Thermally Induced Chemical and Structural Changes in Alumina–Zirconia–Silica Gels during the Formation of Ceramic Composites[1]

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Ceramic composites have been prepared from the system Al_2O_3–ZrO_2–SiO_2 using the sol–gel technique. The influence of catalyst acids and bases on the chemistry, structure, and morphology of the products obtained after heat treatment at various temperatures (800–1400°C) have been studied using powder X-ray diffractometry and transmission electron microscopy. Formation of compounds at higher temperatures have been shown to be related to the various acid–base reactions between the oxides and the catalyst acid or base in the sol. Formation of zircon ($ZrSiO_4$) in the presence of mullite and by direct SiO_2–ZrO_2 reactions in different compositions has been discussed. A new approach based on the molecular electronegativity differences of the component oxides has been made in order to rationalize the observed reactions. Partial charges on oxygen in various oxides have been evaluated using molecular electronegativities and are shown to be consistent both with well-known basicities of component oxides and the observed reactions. The importance of considering electronegativities in oxide reactions is emphasized. © 1990 Academic Press, Inc.

Introduction

It is well known that ZrO_2 imparts very desirable mechanical properties such as high toughness and strength when it is present in composite ceramics (*1–3*). Al_2O_3 and SiO_2 are traditional ceramic materials of great utility. It is therefore necessary to examine the effect of ZrO_2 on ceramics containing both Al_2O_3 and SiO_2. A few investigations have been reported in the literature on the related mullite–ZrO_2 composite systems (*4–6*). Of the three oxides chosen for the study, Al_2O_3 and ZrO_2 react independently with SiO_2 giving rise to well-defined compounds at high temperatures. The compound formation influences the properties of the resulting ceramics. The sol–gel route has been adopted for the preparation of ceramic composites from Al_2O_3–ZrO_2, ZrO_2–SiO_2, Al_2O_3–ZrO_2–SiO_2 systems by many workers (*7–10*). Catalysts appear to influence the sol–gel preparations as noted by Brinker *et al.* (*11*) and Nogami and Moriya (*12*). However, not much information is available in the literature regarding the precise role of catalysts in the preparation of gel-based high temperature ceramic materials. In this paper we examine the effect of acid and base catalysts on selected Al_2O_3–ZrO_2–SiO_2 compositions prepared by the gel route. Our observations

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suggest that the catalysts affect the gel structure which therefore determines the ultimate chemistry, structure, and morphology of high temperature products obtained after sintering.

Experimental

Gels whose compositions are given in Table I were prepared by using ethylsilicate (Mettur chemicals, Mettur, India), aluminium nitrate (E. Merck India Ltd., Bombay, India), and zirconyl nitrate (Loba Chem., India) as starting materials. The procedure for the preparation of base-catalyzed gels has been reported earlier (8). In the present case a mixture of zirconyl nitrate and aluminium nitrate solutions was added to ethylsilicate and stirred well for a few hours. Aqueous ammonia solution was slowly added to coax the gelation. For the preparation of acid-catalyzed gel, partially hydrolyzed ethylsilicate (obtained by refluxing ethylsilicate with water for a few hours at 60°C) was added dropwise to a mixture of zirconyl nitrate and aluminium nitrate. The sol mixture was further refluxed for 2–3 hr at 60°C with the addition of dilute nitric acid (0.01 molar) as a catalyst (acid to alkoxide mole ratio was taken to be 0.03). The mixture was then transferred to a beaker and kept at 70°C for a day to complete the gelation. The gel thus formed cracked into pieces when dried at 70°C for a week. These gel pieces were heated at 200°C (3 days). Powdered samples of the gels were heat treated to temperatures ranging from 600 to 1400°C by employing a heating rate of 100°C/hr. The heat-treated powders were analyzed using powder X-ray diffraction (XRD) (Phillips, Holland), with Ni-filtered Cu$K\alpha$ radiation and high resolution transmission electron microscopy (HRTEM) (Jeol 200 CX, 200 KV, Japan). The fraction of the t-ZrO_2 present in

TABLE I

TEMPERATURE–PRODUCT PHASE EVOLUTION OBSERVED THROUGH XRD STUDIES
IN THE SYSTEM Al_2O_3–ZrO_2–SiO_2

Composition Al_2O_3–ZrO_2–SiO_2 (mol%)	800°C	1000°C		1200°C		1400°C		1500°C	
		Major phase	Minor phase	Major phase	Minor phase	Major phase	Minor phase	Major phase	Minor phase
10-20-70 (BC) GB-1	a	C/T	—	C/T	—	C/T	C_1	—	—
40-20-40 (BC) GB-2	a	C/T	—	C/T	—	C/T	M	—	—
25-50-25 (BC) GB-3	a	C/T	—	C/T	—	m	A C/T Z	Z	m A
10-20-70 (AC) GA-1	a	C/T	—	C/T	A	C/T	A C_1	—	—
40-20-40 (AC) GA-2	a	C/T	—	C/T	A	C/T	Z A M C_1	—	—

