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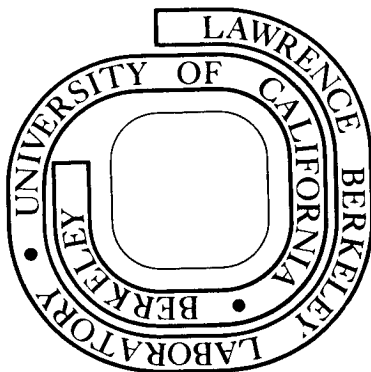
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Edward Orton Jr. Memorial Lecture
American Ceramic Society Annual Meeting, 1979

CERAMIC PROCESSING — A CERAMIC SCIENCE

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It is a great honor to be invited to present the Edward Orton Jr. Memorial Lecture and one greatly appreciated. I have always maintained an interest in the basic fundamentals of ceramic processing. I have thus selected the topic of ceramic processing for my lecture today, but because of time limitations I will restrict my specific remarks to the processing of crystalline materials, in contrast to amorphous or glassy materials, and to structural applications.

As you know, ceramic materials are of great interest for various energy applications because of their potentially good mechanical properties at high temperatures and capability of withstanding exposure to high temperature hostile environments. A very undesirable characteristic of ceramic materials is their brittleness which means that any irregularity in the character of the bulk or surface generally behaves as a defect with a detrimental effect on the mechanical behavior of the material. The presence of an occasional defect in the microstructure thus becomes frustrating to designers and engineers who are forced to use property values in their designs considerably below the potential of the material in order to realize almost absolute safety or integrity in the use of ceramic material components in critical and high cost devices. The occurrence of such irregularities is attributed to the lack of reliability and reproducibility on the part of ceramic materials. Furthermore, it is generally accepted that reliability and reproducibility are poor due

to a lack of a science of ceramic processing and thus a lack of a fundamental understanding of ceramic processing. I do not believe that such a statement should be left unchallenged or at least not subjected to some analysis and discussion as to why this impression exists. This is the reason for my selecting the specific topic of "Ceramic Processing - A Ceramic Science."

Reliability and reproducibility can be equated to homogeneity and uniformity on a microscale from piece to piece and also on a macro-scale. Such an achievement would reduce the scatter of property values and thus result in a higher effective value and a more reliable value for strength for design purposes. There is no question of the fact that good engineering practice and quality control during the operation of specific machinery during fabrication is necessary to maintain homogeneity and uniformity. However, understanding the nature of the response of the material on an atomistic and particulate basis to each of the processing steps and controlling them is equally important in realizing homogeneity and uniformity. Understanding the material response during the fabrication steps could actually be considered to be more important in the sense that such knowledge would also provide capabilities of attaining new designed microstructures as well as controlled microstructures. This kind of fundamental understanding and predictability is the basis for a science of ceramic processing.

An extensive and comprehensive review of the status of ceramic processing was made by a committee of the Materials Advisory Board about twelve years ago which appeared as a National Academy of Sciences publication (Publication 1576) in 1968. That report had a significant

impact on ceramic science as a whole. The chart shown in Fig. 1 appeared in that report. It shows the successive interrelationships between ceramic processing, character, properties and uses. It emphasizes that each category is dependent on the one preceeding it, i.e. uses of a material are dependent on its properties, its properties are dependent on the character or structure of the material, and the characters of materials are dependent on their processing. It also indicates the particularly close relationships between character and properties. Since these relationships have not been completely evaluated as yet, some properties are frequently used as parameters for characterization. The chart also makes it clear that the whole sequence is repeated for any subsequent finishing. The indicated character/property evaluation constitutes the area of physical ceramics which is comparatively far advanced, and is now generally accepted as a ceramic science. It is also considered to be part of Materials Science. On the other hand, the processing/character correlation is not as extensively accepted as a science. It is important to explore the reasons for this attitude and situation, and to determine if there is justification for this attitude.

