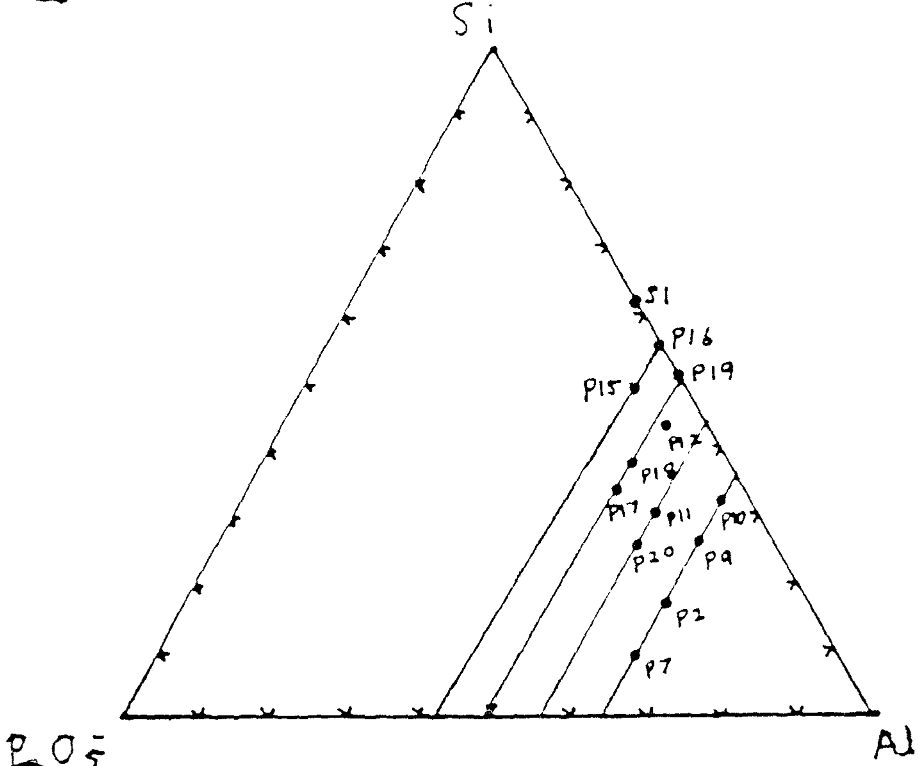
NA
S
AL
CA
SI
CE
ZR
B
CD
CR
100 Microns



FORMULATION - I

CALCINE 70 WT% (LOADING)
SILICA 25 WT%
(B2O3-TI-AL) 5 WT%

SPHENE CATISIO5
TITANATES
ALUMINOSILICATES



FORMULATION - II

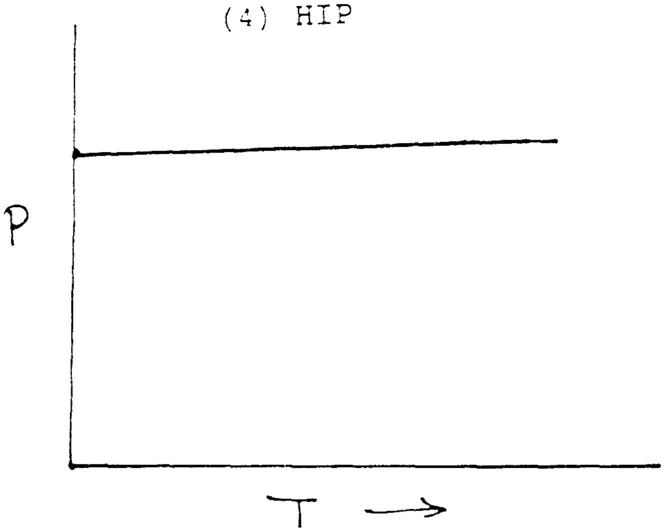
CALCINE 80 WT% (LOADING)
SILICA 10 WT%
(P2O5-AL-SI) 10 WT%

APATITE CA5(PO4)3(OH)
PHOSPHATES
ALUMINOSILICATES

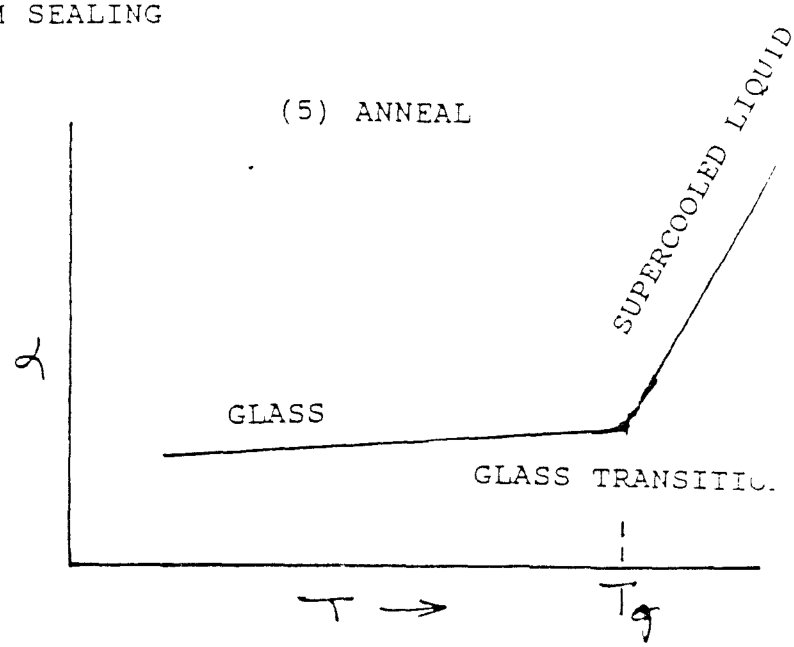
PREPARATION

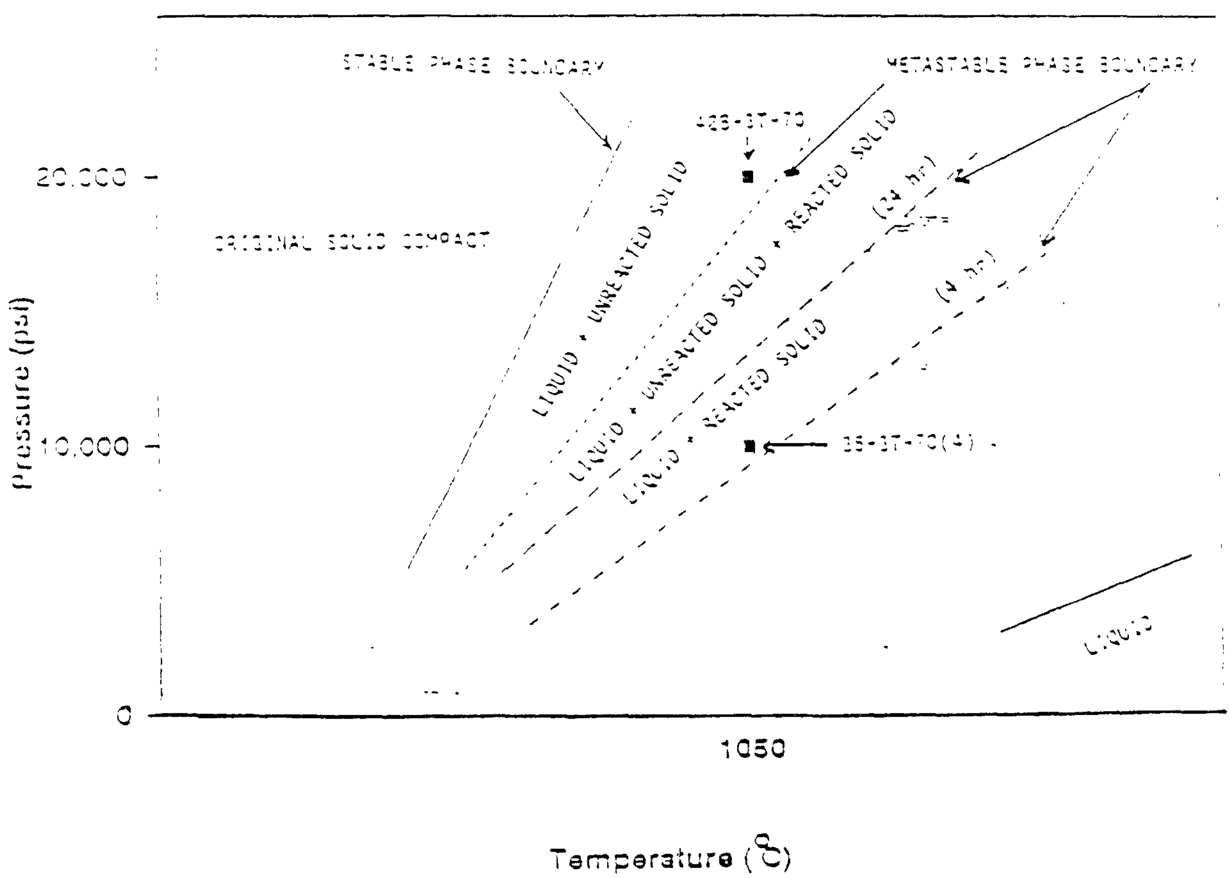
(1) MECHNICAL MIXING OF FRIT AND CALCINE
(2) COLD PRESSING IN STAINLESS STEEL CONTAINER
(3) VACUUM SEALING