Note. a, amorphous; C/T, metastable cubic/tetragonal ZrO_2; C_1, cristobalite; M, mullite; m, monoclinic ZrO_2; A, α-Al_2O_3; Z, zircon; BC, base catalyzed; AC, acid catalyzed.
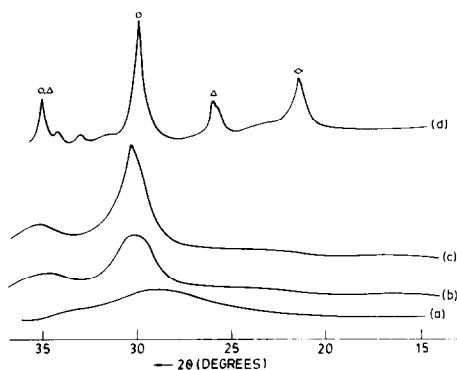
FIG. 1. XRD of GA-1 heat treated at 800°C (a), 1000°C (b), 1200°C (c), and 1400°C (d) (O, C/T ZrO$_2$; △, Al$_2$O$_3$; ◇, cristobalite).
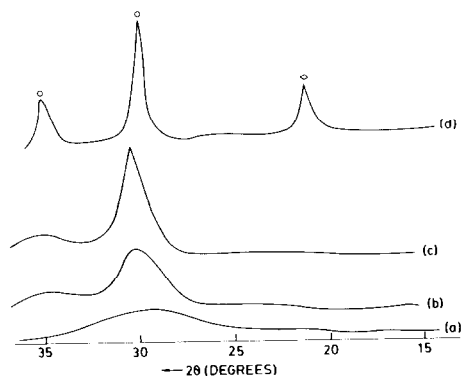
FIG. 3. XRD of GB-1 heat treated at 800°C (a), 1000°C (b), 1200°C (c), and 1400°C (d). (O, C/T ZrO$_2$; ◇, cristobalite).

the sample was estimated using the equation (13)

$$F_t = \frac{I_t\,(111)}{I_t\,(111) + I_m\,(111) + I_m\,(11\bar{1})}$$

where $I_t\,(111)$, $I_m\,(111)$, and $I_m\,(11\bar{1})$ refer to the intensity of (111) reflection of tetragonal, monoclinic, and (11$\bar{1}$) reflection of monoclinic, respectively.

Results and Discussion

The XRD patterns of the heat-treated powders obtained from both acid- and base-catalyzed gels at various temperatures are given in Figs. 1–5. It may be noticed that crystallization occurs in most cases around 1000°C, while at lower temperatures the pure gel phases are amorphous in all the cases. In the region of 1200–1400°C crystallization is quite extensive and characteristic diffraction peaks are apparent in all figures. The evolution of crystalline patterns were followed, major and minor phases were identified as a function of temperature, and approximate estimates of the quantities of the products were made from the intensities of the appropriate prominent peaks in the
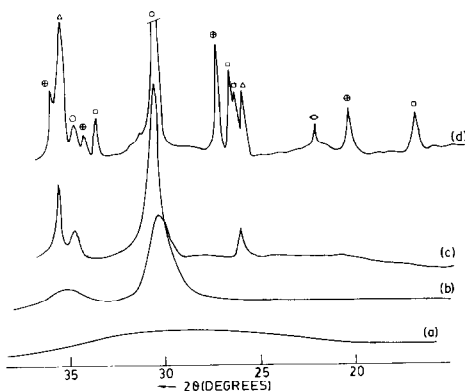