The section on controlled processing in Fig. 1 is not broken down into its various components. It will be helpful for the purposes of our analysis and discussion to make an effort to identify the fundamentals of ceramic processing and to get some impression of the status of knowledge or understanding with regard to the identified fundamentals. A chart indicating a proposed breakdown of the controlled processing indicated in this figure into its components is shown in Fig. 2. A key factor to note is that controlled processing is broken down into

Processing Steps and Materials Response. The indicated successive processing steps then are starting material, formation of particulates, formation of assemblies, drying and pre-firing, and firing. In this concept the Processing Steps or fabrication deal with engineering aspects such as machines, equipment, and procedures involved in fabricating the size and shape of the piece. The parallel or Materials Response steps deal with the behavior of the material as it is exposed to the fabrications steps, and it can be considered to constitute the fundamentals of ceramic processing from a materials viewpoint. The correlation of these processing fundamentals with the resulting material character at each step, and a corresponding understanding of the associated behavior, constitutes the basis of a ceramic processing science. This classification should help eliminate some confusion, or at least point out why some confusion exists, in terminology. Here, I am proposing that ceramic fabrication emphasizes the engineering aspects of processing, and ceramic processing emphasizes the scientific aspects of materials response or behavior. In any case, both aspects must be considered and correlated with the character of the material at each step. It should be obvious that any material characteristic or feature that is introduced at any point in the sequence persists and exerts its influence in each subsequent processing step. The logical objective at every step is to achieve homogeneity, and uniformity and reproducibility and to maintain this condition throughout the entire processing sequences.

Let us now examine some details of each of the fabrication or processing steps. No more will be said about the starting material at this time other than that it should be characterized and that it itself

should maintain uniformity and reproducibility. Some of the processes that are used for the formation of particulates are indicated in the figure. Examples of some fundamentals of materials response that play a role are fracture mechanics of small particles or solid state chemistry depending on the method of particle formation. Of particular importance is understanding of the factors that cause agglomeration and subsequent aggregation and their probable initial dependence on the development of charges on particles in the presence of water as a medium. An understanding is also needed of the effect of small amounts of impurities on such properties. An example of the effect of a small amount of active silica on the zeta potential of alumina particles is shown in Fig. 3 which shows the zeta potential of alumina particles vs. pH of the suspension medium. Curve (e) for an alumina which contains 0.12 wt% SiO_2 that had been aged in a suspension at a pH of ~ 7 for 1 day shows an isoelectric point (i.e.p.) at a pH of ~ 8.9 , and curve (g) shows that the i.e.p. dropped to a pH of ~ 5.2 after aging for 16 days. Curve (e) also represents the same alumina after leaching with HF to remove the SiO_2 and then aging at a pH of ~ 7 in a polyethylene bottle for 16 days; the i.e.p. did not shift to ~ 5.8 as did the unleached specimen but remained at ~ 8.7 . However, when a small amount of sodium metasilicate (Na_2SiO_3) was added to the suspension with the HF-leached alumina and aged for 3 days, the i.e.p. shifted to ~ 6.0 as shown by curve (f). This series indicates that silica polymerizes slowly with aging and affects the surface change of the alumina particles. The details of this study will appear in a paper with Professor Jose Moya who is spending a year with us while on leave of absence from the Institute of Ceramics and Glass,

Madrid, Spain. These curves are shown here as an example of the importance of characterizing a powder and its behavior by showing the sensitivity of its i.e.p. and surface charge on the treatment to which the powder is exposed and the presence of small amounts of silica. The significance of this fact is that with high zeta potentials, positive or negative, the particles repel each other or disperse, and at the i.e.p. the particles have no charge and flocculate or agglomerate. Figure 4a is an S.E.M. photograph of a fracture surface of an unfired alumina compact made with particles of $\sim 4\mu\text{m}$ treated under i.e.p. conditions; agglomeration is observed. On the other hand, the powder's treatment under high zeta potential conditions results in dispersion and no indication of agglomeration as seen in Fig. 4b. Obviously, variations during processing that lead to changes of zeta potential over a period of time can lead to non-uniformity and non-reproducibility.

Let us now look at some of the processes that are used for the formation of assemblies, compacts or green bodies as outlined in Fig. 2. Identified fundamentals are stereology which deals with packing characteristics of particles with and without agglomeration and aggregation. It also deals with problems related to quantifying the size and distribution of particles. Rheology, or flow under stress, during forming including the effect of binders and plasticizers is another fundamental that has not received enough attention, particularly in dry pressing. Some of the factors associated with drying and prefiring are also outlined in Fig. 2. The fundamentals in this case are chemical reactions related to the removal of plasticizers, and the evolution of fluids used during the forming step.