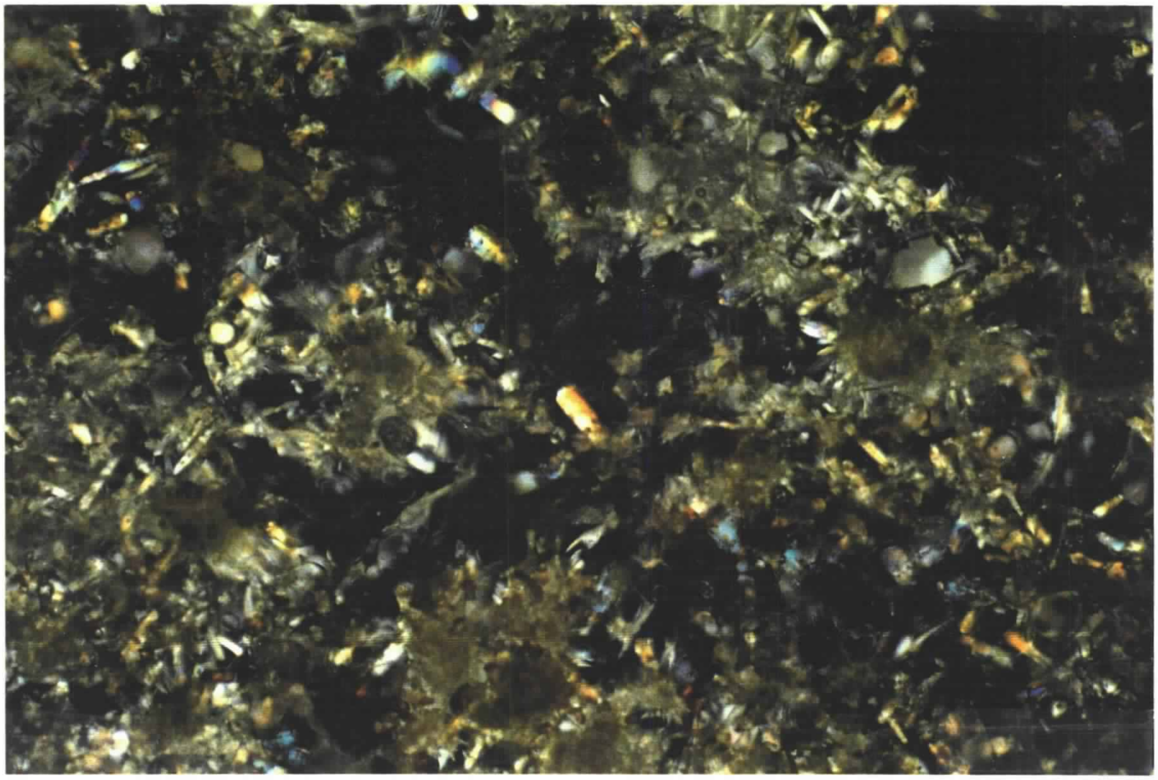
(4) HIP

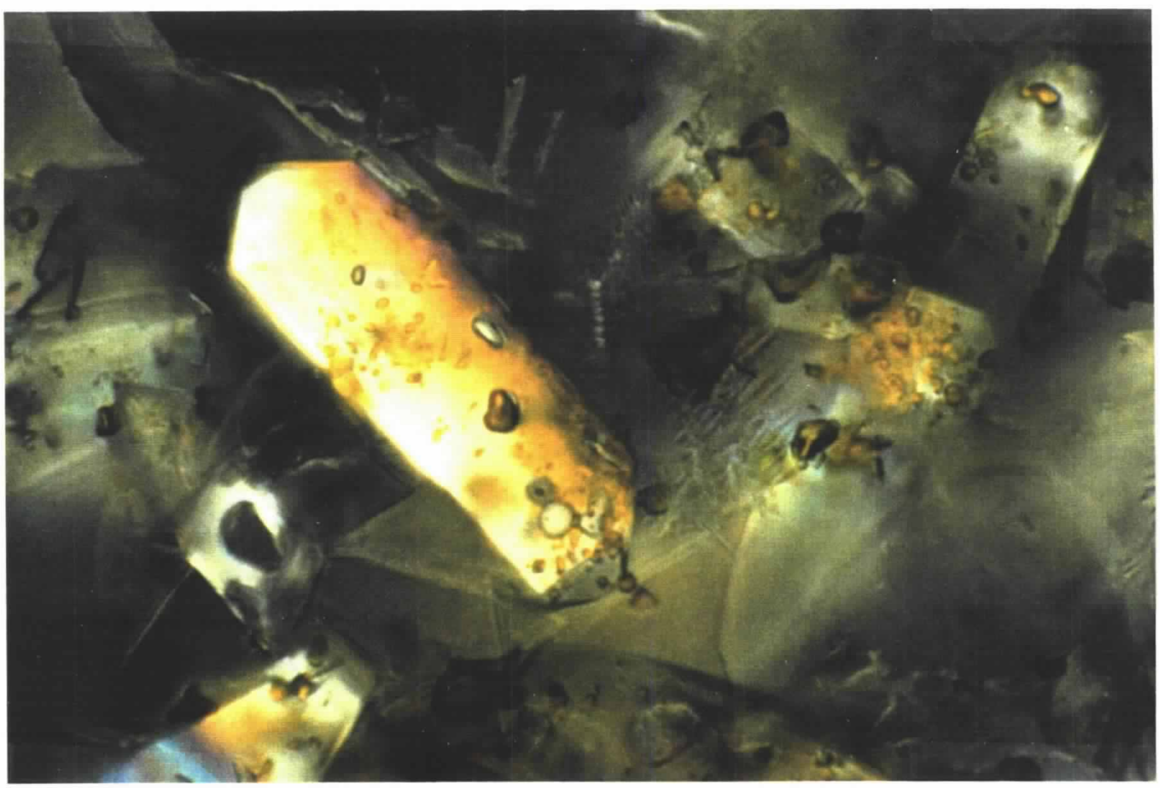


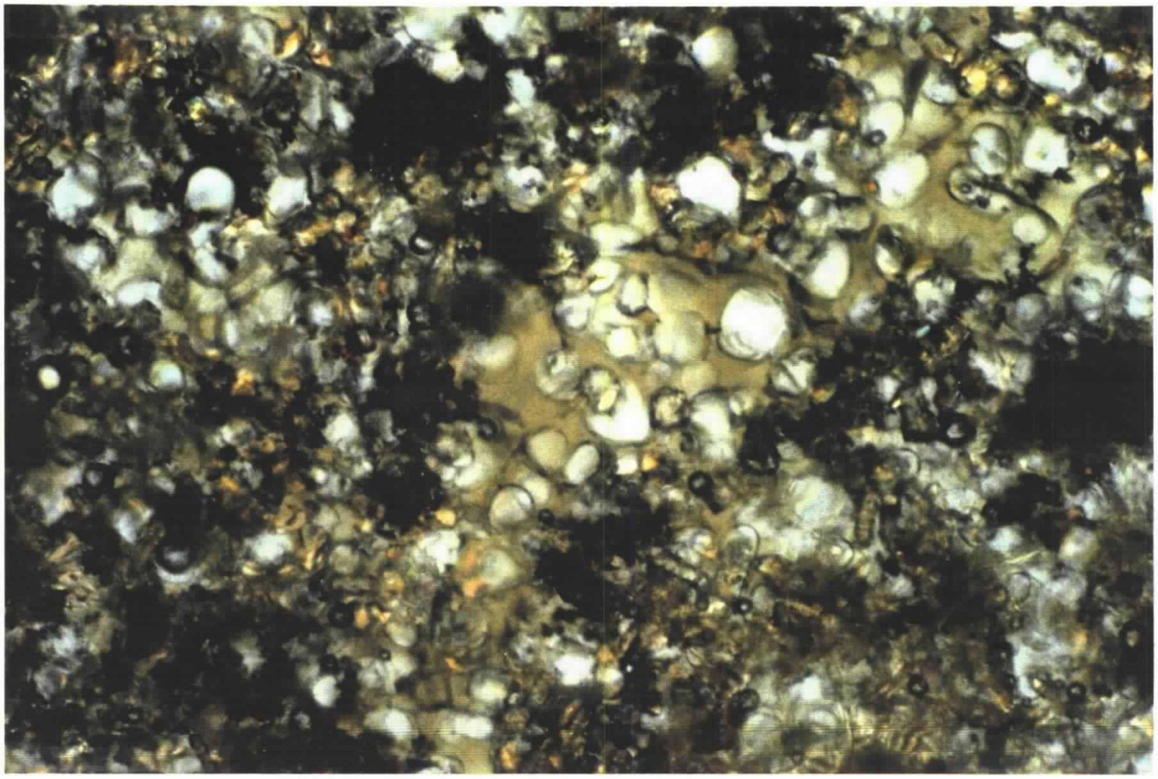
(5) ANNEAL