FIG. 2. XRD of GA-2 heat treated at 800°C (a), 1000°C (b), 1200°C (c), and 1400°C (d) (O, C/T ZrO$_2$; ⊕, zircon; □, mullite; △, Al$_2$O$_3$; ◇, cristobalite).
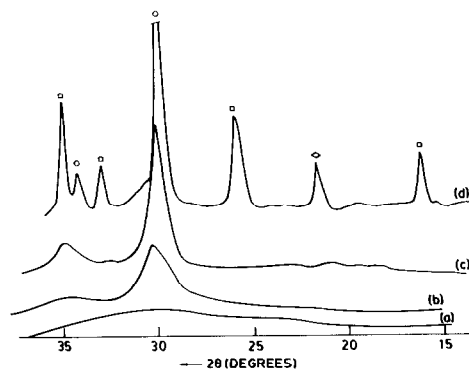
FIG. 4. XRD of GB-2 heat treated at 800°C (a), 1000°C (b), 1200°C (c), and 1400°C (d). (O, C/T ZrO$_2$; □, mullite; ◇, cristobalite).
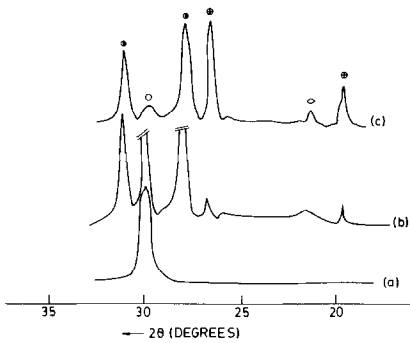
FIG. 5. XRD of GB-3 heat treated at 1200°C (a), 1400°C (b), and 1500°C (c) (◑, m-ZrO_2; ○, C/T ZrO_2; ⊕, zricon; ◇, cristobalite).

Microstructure

Base-catalyzed gels. The morphologies and ultramicrostructures were examined by electron microscopy. HRTEM of a typical base-catalyzed sample (GB-1 of Table I) heat treated at 1200°C (2 hr) is shown in Fig. 6. The particles of ZrO_2 are generally small and possess cubic/tetragonal (C/T) structure as examined by XRD. (It is difficult to assign their crystal structures uniquely since the diffraction patterns can be indexed reasonably satisfactorily for both cubic and tetragonal structures.) This aspect has been discussed by us earlier (*8*). The particle sizes are typically of the order of 50 Å. Figure 6 indeed shows fringes within the particulates. Light regions between the particles in Fig. 6 may arise from cristobalite which also begins to crystallize together with ZrO_2 around this temperature. However, cristobalite peaks in XRD

diffraction pattern. The temperature–product phase evolution is summarized in Table I; the product phases are listed in the decreasing order of their estimated quantities.
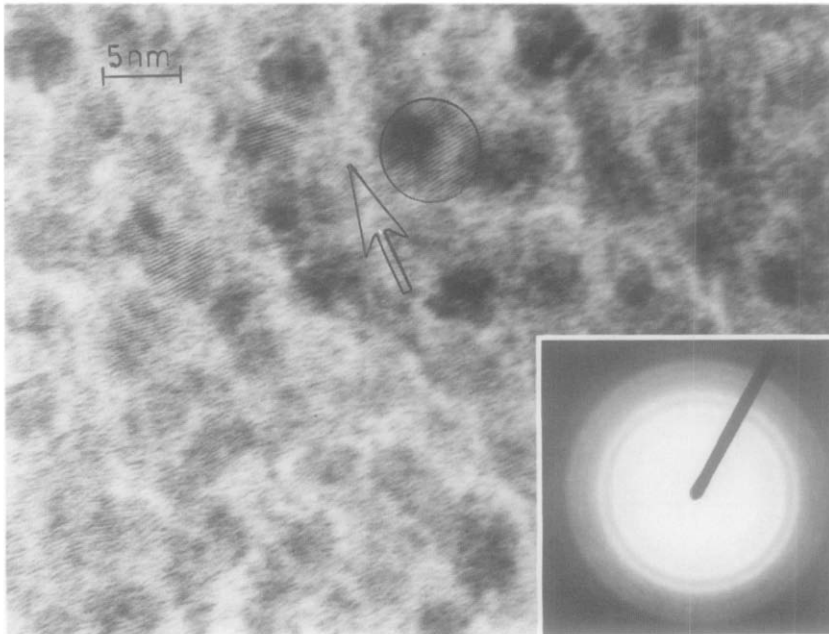

