

Catalysis of low temperature synthesis of ceramics

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The desirability of the synthesis of materials at low temperatures is becoming evident in many major technologies. The principal obstacle is the slow kinetics of both combination and re-ordering to, and within, crystalline arrangements of ions at these low temperatures. This paper reviews several different methods, used by his group over the last 40 years. Results very recently developed in the author's laboratory are described in some detail. The methods for accelerating reactions in oxide materials at temperatures in the range of 0°-500°C include:

1. Utilizing precursors made via solution-sol-gel and, recently, epitaxy via nanocomposite gel routes.
2. Using low melting "fluxes."
3. (a) Hydrothermal processes.
(b) Hydrothermal process with superimposed electric fields.
(c) Hydrothermal process with mechanical forces.
4. Mechano-chemical effects including very high uniaxial pressure and shear.
5. Acoustic wave stimulation (sonochemical).
6. Using of ionizing and non-ionizing radiation.
7. Hydrothermal process with microwave fields.

The results will show that several of these methods can accelerate reactions of the most common oxides by 1-2 orders of magnitude, and will therefore be technologically significant. The basic science behind the processes is still primitive.

1.0 INTRODUCTION

Since 1962 the author, and the Materials Research Laboratory he directed, categorized materials research under these headings: materials **preparation**, materials **characterization**, materials **properties**. In recent years materials preparation has been referred to as materials "synthesis and processing" and the synthesis of new ceramic materials has become the goal of hundreds of groups across the world. The record shows that in spite of thousands of person years of recent effort, not much in the way of really new phases has emerged. Among HTSC materials, for example, not a single new structural family has emerged—with modest success attained by rather obvious compositional tailoring of the perovskite plus Cu-O layers. The spectacular neodymium iron boride hard magnets constitute perhaps the most significant

example of a serendipitous discovery of a significant new phase. These issues have been treated by the author¹ in a recent detailed review of the status of the content and context of ceramic materials synthesis.

While the vast majority of the research effort is devoted to (very) high temperature materials, ZrO₂, SiC, Si₃N₄, there have been few advances in any synthesis aspects of such materials. As far as really new materials are concerned, there have been much greater successes of significance in low-temperature materials. In the last three decades completely new families of zeolites with very considerable commercial value have been synthesized starting with Linde's 4A and 5A and 3X, and moving through the AlPO's to the new large pore phases. New synthetic layer structures which serve as selective adsorbers have also been synthesized. Thus low-temperature

materials are in many ways the leading edge of *new* ceramic materials synthesis. Moreover, the gradual recognition that materials made at low temperatures can be much purer and more perfect structurally also are bringing low-temperature processes into focus.

Still the vast majority of ceramic materials are made at high temperatures in the 1000°–2000°C range. The reason is simple. In solid state reactions, where solid state diffusion controls the kinetics, reaction rates are unworkably slow below that. To take the most obvious example SiO₂-quartz and Al₂O₃-corundum are not in equilibrium together in any part of the p-t plane. Yet an intimate mixture of fine powders would not react at all below nearly a thousand degrees Celsius, although thermodynamically they are less stable together than mullite, or andalusite, sillimarite and kyanite. And certainly they would not react with water, even though they should, thermodynamically to form kaolinite or pyrophyllite. The kinetics are too slow.

Hence the problem confronting the low-temperature materials synthesizer is how to increase the *kinetics* of reaction of ceramics to catalyze reactions, say, below 500°C. This is the problem I address in this paper.

2.0 OVERVIEW OF EARLIER AND CURRENT METHODS

In the following the author attempts to bring together and show the connections among many different approaches to catalyzing low-temperature reactions among solids. Table 1 groups the methods into three categories each subdivided further into several subcategories.

Category A includes six subcategories starting with reactive precursors, fluxes and hydrothermal reactions and ending with radiation catalysis. We will treat each in turn. Then we will discuss our current work on Category B methods.