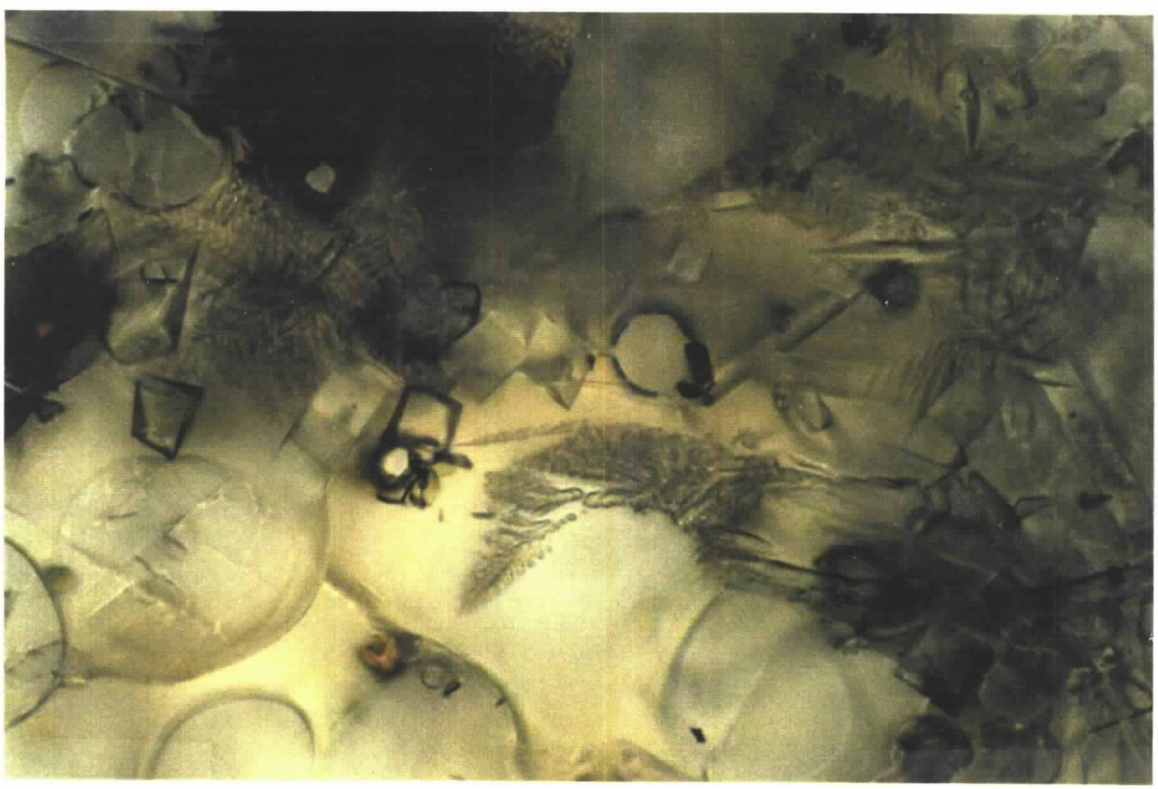


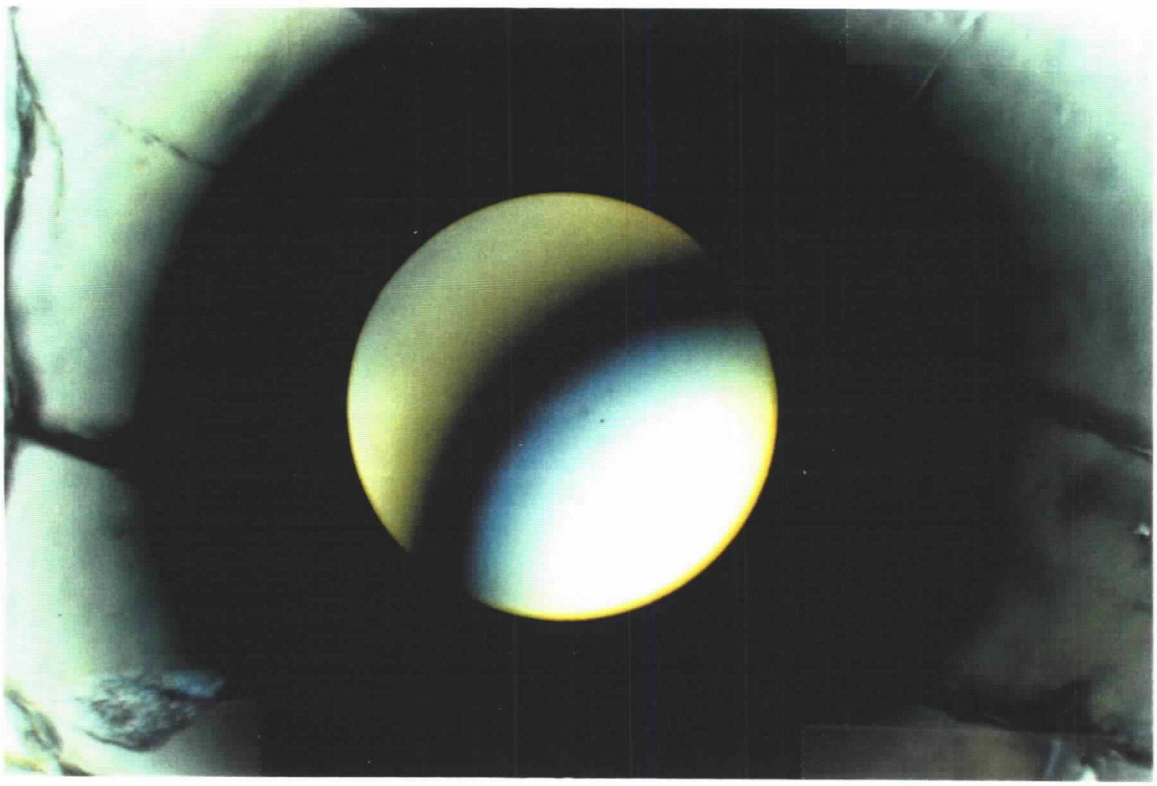


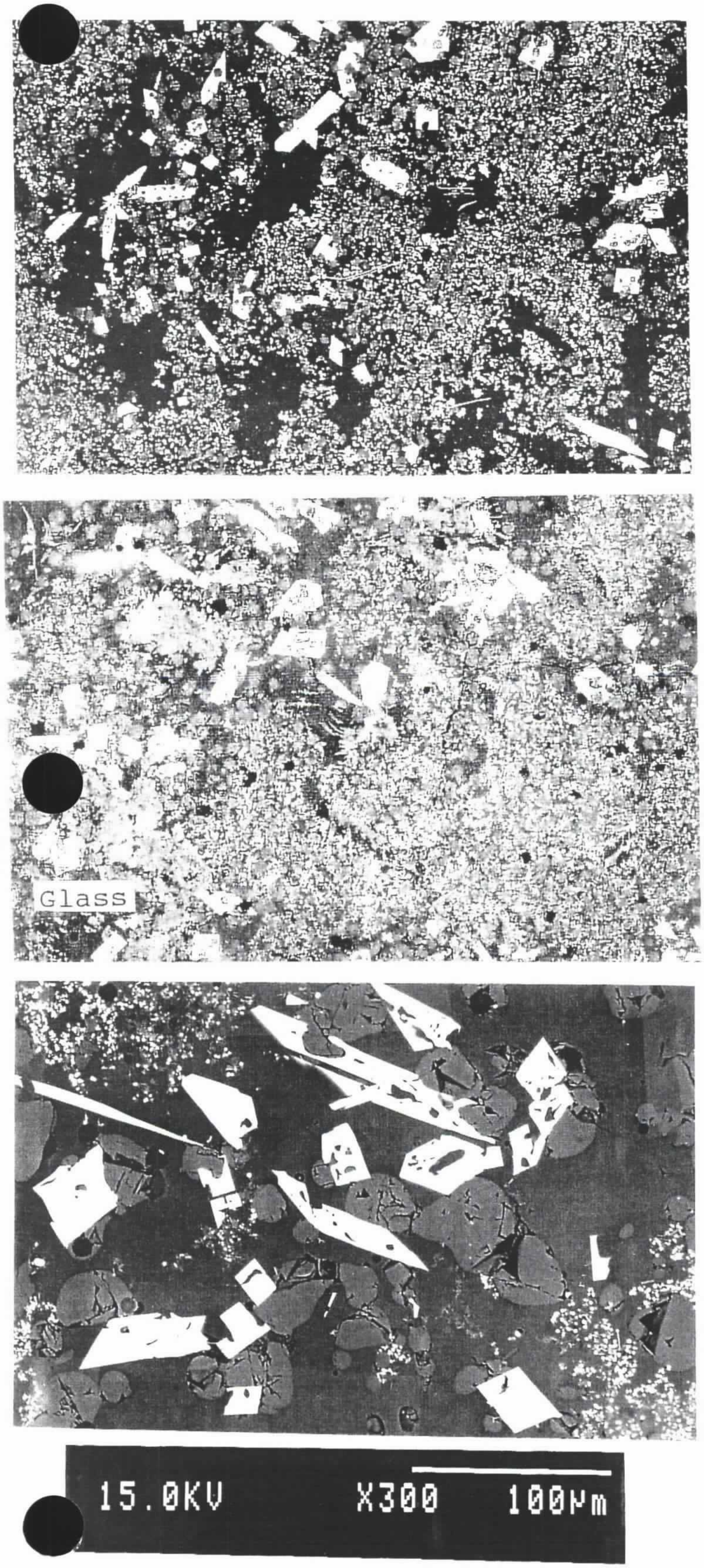


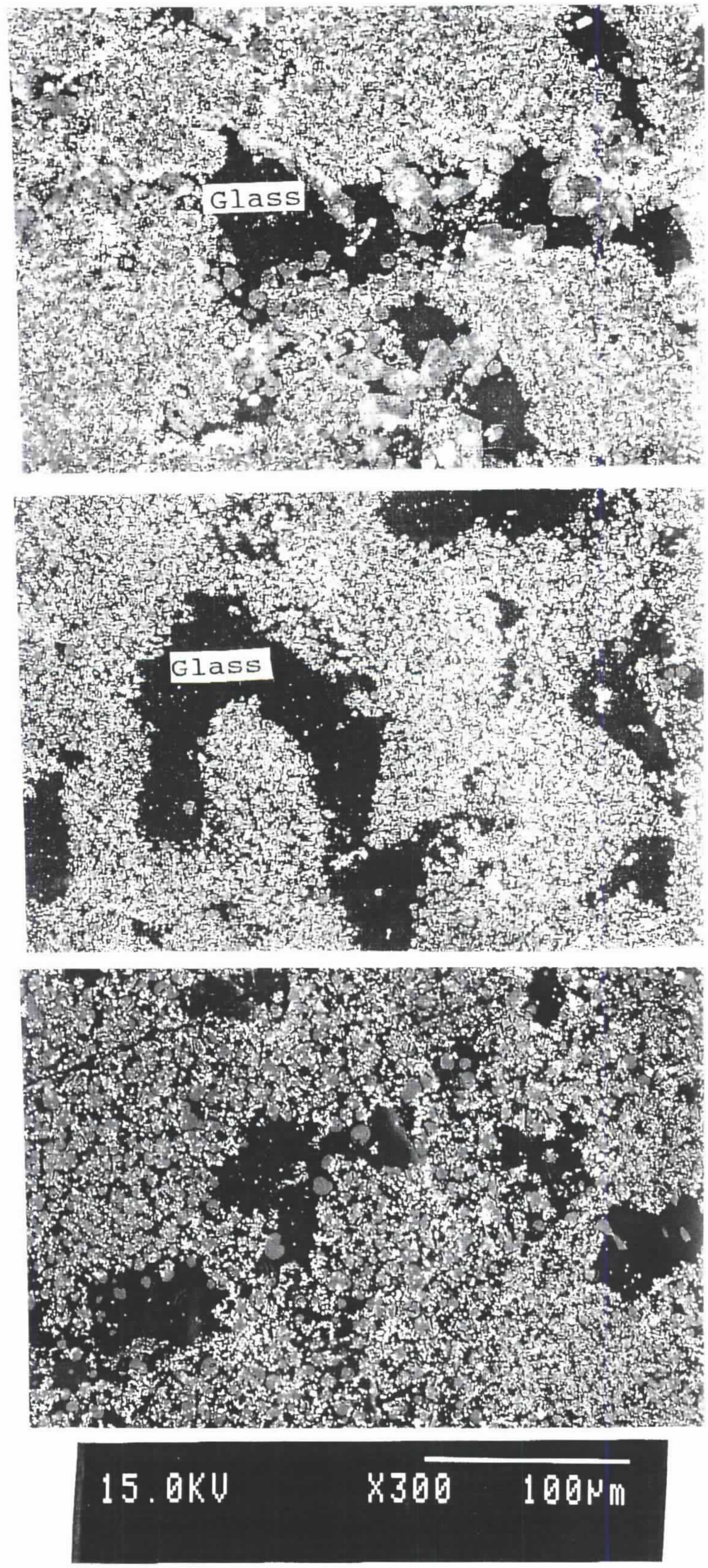