Lastly, some of the fundamentals associated with firing are shown in Fig. 2. Sintering and microstructure development are part of this category. This area has received a great deal of attention, and is perhaps the furthest advanced among the ceramic processing fundamentals, but there are still many problems and deficiencies in our understanding. Let us now look at examples of some of the difficulties encountered in characterizing particulates, particulate assemblies and the corresponding developing microstructures. These examples are taken out of Michael D. Sacks' Ph.D. thesis studies which will be finished this summer. In the preparation of mullite powders by a modified gel process mixtures of Al_2O_3 and SiO_2 were calcined at 1450°C for 24 hrs; considerable aggregation occurred. The calcined powder was ground for various lengths of times in an effort to continuously break down the aggregates. Each resulting powder was then compacted by adjusting the pressure so that the same green or unfired density was obtained ($54 \pm 1\%$ of theoretical density). The compacts were then broken, and scanning electron microscopy (SEM) photographs were obtained of the fracture surfaces. The fracture surfaces are shown in Fig. 5. It can be seen that the individual grain or particle sizes remained essentially constant but the aggregate sizes decreased with grinding time. Sintering equations are based on the use of a single grain size in the initial stage or some mathematical relationship indicating grain growth in the intermediate stage. Realistically, there is a dilemma as to what size parameter or parameters should be used to represent what is seen in the figure. At present we do not have this mathematical capability or, if we do, it has not been applied to this problem. This is an important question since

these visual differences persist into the microstructures fired at 1660°C for 18 hours as seen in Fig. 6. The observed differences are reflected in the plots of percent theoretical density vs. time of firing at 1660°C for powders ground for different times, as shown in Fig. 7. The large pores that formed in compaction and persisted through firing have affected the final bulk density significantly. Consequently, the use of a single value for the individual grain size is incorrect and the grain size value should somehow include the aggregate size and size distribution. Figure 8 is an SEM photograph of a specimen prepared with the powder ball milled for 12 hrs and fired at 1580°C for 6 hrs. It illustrates the fact that bulk theoretical density was not reached only because of a lack of homogeneity in the powder compact. The information obtained by SEM with its capabilities of large magnification and depth of focus indicates that we now have an analytical tool that can show microstructures and particulate structures. It can at least provide an explanation and understanding of the nature of the problem and the consequences.

Another contribution of SEM to the understanding of sintering mechanisms and providing information for development of sintering models is its use for the observation of the geometry of neck structures that form between grains in contact during sintering. The generally accepted models picture necks with reverse curvature and large dihedral angles. Actual observations with SEM of sintering MgO compacts fired in a gas-fired furnace after 6 hrs at 1350°C indicate necks with normal dihedral angles. Figure 9 shows an example, by courtesy of Nick Cassens of Kaiser Refractories at the Center for Technology in Pleasanton,

California. Another example is one of sintering SnO_2 powder with normal dihedral angles as shown in Fig. 10 by courtesy of Dr. Boon Wong and Dr. J. T. Smith of G.T.E. Laboratories.

Now let us take another look at the overall classification shown in Fig. 2. The character/properties coupling under the firing step constitutes the area of physical ceramics or materials science. We have taken the processing category from Fig. 1 and broken it down into its various steps which constitute the balance of this chart. The affectiveness of this chart toward contributing to an overall understanding of ceramic processing, as mentioned, is that it separates technology and engineering from the fundamentals of materials response, but the chart still emphasizes that in production they can not be isolated and constitute a sequence for each step from the starting material to the characterized finished product. At each processing step good technology based on quality control is dependent on understanding the materials response and both determine the character of the material at that step. This chart also emphasizes the realization and understanding that any character modification or defect introduced at any step carries on through the whole processing sequence to the final product. It thus can not be overemphasized that control is necessary at every step both from the viewpoints of engineering quality control and understanding the fundamentals of materials response to realize uniformity and homogeneity, and thus reliability and reproducibility.

Although technology can not be separated from materials response, the materials response/character/property couplings can be isolated studies and constitute the area of ceramic processing fundamentals.