Table 1
Different methods for catalyzing low-temperature reactions

A. Widespread Use Before 1980	
1.	Utilization of reactive precursors; the sol-gel approach
2.	Use of low melting salts as fluxes
3.	(a) The hydrothermal process (high p-t water)
	(b) Ditto with electric fields added
	(c) Ditto with mechanical grinding added.
4.	Mechano-chemical effects
	(a) pressure alone
	(b) pressure with shear
5.	Use of ionizing and non-ionizing radiation
B. Recent Research	
6.	Nanocomposite xerogels via Sol-Gel II
7.	Acoustic wave stimulation (sonochemistry)
8.	Hydrothermal with microwave

2.1 Known Strategies for Catalysis of Low-Temperature Reactions

2.1.1 Reactive Precursors: The Sol-Gel Process, I. The author developed the sol-gel process starting in 1948 originally explicitly to respond to the utter lack of reactivity of Al₂O₃ and SiO₂ below 500°C. By creating atomic mixing in solution both from organic or inorganic precursors, it became possible to *create highly reactive starting materials*. This is a very general solution of universal applicability in low-temperature ceramic material synthesis: use solution mixing. By the mid-fifties we had made some 5,000 such compositions in one-, two-, three-, four- and five-component systems for use as starting materials precisely for this purpose. Indeed the title of the first review of the sol-gel process² is titled, "Aids in Hydrothermal and 'Wet' (Low Temperature) Phase Equilibrium Studies." The variety of hydroxylated

phases—dozens of them quite new—range from complex clays, zeolites, micas to the simple hydroxide and oxyhydroxides all made via the sol-gel route is very large and references may be found in a later review.³

2.1.2 The Sol-Gel Process II: Nanocomposites. In 1981 the author redirected the main thrust of all sol-gel research away from homogeneity of mixing on the atomic scale to heterogeneity on a nanometer scale (see details in Ref. 3). He thereby started work on what he called nanocomposites. The rationale was twofold. Compositional heterogeneity provided an additional thermodynamic driving force in the ΔH_{react} for lowering temperatures of reaction. This was commercialized early by the Chichibu Cement Company in its mullite powder. Structural heterogeneity or epitaxial seeding provided a lower temperature route to completing a solid state reaction at a lower temperature or directing the reaction to a (metastable) lower temperature phase. The concept of seeding of gels, first of boehmite gels with Al_2O_3 -corundum practiced in 1949 in hydrothermal research, was extended to all ceramic systems under “dry” firing conditions between 1982 and 1985.⁴⁻⁵ Starting with this work nanocomposite xerogels and gels have been a major asset and tunable resource for *all* low-temperature materials synthesis in oxides and similar materials.

2.2 Fluxes

A flux is typically a low-melting halide or oxysalt mixture. While little sophisticated detailed work has been done on the *mechanisms* of how fluxes work in oxide reactions, the empirical fact that one can use fluxes for inducing subsolidus reactions in oxides goes back at least to C. N. Fenner’s work on SiO_2 polymorphism.⁶ By using Na_2WO_4 (or Li salts) one is able to transform, e.g., quartz to tridymite and tridymite to cristobalite reversibly near 870° and 1470°C, respectively. Even today the tungstate flux is the method of choice to synthesize large amounts of tridymite.

A variety of low-melting halide salts of Al, Zn, Mg, Li have been used as fluxes in a variety of syntheses. In the recent past, fluxes have been used extensively mainly in crystal growth. The use of a flux or low-melting eutectic from which (small) crystals precipitate is often the fastest method to obtain single crystals in the mm range for structural characterization.

A search of *Chemical Abstracts* reveals that from 1967-1993, that out of some 35638 entries on crystal growth, some 1100 involved growth from fluxes. A scan of these titles reveals that three-quarters of them describe the attempts to grow even very modestly sized crystals of YBC superconductors and hard ferrites.

The disadvantage of using fluxes, which has not proved to be a serious deterrent, is the possible inclusion of the flux ions in the growing crystal lattice. To avoid this, one uses either a common ion (e.g. BaCl_2 for BaTiO_3) or cation and anion sizes with very different sizes (Cl instead of F for growing oxides in flux and crystal).

In the opinion of the author, the use of fluxes has been neglected in recent materials synthesis, especially in the low-temperature regime. There are many ternary halide eutectics and even binary eutectics involving Zn and Pb which have melting points from 250°–350°C which could be explored as fluxes for oxide reactions.