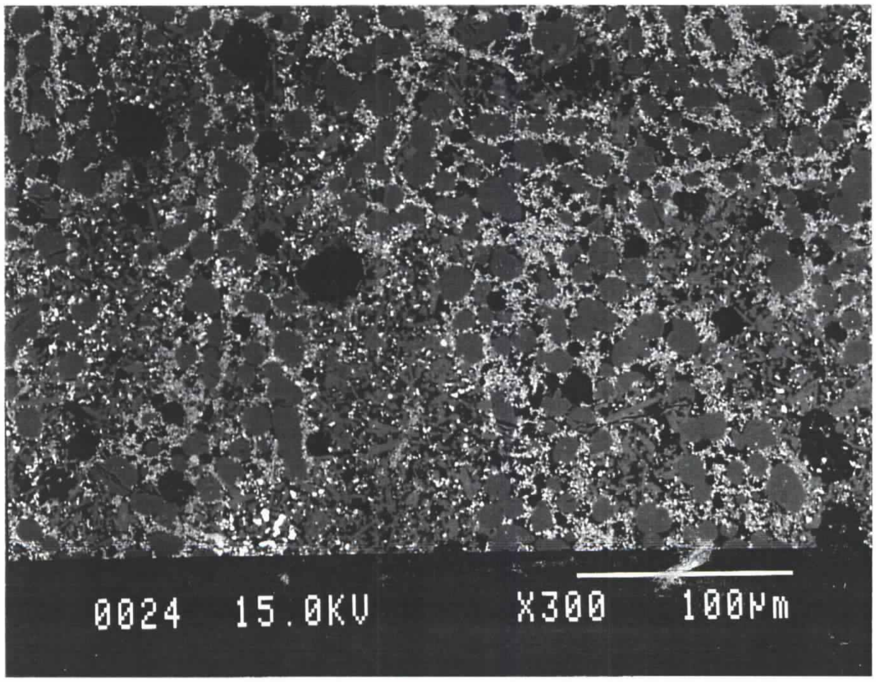







Glass
15.0KV X300 100μm


Glass
Glass
15.0KV X300 100μm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