FIG. 6. High resolution image of GB-1 heat treated at 1200°C for 2 hr, showing fine fringes corresponding to C/T ZrO_2 (encircled). The glassy phase (arrow-marked) is seen as light regions. Inset shows electron diffraction pattern of polycrystalline C/T ZrO_2.
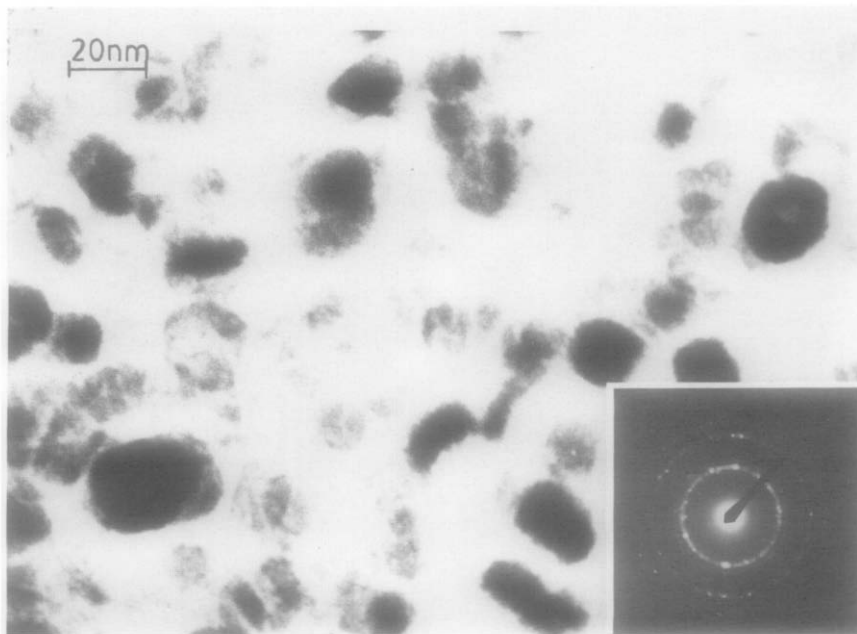
FIG. 7. TEM micrograph of GB-3 heat treated at 1200°C for 2 hr, showing C/T ZrO_2 particles. Inset: Electron diffraction pattern of polycrystalline C/T ZrO_2.

become evident only at 1400°C (Fig. 1). GB-3 heat treated to 1200°C gives rise to products whose microstructure is quite complex. Faceted particles of (C/T) ZrO_2 are seen often surrounded by an amorphous matrix of alumino silicates (Fig. 7). When heated to 1500°C zircon crystals grow in size typically up to 2000 Å, and appear to be coated with a second phase of aluminosilicates. A micrograph of one such large particle and its diffraction pattern is shown in Fig. 8. The diffraction pattern has additional spots and we feel that they arise from Al_2O_3-rich aluminoslicates (see later) adhering to the surface of zircon with a specific orientation relation although we are unable to confirm it.

Acid-catalyzed gels. The microstructures of GA-1 indicate the formation of the (C/T) phase of ZrO_2 below 1200°C. Cristobalite and Al_2O_3 are formed only at 1400°C. In GA-2 composition, however, large Al_2O_3

crystallites formed around 1200°C are surrounded by finer particles of ZrO_2 of typical spheroidal morphology (Fig. 9). Heat treatment of GA-2 to 1400°C gives rise to zircon, Al_2O_3, mullite, and cristoballite. However, the presence of the minor phases (like zircon) could be identified only in X-ray diffractograms. Our X-ray work did not enable us to follow the structural evolution of the many Al_2O_3 phases reported in the literature (*14*).

The role of acid–base catalysts. One striking observation in our studies is that even gels of identical compositions like GA-2 and GB-2 give rise to differences in chemistry and morphology of products obtained by heating up to 1400°C. It is an indication that catalysts control the initial gel structures although they are fully eliminated from the systems upon heating well below the sintering temperatures. Catalysts, therefore, set the complexion of the
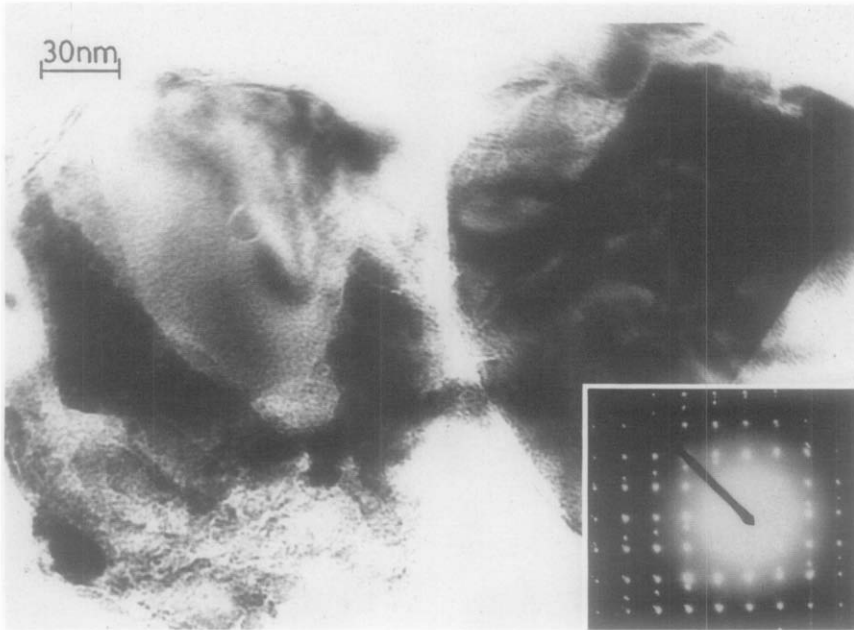
FIG. 8. TEM micrograph of GB-3 heat treated at 1500°C for 2 hr, showing zircon crystals with probable adhesion of an aluminosilicate phase. Inset shows single crystalline diffraction pattern of zircon, with additional spots (see text).