2.3 Hydrothermal

By far the most general catalytic tool for materials synthesis of oxygen lattice phases is the use of high pressure and modest temperature water—the so-called hydrothermal process. Many regard the water as the limiting case of a flux. In the U.S. this tool owes its development to G. W. Morey⁷ and his group at the Carnegie Institution in Washington. He not only designed the pressure vessel which bears his name but did systematic phase diagram studies on the alkali-silicate-water systems. The “Morey bombs” were used worldwide for low-temperature materials synthesis—including clays and zeolites in the 1930’s and 1940’s by Hall and Insley, and later by Roy and Osborn and Barrer. The Morey vessels were limited to about 450°C and 1 kbar. Nineteen forty-eight saw the

appearance of the Tuttle apparatus and 1949 the test-tube or cold-seal bomb as reviewed by Roy and Tuttle.⁸ The latter has become the worldwide standard for 40 years. It is used in the range to $\approx 1000^\circ\text{C}$ and ≈ 5 kbars; with special modifications helping it to reach 1200°C and 5 kbars.

Convenient apparatus is essential to exploiting any process for synthesis and the multiple test-tube vessel facility provided this. Using it, an enormous number of syntheses have been carried out. For lower temperatures and pressures, very large autoclaves have been designed for quartz growth $\approx 400^\circ\text{C}$, ≈ 1 kbar. The very important hydrothermal synthesis of zeolites is carried out worldwide in very simple autoclaves.

2.3.1 Low-Temperature Synthesis. The syntheses which could not be done by any process other than the hydrothermal approach include:

- a. Hydroxylated phases such as clays, zeolites, micas, some oxyhydroxides, etc., since the water must be maintained as a component and modest temperatures are needed for finite rates.
- b. Reaction between highly refractory oxide phases through solution in H_2O .
- c. Crystallization of glasses and noncrystalline oxides is accelerated by several orders of magnitude.
- d. Exsolution and order-disorder in oxide crystals at low temperatures have *only* so far been catalyzed by the use of hydrothermal conditions. The classic example is the work of Roy and Roy⁹ tracing the exsolution of Al_2O_3 from spinel- Al_2O_3 crystalline solutions, and Datta and Roy¹⁰ on spinels.

Since the seventies, a great deal of the activity in the use of hydrothermal oxide reactions in ceramics moved to the laboratories of Professor S. Somiya, then at the Tokyo Institute of Technology. He specialized in the application of hydrothermal processes to supplement traditional ceramic processes. Excellent reviews of this work are available.¹¹⁻¹³

2.3.2 Hydrothermal with Superimposed Electric Field. In 1967, Hawkins and Roy¹⁴ introduced electrodes into a hydrothermal bomb and studied the influence of an electric field on the synthesis of kaolinite. They showed a very substantial effect ($+100^\circ\text{C}$) of lowering the temperature of crystallization of recognizable kaolinite. More recently, Yoshimura, Hirano and Somiya have extended this concept to the synthesis of electroceramic materials such as BaTiO_3 and related materials.¹⁵ Several other papers^{16,17} have established that the use of an electric field in a hydrothermal environment can play a useful role in accelerating and changing products in low-temperature synthesis.

2.3.3 Hydrothermal with Superimposed Mechanical Forces. The concept behind these experiments first carried out by Dachille and Roy¹⁸ was that the exposure of fresh highly reactive surfaces formed by grinding and consequent fracture, to the reactive hydrothermal ambient would give rise to the equilibrium phases.

In fact we were able to demonstrate quite substantial improvements in reaction kinetics especially in hydration reactions of highly stable oxides to make clays. Again, this was made possible by a simple innovation in apparatus. In effect the Morey bombs were converted into ball mills or rod mills.

2.3.4 Mechano-chemical Effects Including High Uniaxial Pressure With and Without Shear. It is not unreasonable that the process of grinding itself and the attendant repeated fracture with the high "local" temperatures involved could serve to catalyze reactions. But this is an effective technique for catalyzing low temperature reactions. V. I. Boldyrev in Novosibirsk is the best-known worker who has specialized in the field and the interested reader is referred to his work.¹⁹ He summarizes the mechanisms he finds in Figure 1.