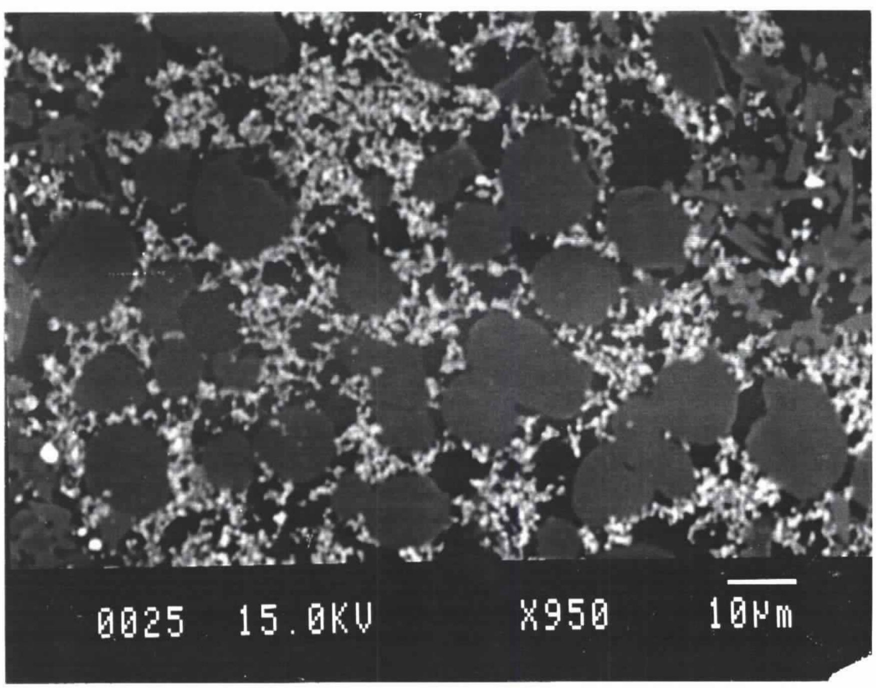
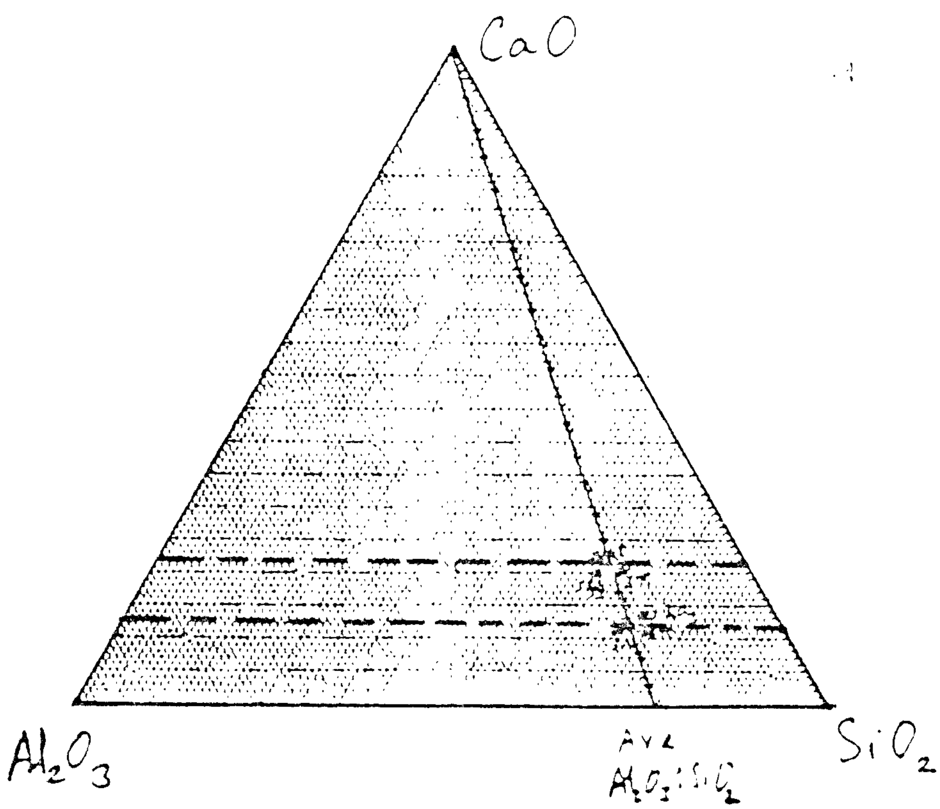

0025 15.0KV X950 10µm

ELECTRON MICROPROBE ANALYSIS OF GLASS COMPOSITIONS (WT%)