FIG. 9. TEM micrograph of GA-2 heat treated at 1200°C for 2 hr, showing bigger α-Al_2O_3 particles (A) with finer C/T ZrO_2 particles in the background (C/T). Inset shows electron diffraction pattern of single crystalline α-Al_2O_3.

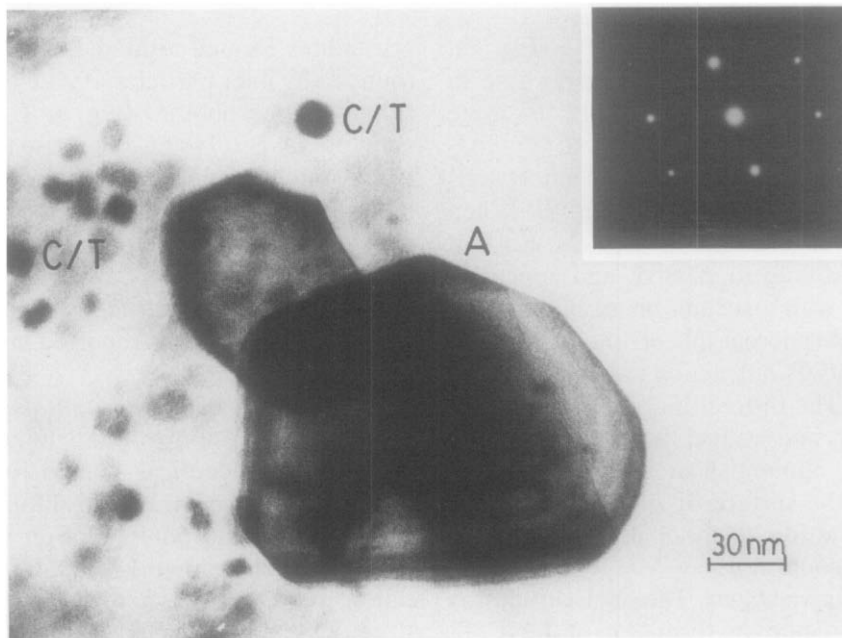reactive components in the gel. We visualize this as the nucleating step. We may note that of the three oxides involved in this study SiO_2 is acidic, Al_2O_3 is amphoteric, and ZrO_2 is basic in their chemical nature. Hence at the stage of sol–gel consolidation, presence of acids and bases can influence the gel structure via their chemical affinities. Oxides in the sol would cohere into microphases in the presence of catalyst acids or bases if there is a reaction between the oxide and the catalyst. We examine below this aspect in slightly greater detail.

SiO_2, Al_2O_3, and ZrO_2 may be represented as a_1, (a_2/b_2), and b_3 implying that they are acidic (a), amphoteric (a/b), and basic (b), respectively. The added catalysts are represented as A (acid) and B (base). A and B are strong acid and strong base respectively compared to the oxides themselves. We consider first the case of an acid (A)-catalyzed gel, GA-1. Several acid–base products are expected to form in the gel. In order to determine the possible acid–base reaction products we ignore acid–acid reactions like $a_1 + A$ (although in presence of a strong acid, SiO_2 may behave like a weak base) and the trivial self reaction like $a_2 + b_2$. Further, reactions with A such as $b_2 + A$ and $b_3 + A$ will ultimately leave behind b_2 and b_3 respectively when the gel is heated to higher temperatures. Thus the acid-catalyzed gel should consist of a_1, b_2A, b_3A, b_2a_1, and b_3a_1. Since there is no reported compound formation between ZrO_2 and Al_2O_3 (15, 16), (b_3a_2) is also ignored. The expected products are therefore cristobalite, Al_2O_3, ZrO_2, mullite, and zircon. However, preferences for strong acid–strong base reactions are well known in acid–base chemistry. Therefore the gel structure would be dominated by the formation of b_3A compared to b_3a_1. Aggregation of b_3A causes microscopic unmixing of b_3A and a_1. Hence it leads to a suppression of the formation of b_3a_1 (zircon) in acid-catalyzed gels. Thus the product from the heated gel

may be expected to contain crystobalite (a_1), alumina (b_2/a_2), zirconia (b_3) along with mullite (a_1b_2). This is clearly borne out in Table II.