2.3.4.1. At Penn State, during the same time as Boldyrev, Dachille and Roy took a different tack. First, they established that

simple uniaxial pressure in the 10-100 kbar regime was sufficient to bring about reactions at low temperatures which could not be accomplished by any other means at all.

The most direct evidence for this is the crystallization of simple glasses such as SiO_2 , B_2O_3 , GeO_2 ²⁰ by the application of pressure at much lower temperature than is possible by any other means, specifically in opposed anvil devices. It was argued that the effect may not only be due to pressure, *but the shearing actions at high pressure*, which are unavoidably present in simple anvil experiments with powders. Nevertheless it is empirically true that high pressures (> 10 kbars) catalyze low-temperature reactions in ceramic materials.

2.3.4.2 Influence of Grinding Alone. The earliest clean experiment showing the remarkable effects of grinding in ordinary agate mortars was that of Burns and Bredig²¹ who claimed that calcite could be partly transformed to aragonite merely by grinding in a mortar. Dachille and Roy²² not only confirmed this observation but extended it to include a whole range of phases such as PbO , PbO_2 , CaCO_3 , MnF_2 , Sb_2O_3 and BeF_2 . The extraordinary finding was that all these crystalline phases stable at 1 atm. and room temperature could be transformed by mere grinding for several hours in an automatic agate mortar and pestle, to the high pressure polymorphs. Dachille and Roy estimated from the p-t equilibria for these phases that the grinding generated pressures of the order of 15 to 20 kbars and that the shearing action was responsible for the increase of several orders of magnitude in the kinetics of these solid-solid reactions at room temperature.

2.3.4.3 Influence of the Combination of Shear and Very High Pressures. The logical extension of the results reported was to try to separate the effects of pressure from shear. The study of the influence of shearing stresses superimposed upon quasi-hydrostatic pressures of up to 100,000 bars at temperatures below 550°C was made possible by the development of a simple apparatus by Dachille and Roy.²³ This

consists of the Bridgman uniaxial-type apparatus—with a provision for continuous rotation of the bottom piston very slowly back and forth through a 2° arc. The sample is heated externally; and displacive-shearing runs with pressure and temperature automatically controlled can be made for periods exceeding several days if desired. The results clearly separate the influence of “hydrostatic” pressure itself upon reaction rates from the effect of the added “displacive-shearing” stresses. Further, from the results it becomes clear that equilibrium relations between phases are not altered by the shearing stresses. The influence of this type of stress is illustrated for the transformations $\text{SiO}_2_{\text{qtz}} \leftrightarrow \text{SiO}_2_{\text{coesite}}$; $\text{PbO}_2(\text{MnF}_2)_{\text{rutile}} \leftrightarrow \text{PbO}_2(\text{MnF}_2)_{\text{orthorhombic}}$; $\text{PbO}_{\text{litharge}} \leftrightarrow \text{PbO}_{\text{massicot}}$; $\text{CaCO}_3_{\text{calc.}} \leftrightarrow \text{CaCO}_3_{\text{arag.}}$ and the formation of $\text{NaAlSi}_2\text{O}_6$ (jadeite). Reactions which cannot usually be made to proceed below 300°-350°C can be performed at temperatures between 0°-150°C.

Increases in rates of reaction of two or three orders of magnitude can be attained at a given pressure and temperature. It is not clear whether this should be ascribed to strain energy stored in the lattice or merely to breakage of bonds.

Boldyrev¹⁹ in his extensive work with mechano-chemical effects comes to virtually the same conclusions for many reactions: it is possible to increase the kinetics by about two orders of magnitude.

2.3.6 Use of Ionizing and Non-ionizing Radiation. The radiation damage caused by uncharged particles (neutrons, α particles and heavy atoms) have been studied by dozens of workers. However they have not examined the effects on kinetics of solid state transformation. Roy and Buhsmer²⁴ studied a variety of phase transformations, in SiO_2 , $\gamma\text{-Ca}_2\text{SiO}_4$, PbO , and showed that only modest changes in kinetics were caused by neutron radiation damage.