Component	3Ti	6Ti	1Al	3Al	5B_2O_3	3B_2O_3
Al_2O_3	14.51	13.38	15.69	20.11	17.19	15.63
B_2O_3	5.32	7.21	6.36	6.70	4.51	1.67
CaO	14.66	8.09	16.12	10.07	13.55	10.30
CaF_2	3.43	3.30	4.76	0.27	3.33	2.86
CoO	0.08	0.00	4.46	0.01	0.35	0.46
Ce_2O_3	1.28	1.36	0.88	0.51	0.99	0.73
Cr_2O_3	0.13	0.00	0.17	0.06	0.00	0.06
Cs_2O	0.00	0.28	0.13	0.29	0.18	0.31
FeO	1.21	0.00	0.41	0.01	0.77	0.65
K_2O	1.65	1.37	1.65	1.92	1.55	1.73
Na_2O	2.19	4.39	1.01	1.30	4.89	4.36
SiO_2	47.93	50.72	44.11	55.10	48.31	56.39
SrO	0.78	0.70	0.64	0.51	0.53	0.52
TiO_2	2.76	3.59	0.00	0.00	0.00	0.00
ZrO_2	4.02	4.62	3.11	3.14	3.85	3.33
Total	100.00	100.00	100.00	100.00	100.00	100.00



$-B_2O_3-SiO_2$

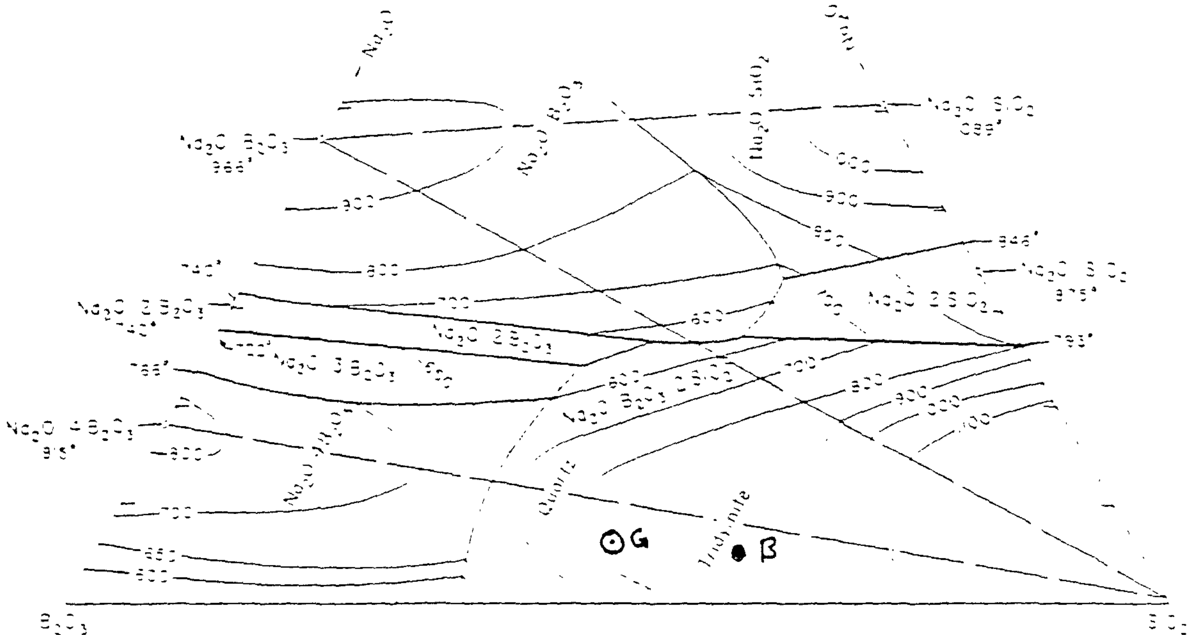
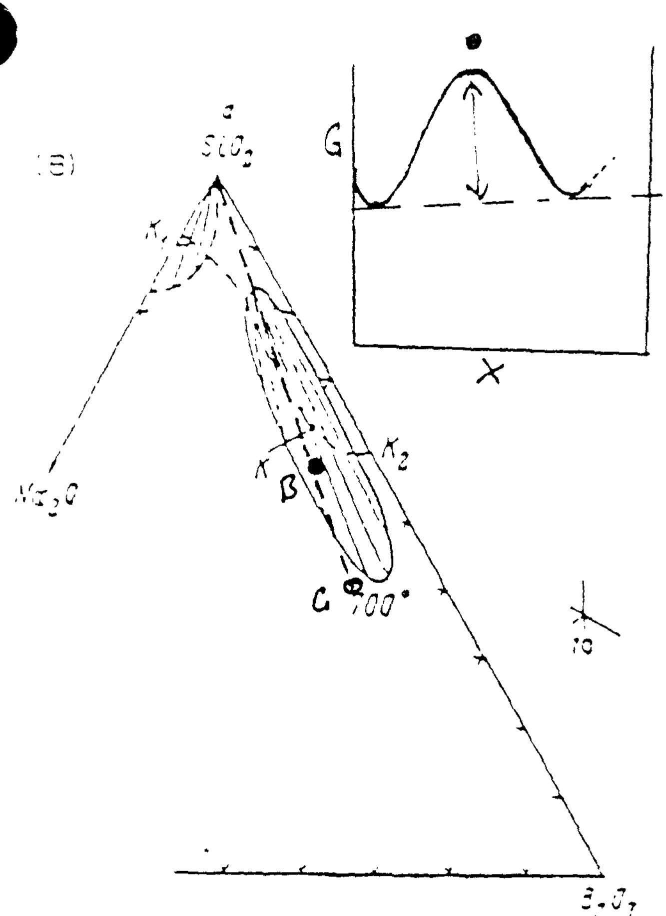
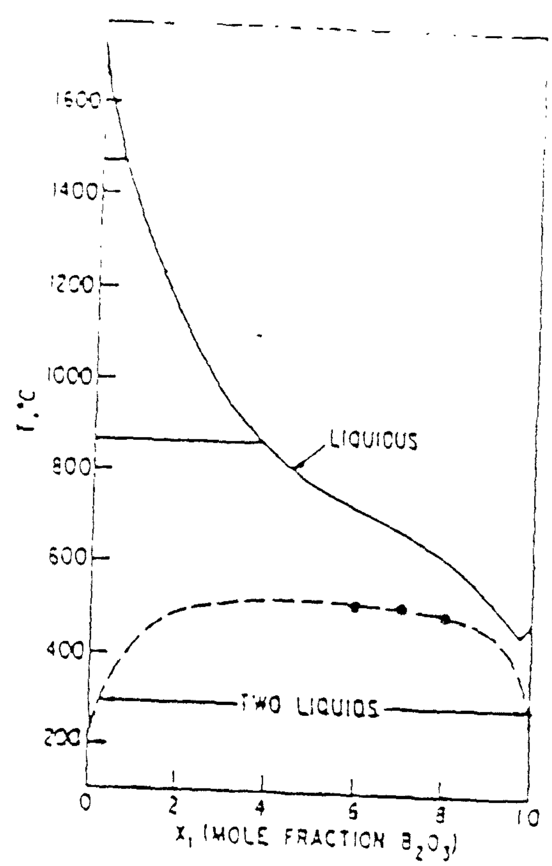
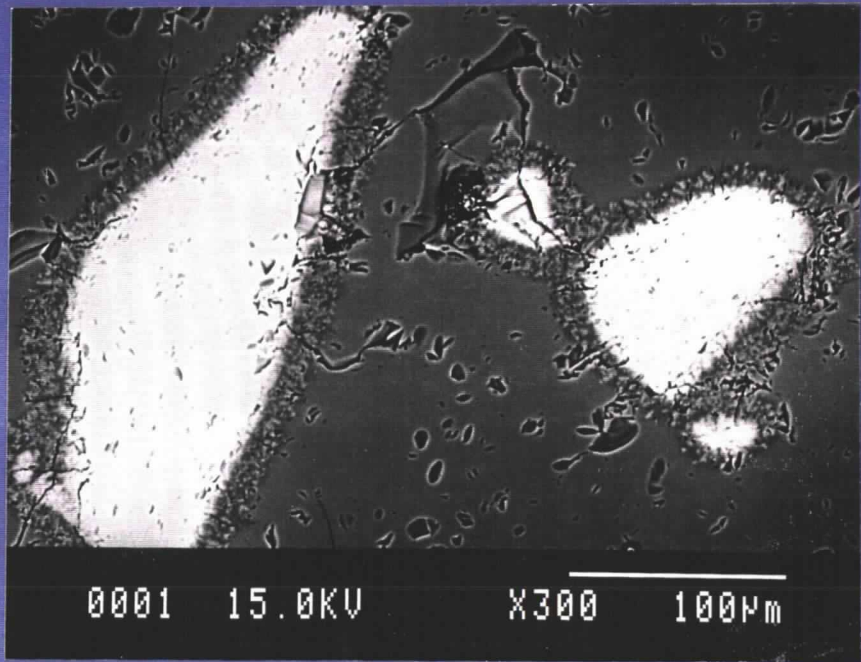


FIG. 515.—System $Na_2O-B_2O_3-SiO_2$.