When alumina concentration is very high as in GA-2, formation of b_2a_1 (mullite) is expected to be the dominant mass law dictated reaction. However, mullite in turn can dissolve ZrO_2 and SiO_2 and this may result in the formation of zircon in the mullite matrix at higher temperatures. Indeed zircon formation as a minor phase in GA-2 is confirmed by XRD. We will see later that mullitic (aluminosilicate) phases are often present surrounding zircon crystals which supports the above viewpoint. We have examined all possible reactions in GA-2 and all the expected phases namely cristobalite, mullite, and Al_2O_3 along with zircon have been identified from XRD studies and listed in Table I.

Base catalysis can also be examined in a similar manner. Ba_1 (reaction with SiO_2) is the most significant product of catalyst reactions. ZrO_2 would not be expected to react chemically with B. Thus ZrO_2 would be rather evenly distributed in the gel structure with isolated regions of SiO_2. Al_2O_3 should also exhibit a tendency to form isolated regions in the gel as it reacts with the base catalyst. In the gel one would therefore expect SiO_2 and Al_2O_3 regions isolated by surrounding ZrO_2. At high temperatures SiO_2 may be expected to react with the sur-

TABLE II

Acid–Base Reactions Considered
in the Acid-Catalyzed Gel GA-1[a]

$b_2 + A$	$\longrightarrow b_2$
$b_3 + A$	$\longrightarrow b_3$
$a_1 + b_2$	$\longrightarrow a_1b_2$ (mullite)
$a_1 + b_3$	$\longrightarrow a_1b_3$ (zircon)
$a_2 + b_3$	$\longrightarrow$ No compound formation

[a] See text for abbreviations.

rounding ZrO_2. However, zircon is surprisingly not found to form in GB-1. The SiO_2-rich GB-1 composition forms only cristoballite at high temperatures. This may be so partly because GB-1 is compositionally poor in both ZrO_2 and Al_2O_3. However, we may note that SiO_2 and ZrO_2 do not react readily even at high temperatures. It suggests simply that mere presence of Al_2O_3 is not enough for the ZrO_2–SiO_2 reaction. It is possible that formation of mullite by the reaction of SiO_2 and Al_2O_3 is a necessary precondition. As noted earlier, SiO_2 and ZrO_2 dissolve in mullite and may then react to form zircon. An increase of Al_2O_3 content in GB-2 indeed results in the formation of mullite as expected. But ZrO_2 is not concentrated enough and therefore a detectable quantity of zircon is still not formed.

GB-3 is, however, a ZrO_2-rich composition where the minor components Al_2O_3 and SiO_2 can be expected to form small separated islands in the gel, due to reactions with the added base. Since somewhat larger and perhaps continuous (unrestrained) regions of ZrO_2 are present in the gel structure the latter transforms from metastable tetragonal to the monoclinic phase at temperature higher than 1200°C. Al_2O_3 remains as an essentially unreacted phase. The monoclinic form of ZrO_2 appears to react with the fine particles of SiO_2 and form zircon. This situation is microstructurally different from what we encountered earlier (8) in the binary ZrO_2–SiO_2 system where ZrO_2 particles were always surrounded by SiO_2. This may be due to at least two important reasons. First, the so-called Hedvall effect (17) which enhances the reactivity of ZrO_2 at its (t–m) phase transformation temperature. Second the increased volume of m-ZrO_2 (compared to t-ZrO_2), which can reduce the barrier for reactive mixing of ZrO_2 and SiO_2. Nevertheless, formation of zircon in GB-3 we feel may not be mediated by the presence of mullite.