Boldyrev²⁵ in work on the CaO-SiO_2 system was able to increase the kinetics of reaction by two orders of magnitude—albeit at a modest temperature—by using 2 Mev electrons (see Figs. 2 and 3).

Change of the Way of Stress Field Relaxation Depending upon Intensity of Mechanical Energy Delivered

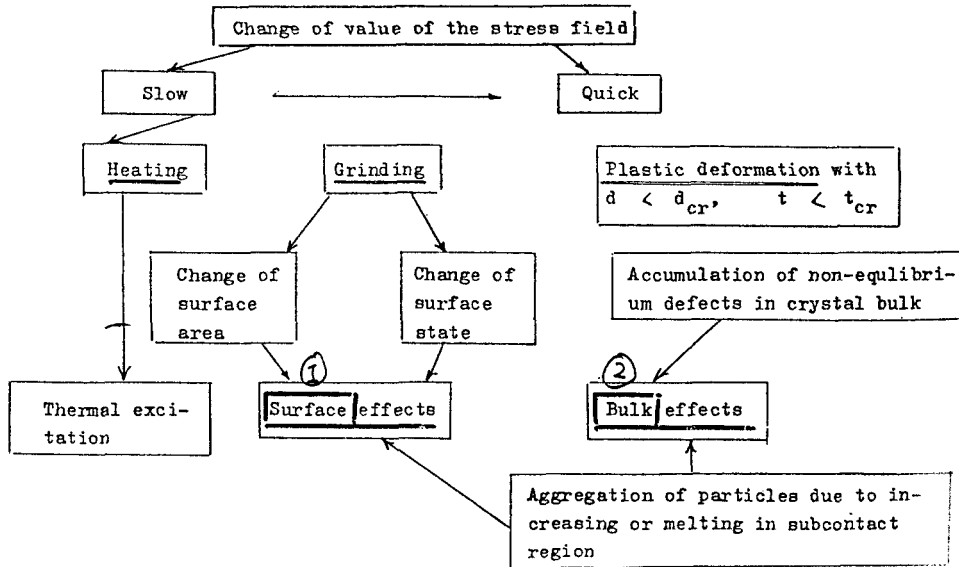


Figure 1. Boldyrev's analysis of how mechanochemical effects work; principally by surface (1) and to a lesser degree bulk (2) effects.

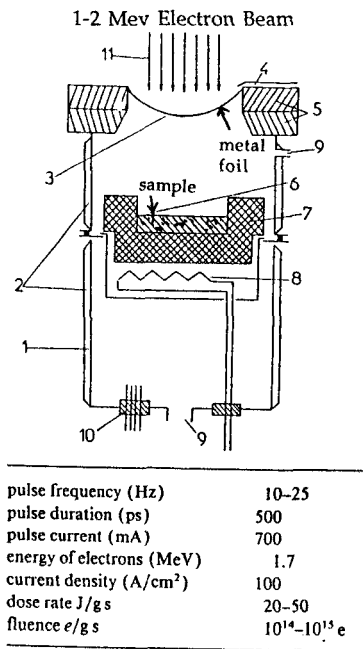


Figure 2. Apparatus for electron beam excitation of solid state reactions.

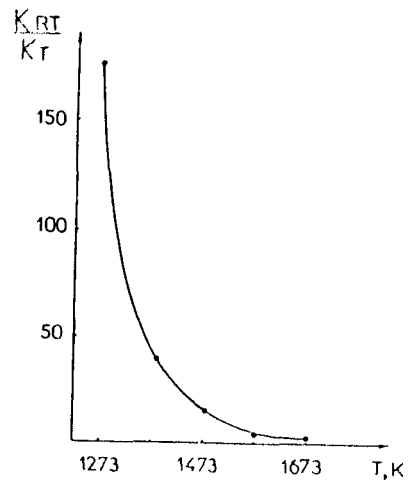


Figure 3. Change of reaction rate by factor of 20 at lower temperatures for the reaction $2CaO+SiO_2 = Ca_2SiO_4$.