G. W. Morey, J. Soc. Glass Tech., 35, 270 (1951). On the Na_2O-SiO_2 boundary, the lower of the two compounds labeled $Na_2O \cdot SiO_2$ should read $Na_2O \cdot 2SiO_2$.



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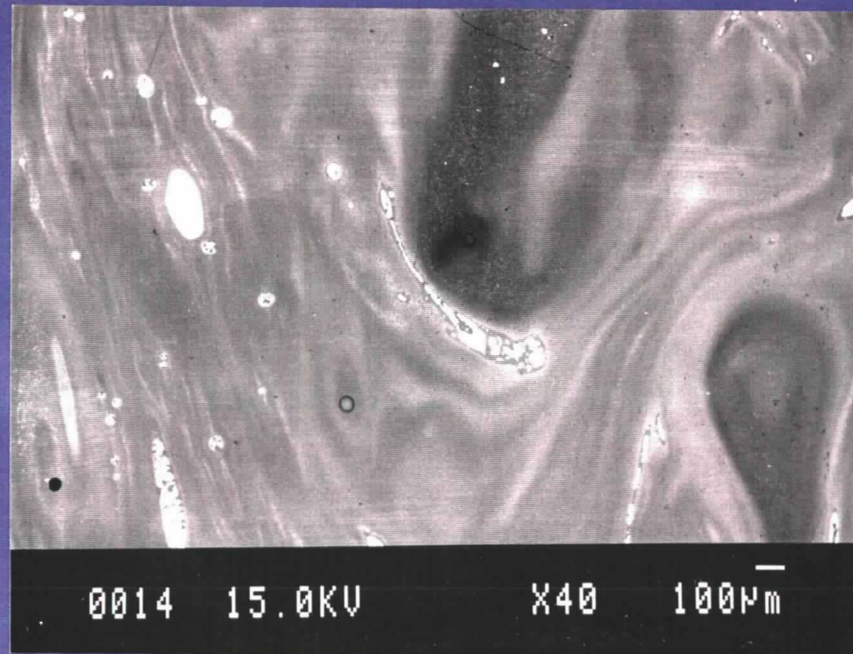
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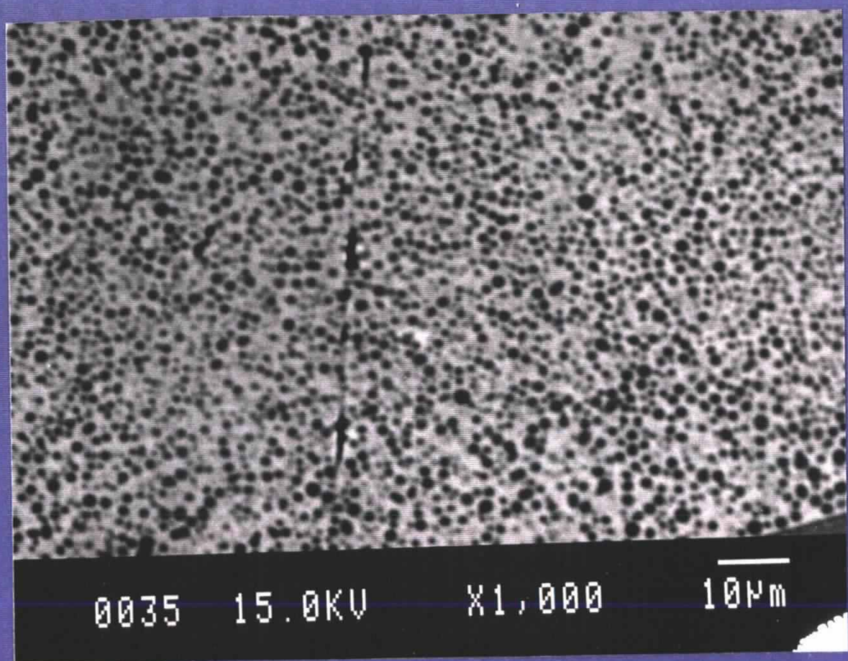
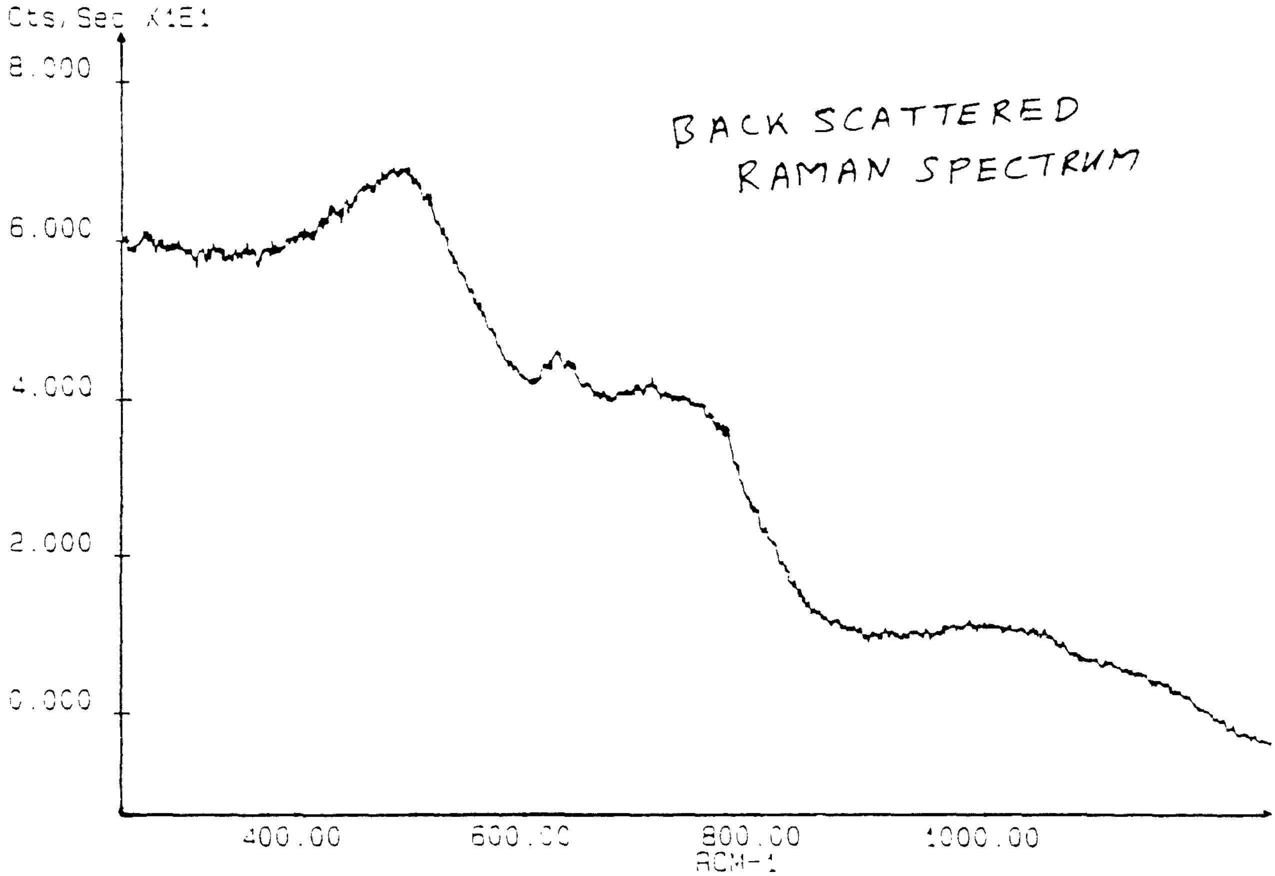
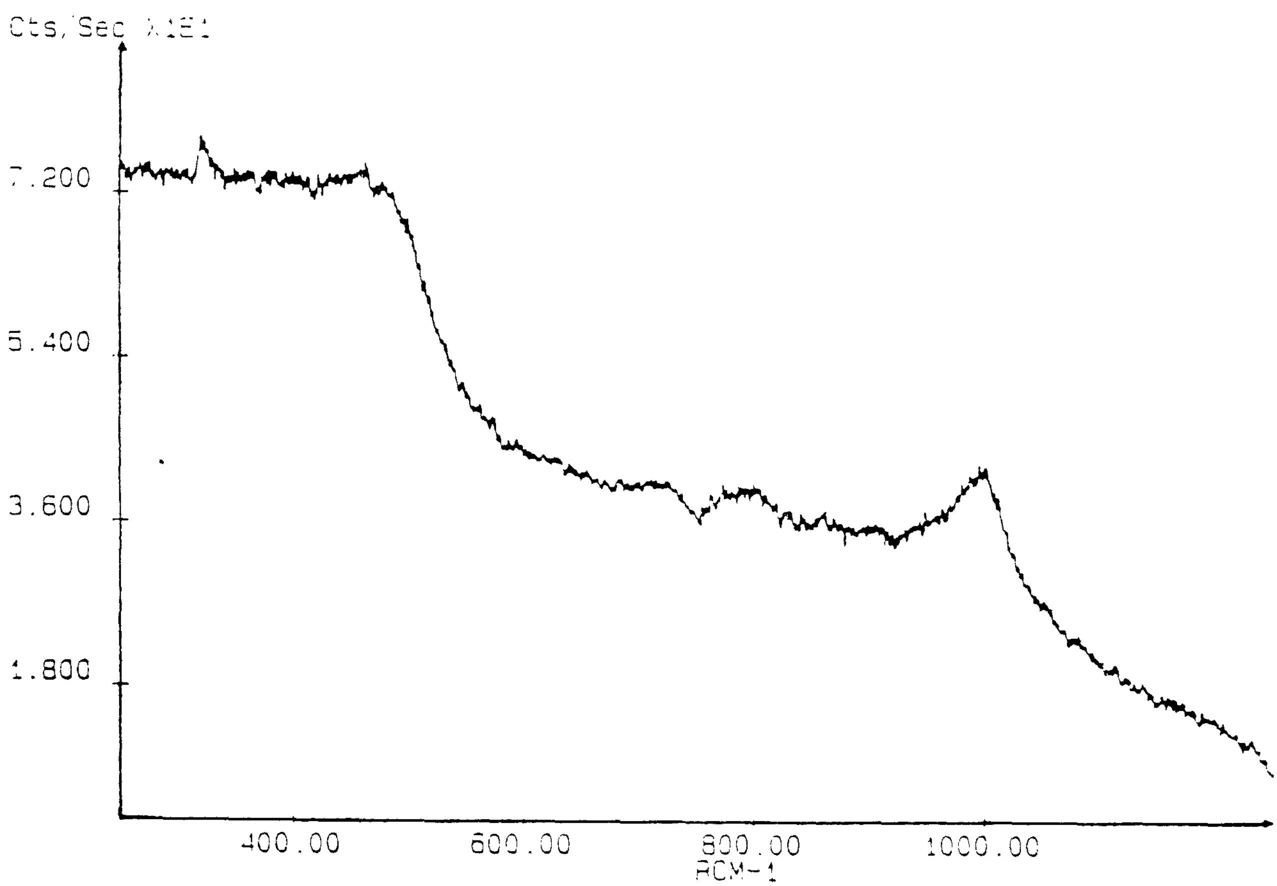