Electronegativity and Oxide Reactions

An important driving force for the direct ZrO_2–SiO_2 reaction in GB-3 could be the difference in the molecular electronegativities of ZrO_2 and SiO_2. These molecular electronegativities are defined here as the geometric mean of the electronegativities of atoms in a formula unit (18). The electronegativities of atoms for the evaluation of molecular electronegativities have been taken from Ref. (19). The molecular electronegativities so evaluated for SiO_2, Al_2O_3, ZrO_2, $ZrSiO_4$ (zircon), and $Al_6Si_2O_{13}$ (mullite) are given in Table III. SiO_2 and ZrO_2 have the highest electronegativity difference which is the chemical driving force for the reaction between ZrO_2 and SiO_2 much in the same manner as basicity differences which are inversely related to molecular electronegativities (see later). While a somewhat similar driving force exists between SiO_2 and Al_2O_3, we may recall that in GB-3 they are minor constituents and occur as separated regions in the catalyst-manipulated gel structure; they are almost entirely surrounded by ZrO_2. Thus at high temperatures, formation of zircon becomes possible by direct reaction of SiO_2 and ZrO_2 which is clearly identified in the micrograph (Fig. 8). We may note here that while electronegativity differences like free energy differences indicate feasibility of reactions, ki-

TABLE III

MOLECULAR ELECTRONEGATIVITIES OF VARIOUS COMPOUNDS AND PARTIAL CHARGES ON THE IONS IN THEM

| System	X_{av}	Partial charge on			
		O	Si	Al	Zr
SiO_2	2.820	−0.2143	+0.4278		
Al_2O_3	2.537	−0.3121	—	+0.4683	—
ZrO_2	2.500	−0.3249	—		+0.6503
$ZrSiO_4$ (zircon)	2.654	−0.2718	+0.3504	—	+0.7356
$Al_6Si_2O_{13}$ (mullite)	2.615	−0.2853	+0.3323	+0.5075	—

netic barriers have to be overcome. In the present case strong covalent Si–O bonds are to be excited before it can react with ZrO_2 and hence the requirement of high temperature for the reaction. Al_2O_3 present in GB-3 also crystallizes. When Al_2O_3 crystallizes in the neighborhood of zircon crystals, it appears to stick to the zircon surface. Al_2O_3 and zircon can indeed react (see below) because of electronegativity differences and thus zircon appears to be bound to an aluminosilicate product with some specific epitaxial relation which we believe is the origin of the additional reflections seen in Fig. 8. It is interesting to note here that Al_2O_3 and ZrO_2 have almost equal molecular electronegativities and have no chemical driving force for reactions. This is substantiated by the fact that there is no reported compound formation between ZrO_2 and Al_2O_3. Indeed recently it is observed that they form solid–solutions over a wide range of compositions (16).

That the molecular electronegativities do play an important role in the reactions can be further supported. Molecular electronegativities can be used to determine partial charges on oxygen atoms by the procedures of Sanderson (18). The calculated partial charges on the ions are listed in Table III. It can be seen that the most basic ZrO_2 carries maximum partial negative charge on oxygen and the acidic SiO_2 carries the least. The partial charge on oxygen in Al_2O_3 is close to that of oxygen in ZrO_2. Basicity may thus be reckoned on the scale of the partial charges on oxygen and therefore molecular electronegativities and basicities are inversely related. The reaction of ZrO_2 and SiO_2 ameliorates the basicity differences by the formation of zircon of intermediate basicity (Table III). Molecular electronegativities are therefore in conformity with known acid–base properties of component oxides. Further, in the spirit of thermochemical basis of Pauling electronegativities, we can relate the heats of reac-

tion to molecular electronegativities (20); $\Delta H_f^\circ = 30(\Delta\chi)^2$, where ΔH_f is the standard enthalpy of formation and $(\Delta\chi)$ is the difference in the molecular electronegativities. The heat of reaction for $ZrO_2 + SiO_2 \rightarrow ZrSiO_4$, as calculated from standard heats of formation of ZrO_2 (−262.3 kcal/mole), SiO_2 (−217.72 kcal/mole), and $ZrSiO_4$ (−483.7 kcal/mole) is 3.68 kcal/mole (21). This value may be compared with that calculated from molecular electronegativities given in Table III which is equal to $30 \times (2.8 - 2.5)^2$ and approximately equal to 3 kcal/mole; thus there is reasonably good agreement with the thermochemical data. We emphasize that the electronegativity considerations particularly in relation to reactions in GB-3 are very useful. It can be of value in considering a variety of similar reactions in ZrO_2 and related ceramics.