2.4 Recent Research on Low-Temperature Reaction Catalysis

During the last several we have re-opened the question of the possibility of increasing the kinetics of low-temperature reactions in ceramic systems. We report below the results of three different families of approaches:

1. epitaxial nanocomposites as precursors;
2. acoustic wave stimulation (sonochemistry);
3. microwave hydrothermal reactions.

2.4.1 Epitaxial Nanocomposites. In Section 2.1.2 above we referred to our extensive work on the remarkable effects on crystallization temperature and kinetics of using nanocomposites in *dry* ceramic systems. We first established these effects in one-component systems such Al_2O_3 , TiO_2 , etc.,²⁶ next in binary systems such as Al_2O_3 - SiO_2 , ZrO_2 - SiO_2 , etc.²⁷ Figure 1 below summarizes what can be achieved in the crystallization of ZrSiO_4 .²⁸ The case of ThSiO_4 ²⁹ with its two polymorphs was, however, by far the most instructive. Not only could one lower the temperatures of reaction, but one could *totally* direct the ThSiO_4 gel to form (and retain at 1400°C for days) the huttonite or the thorite structures merely by nanocompositing with seeds of the respective phases.

		Compositionally	
		Nanocomposite	Homogeneous
Structurally	Homogeneous	1175°C	1350°C
	Nanocomposite	1075°C	1100°C

Figure 4. Effect of using compositional and structural nanocomposite gels of the ZrSiO_4 composition compared to a single phase homogeneous gel.

In a study designed to test whether these effects could be realized *at lower temperatures*, we studied crystallization in the Al_2O_3 - P_2O_5 - H_2O system.³⁰ Our results clearly showed that below 400°C one can *direct* the phase formation by "seeding," as summarized in the following.

Crystal growth under hydrothermal conditions in the binary join SiO_2 - AlPO_4 were investigated up to 400°C using several starting materials made by a partial solution route. Precursors used were boehmite (AlOOH), H_3PO_4 , noncrystalline silica (Ludox, Cab-O-Sil), and quartz. Studies up to 400°C showed that SiO_2 , AlPO_4 , and its hydrate were the only crystalline and noncrystalline phases present along the binary join, and no substantial crystalline solution of any ternary phase was observed. Three polymorphic forms of AlPO_4 , namely, berlinite, tridymite form, and cristobalite form, existed at as low as 75°C . The nature of the silica precursors greatly influenced the development of the polymorphic phases of AlPO_4 . The low quartz precursor suppressed the formation of the cristobalite form of AlPO_4 and favored berlinite production. On the other hand, noncrystalline silica with a cristobalite-like broad XRD peak suppressed the formation of berlinite and enhanced that of the cristobalite form of AlPO_4 . The silica precursors acted as structural seeds for the growth of AlPO_4 . These precursor effects indicate that heteroepitaxy is very significant during the nucleation and growth of AlPO_4 phases on the surface of SiO_2 particles even in these low temperature reactions. Clearly the potential for exploitation of final phase direction and the kinetics of its formation exists in the low temperature hydrothermal regime.

2.4.2 Acoustic Wave (Sonochemical) Stimulation. In the last decade considerable work has appeared in the field of "sonochemical" breakdown of liquid phases. This work was limited almost exclusively to organic materials and to decomposition of homogeneous liquids. Excellent reviews by Suslick³¹ give an overview of the field and Suslick did in fact show that metallic phases

may be melted and/or corroded in aqueous suspension, the general concept being that in the collapsing bubble during cavitation could generate temperatures in the order of 5000 K and modest local precursors. We decided to see if *novel* materials synthesis or combination reactions could be accelerated by the ASW route. In the event it was clear that many reactions can be accelerated by about two orders of magnitude. In attempting to understand the fundamentals of the process we changed the frequency from 20 KHz to 500 kHz and even 1 Mhz. This had virtually no effect. The more interesting effect was the size effect.³² Our study was the leaching of K^+ into water from a series of micas. The leaching at 60°C was enhanced by more than a factor of ten. But to our surprise, for the 20 kHz field, it was clear that very small particles ($\approx 1\mu$) which on the face of it should react faster, did not. Instead particles of the various micas near 20-40 μ in size coupled better with the cavitation process and reacted faster.