0035 15.0KV X1,000 10µm


0015 15.0KV X1,000 10µm



Cts/Sec X1E1
8.000
6.000
4.000
2.000
0.000
400.00
600.00
800.00
1000.00
RCM-1
BACK SCATTERED
RAMAN SPECTRUM



Cts/Sec X1E1
7.200
5.400
3.600
1.800
400.00
600.00
800.00
1000.00
RCM-1

X-RAY POWDER DIFFRACTION ANALYSIS OF CRYSTALLINE PHASES (WT%)

Glass-Ceramic	CaF_2	ZrO_2	$ZrSiO_4$	$CaTiSiO_5$	CdS	Cd	$Cr_2Ti_7O_{18}$	$Ca_3(Fe,Ti)_2(Si,Ti)_3O_{12}$	$NaAlSi_3O_8$	$CaAl_2Si_2O_8$
3Ti	26.10	22.70	29.90	11.90	-	6.70	2.70	-	-	-
6Ti	31.30	27.20	3.20	-	-	12.00	3.50	8.50	-	-
1Al	38.00	23.00	32.00	-	-	14.00	-	-	-	-
3Al	36.00	37.00	-	-	-	-	-	-	-	12.00
$5B_2O_3$	35.50	20.70	23.90	-	7.20	-	-	-	-	-
$3B_2O_3$	33.80	30.30	11.40	-	8.50	-	-	-	10.10	-

14- DAY MCC-1 LEACH RATES (GRAMS/SQUARE METER-DAY)

		Normalized Elemental Leach Rates g/m^2-d)									
Glass Ceramic	Total Mass Rate (g/m^2-d)	Al	B	Ca	Cd	Cs	Cr	K	Na	Si	Sr
3Ti	0.29	0.92	0.35	0.21	0.06	1.32	0.00	0.84	1.39	0.73	0.31
6Ti	0.17	0.38	0.10	0.27	0.62	0.27	0.00	0.38	0.52	0.30	0.29
1Al	1.45	0.68	0.92	0.81	0.00	2.24	0.00	2.29	9.81	0.74	2.87
3Al	0.40	0.69	0.63	0.37	0.20	0.69	0.00	0.53	0.79	0.82	0.56
$5B_2O_3$	0.32	0.61	0.47	0.26	0.12	0.13	0.00	0.31	0.54	0.66	0.51
$3B_2O_3$	0.27	0.44	0.09	0.25	0.33	0.00	0.00	0.23	0.40	0.54	0.39

SUMMARY AND CONCLUSION

CALCINE ACCOMMODATED BOTH IN GLASS AND CERAMIC PHASES, HENCE HIGH CALCINE LOADING IN GLASS-CERAMIC WASTE FORMS

GLASS-CERAMIC WASTE FORMS CONTAIN NATURALLY COMPATIBLE CRYSTALLINE PHASES AND GLASS, HENCE POTENTIAL FOR HIGH DURABILITY

BOTH GLASS SOLUBLE AND GLASS INSOLUBLE COMPONENTS ACCOMMODATED IN THE GLASS-CERAMIC, HENCE NO ADDITIONAL WASTE GENERATED

DURABLE GLASS AND CRYSTALLINE PHASES FORMED AT LOWER TEMPERATURES UNDER THE INFLUENCE OF VOLATILE PRESSURE

GRAIN BOUNDARIES AND PHASE COMPOSITIONS MUST BE ENGINEERED AS A FUNCTION OF PROCESS VARIABLES TO ELIMINATE MICROSTRUCTURAL DEFECTS