In systems like ZrO_2–SiO_2–Al_2O_3, we should consider other possible reactions also using molecular electronegativity differences. Thus for example, zircon in contact with alumina particles cannot be a stable situation, because the reaction

$$2ZrSiO_4 \text{ (zircon)} + 3Al_2O_3 \rightarrow$$
$$Al_6Si_2O_{13} + 2ZrO_2$$
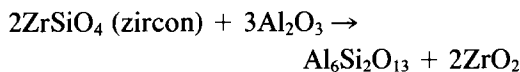
can be driven by basicity differences. Such a reaction can reduce the total basicity to some suitable intermediate value (Table III). We assume that the reaction proceeeds till the weighted sum of the partial charges on oxygen (or equivalently molecular electronegativity) of reactants and products become equal. Then the reaction between zircon and alumina proceeds up to about 60–70% before cessation. We may note in this connection that reaction does not occur between alumina and zircon particles well separated by mullite phases (22).

Summary and Conclusions

Influence of acid and base catalysts on the chemistry structure and morphology of

Al_2O_3–ZrO_2–SiO_2 ceramics has been investigated. Catalysts influence structure through acid–base reactions which take place before gelation. High temperature reactions can be understood through a consideration of molecular electronegativities which are simply related to their basicities.

Acknowledgment

References

1. N. CLAUSSEN AND M. RUHLE, in "Advances in Ceramics," Vol. 3, "Science and Technology of Zirconia" (A. H. Heuer and L. W. Hobbs, Eds.), p. 137, American Ceramic Society, Columbus, OH (1981).

2. A. H. HEUER, J. Amer. Ceram. Soc. 70, 689 (1987).

3. K. T. FABER, in "Advances in Ceramics," Vol. 12, "Science and Technology of Zirconia-II" (N. Claussen, M. Ruhle, and A. H. Heuer, Eds.), p. 293, American Ceramic Society, Columbus, OH (1984).

4. N. CLAUSSEN AND J. JAHN, J. Amer. Ceram. Soc. 56, 228 (1980).

5. M. I. OSENDI et al., J. Mater. Sci. Lett. 4, 1026 (1985).

6. J. M. RINCON et al., Acta. Metall. 35, 1175 (1987).

7. BRUCE FEGLEY, JR., PAUL WHITE, AND H. KENT BOWEN, J. Amer. Ceram. Soc. C 68, 60 (1985).

8. V. S. NAGARAJAN AND K. J. RAO, J. Mater. Sci. 24, 2140 (1989).

9. I. M. MIRANDO SALVADO, C. J. SERNA, AND J. M.

10. M. NOGAMI, K. NAGEAKA, K. KADONO, AND T. KISHIMOTO, J. Non-Cryst. Solids 100, 298 (1988).

11. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER, AND C. S. ASHLEY, J. Non-Cryst. Solids 48, 47 (1982).

12. M. NOGAMI AND Y. MORIYA, J. Non-Cryst. Solids 37, 191 (1980).

13. R. C. GARVIE AND P. S. NICHOLSON, J. Amer. Ceram. Soc. 55, 303 (1972).

14. WEN-CHENG WEI AND J. W. HOLLORAN, J. Amer. Ceram. Soc. 71, 581 (1988).

15. I. SHINDO, S. TAKEKAWA, K. KOSUDA, T. SUZUKI, AND Y. KAWATA, in "Advances in Ceramics," Vol. 12, "Science and Technology of Zirconia" (N. Claussen, M. Ruhle, and A. H. Heuer, Eds.), p. 181, American Ceramic Society, Colombus, OH (1984).

16. OSAMU YAMAGUCHI, MASAKAZU SHIRAI, AND MASARU YOSHINAKA, J. Amer. Ceram. Soc. C 71, 510 (1988).

17. C. N. R. RAO AND K. J. RAO, in "Phase Transitions in Solids," p. 13, McGraw–Hill, New York (1978).

18. R. T. SANDERSON, in "Polar Covalence," p. 39, Academic Press, New York (1983).

19. "Table Of Periodic Properties Of Elements," issued by Sargent–Welch, Skokie, IL (1979).

20. L. PAULING, in "The Nature of Chemical Bond," 3rd ed., p. 64, Cornell Univ. Press, Ithaca, NY (1960).

21. "Lange's Handbook of Chemistry," (John A. Dean, Ed.), p. 9.4, McGraw–Hill, New York (1985).

22. J. S. WALLACE, G. PETZOW, AND N. CLAUSSEN, in "Advances in Ceramics," Vol. 12, "Science and Technology of Zirconia" (N. Claussen, M. Ruhle, and A. H. Heuer, Eds.), p. 436, American Ceramic Society, Columbus, OH (1984).

FERNANDEZ NAVARRO, J. Non-Cryst. Solids 100, 330 (1988).