In another example,³³ ultrasonic energy was used to accelerate the formation of hydroxyapatite (HAP). The experiments were carried out in aqueous systems on two different sets of reactants: (1) a mixture of $Ca_4(PO_4)_2O$ (TetCP) and $CaHPO_4 \cdot 2H_2O$ (brushite) and (2) α - $Ca_3(PO_4)_2$ (α -TCP). The reaction systems were exposed to ultrasound of 20 kHz for various times ranging from 5 to 80 min. The products were characterized by XRD and SEM. Parallel experiments without ultrasound were carried out for calibration. The results show that the ultrasound substantially accelerates both reactions. With ultrasound, the time required for the TetCP-brushite system to complete the reaction forming HAP was reduced from 9 h to 25 min at 25°C, and from 3 h to 15 min at 38°C. At 87°C, α -TCP does not hydrolyze within 1 h in de-ionized water unless the pH is adjusted. Hydrolysis of α -TCP was induced by sonication in less than 20 min, and longer treatment results in the formation of a homogeneous sol of HAP.

Also in a preliminary study of the use of acoustic wave stimulation of cementitious materials³⁴ we have demonstrated that

occasionally a new reaction can be made to occur. In the systems $Al_2O_3 + H_2O$ and $Al_2O_3 + P_2O_5 + H_2O$, it can definitely be concluded that the high power ultrasound influences inorganic reactions near room temperature. The rates were highly dependent on the particle size of the precursor powder used. In the case of Rhonc-Poulenc $Al_2O_3 + P_2O_5 + H_2O$ it was observed that just 20 min exposure of ultrasound had produced a highly crystalline hydrated phase of $AlPO_4$.

2.4.3 Hydrothermal Processes with Superimposed Microwave Fields. The empirical observation that the oxides in common minerals which are very resistant to dissolution in acids, bases and even molten carbonates, could be dissolved in relatively dilute acids at very modest temperatures in short times if, and only if, the slightly superheated systems were placed in a microwave field. This principle again has been incorporated into a simple convenient commercial apparatus and today microwave hydrothermal is in use the world over for rapid sample *dissolution* for chemical analysis.

Our approach was to reverse the direction of the reaction and try to show that we can *synthesize* materials by increasing the kinetics of reactions in the same temperature regime.

Our preliminary study³⁵ clearly demonstrates that microwave-hydrothermal synthesis enhances the kinetics of crystallization of various ceramic oxides such as TiO_2 , ZrO_2 , Fe_2O_3 , $KNbO_3$ and $BaTiO_3$ by one or two orders of magnitude. In addition to catalyzing the reactions, this novel processing may lead to novel phases as we have demonstrated here with a new layered alumina phase. The crystal size, morphology and level of agglomeration of the different ceramic oxides can be controlled by parameters such as concentration of the chemical species, pH, time and temperature. Submicron powders of TiO_2 , ZrO_2 , Fe_2O_3 , $KNbO_3$ and $BaTiO_3$ have been prepared by optimizing the above parameters. It is suggested that microwave-hydrothermal processing may prove to be a valuable process in

the low temperature production of fine ceramic powders including clays and zeolites.

3.0 CONCLUSIONS

Now that the synthesis of fine powders with controlled size, composition, perfection has come into such demand, and since low-temperature processes can produce the best materials, it is very worthwhile to re-examine the various methods available for increasing the kinetics of such reactions. If perfection is not important a wide variety of techniques can be considered; if it is, the hydrothermal process augmented in various ways is clearly going to dominate for some time.

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(short biography)

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He is one of the world's most widely cited and honored materials scientists; elected to membership in the U.S. and four foreign National Academies. Author of 600 papers and six books, he is one of 40 Americans who has been inducted into the Engineers Hall of Fame up to the present. His research has left a permanent mark on his field of science: the sol-gel process, hydrothermal processing, glass ceramics, nanocomposites and diamond films. But he is perhaps most distinctively known as the only working scientist professionally involved in science policy, science education, philosophy and ethics.