The question now is whether this area can be considered a science. The general consensus is that it does not have the status of a science except possibly the step dealing with sintering. We can then first ask the question, "Why does this situation exist?"

The acceptable and popular conception of a scientific activity is based firstly on the capability of identifying and characterizing a material on an atomistic or structural basis, and secondly on the capability of developing a mathematical analysis or expression based on models or numerical data obtained for a phenomenon or behavior characteristic, and thirdly on the capability of predictability. The area of physical ceramics has enjoyed this status to some extent. This has been primarily the result of the availability and development of analytical tools such as transmission electron microscopes, and diffractometers of various types that can be used to characterize fired specimens. Also, and perhaps more important psychologically, physical ceramics has had the capability of attracting researchers who identify themselves as scientists and who insist that everything they do is basic scientific research, which in turn leads to the attraction of research funds. Or, perhaps it is vice versa. Unfortunately, a similar situation does not exist in the case of the overall field of ceramic processing. One of the principal problems is the difficulty of a meaningful characterization of the particulates in terms of size, shape, microporosity, surface characteristics, agglomeration and aggregation. At present these parameters are not subject to complete mathematical expression for purposes of application to packing and sintering analyses. It certainly would be a challenge for our mathematically inclined colleagues to tackle this problem. This

problem has been intensified by the lack of analytical or characterization tools to observe the particulate structures and to characterize surfaces and grain boundaries under realistic environmental conditions. With the advent and development of scanning electron microscopy which has a characteristically large depth of focus and with appropriate analytical attachments like EDAX, we are now in a much better position to tackle these problems and to identify and follow particulate variables at all steps in processing that were previously impossible and thus not subject to direct analysis on an atomic or particle scale.

This concept of science is popularly accepted. I would like, however, to take a few moments to discuss another, and probably more basic, approach to science. Philosophically, science is equivalent to the development of fundamental understanding, in our case of the nature and behavior of materials and processes. The basic objectives of science are to discover the reasons for behavioral patterns so they could be controlled, and to provide answers to the question "why". Before properties or mechanisms can be effectively described or modeled mathematically, they must first be fundamentally understood. Unfortunately, there are some features that have not reached this status of understanding. Particulate parameters are presently in this category. In this case, perhaps we need someone to experience a revelation - it is said that Newton experienced such a revelation when one day the apple appeared to him as not "falling" but "pulled towards the earth." Does this situation exclude the area of particulates from the status of a science? I strongly suggest that it does not as long as the research is done with the objective of developing an understanding and control of the various

processing steps. In time, development of such understanding and attitudes should lead to identification of parameters that would be subject to measurement and mathematical analysis. Such studies from a philosophical viewpoint should be categorized as being scientific. To me, the contemporary processing scientist who has to deal with the problems having many variables is one who pieces together, like a jigsaw puzzle, evidence drawn from many different types of scientific inquiries in physics and chemistry, for purposes of analysis. He is one who is part theoretician, thinker and experimenter.

Another responsible factor for the popularly accepted status between physical ceramics and ceramic processing as sciences has already been alluded to. The field of physical ceramics has attracted and attracts many solid state physicists who have an indoctrinated scientific attitude and approach which they transmit to the field and their colleagues. An equal influx of solid state chemists or scientists into ceramic processing has not occurred. This situation probably is due to the lack of publicized research support in processing. The repeated conclusions reached by workshop committees, the most recent being one sponsored by DOE and chaired by Kent Bowen, that the problem of reliability and reproducibility is due to the lack of a science of ceramic processing, and the current optimism for possible structural ceramics applications being expressed by NMAB, may lead to the provision of further financial support for research which in turn will lead to the attraction of more scientifically inclined researchers to the field of ceramic processing, by the way, popularly known in some sophisticated circles as microstructure development.

In conclusion, may I say that I am optimistic about the future. With the expanding availability of new analytical tools, particularly the SEM, changing attitudes and developing realizations, I expect that the next decade will witness a great advance in our understanding of ceramic processing, specifically in the areas of particle technology and stereology, rheology of particulate assemblies, solid state chemistry of ceramic materials, and sintering from an atomistic and particulate approach instead of a continuum mechanics approach. Thank you for giving me an opportunity to share my thoughts with you on this vital and critical subject.

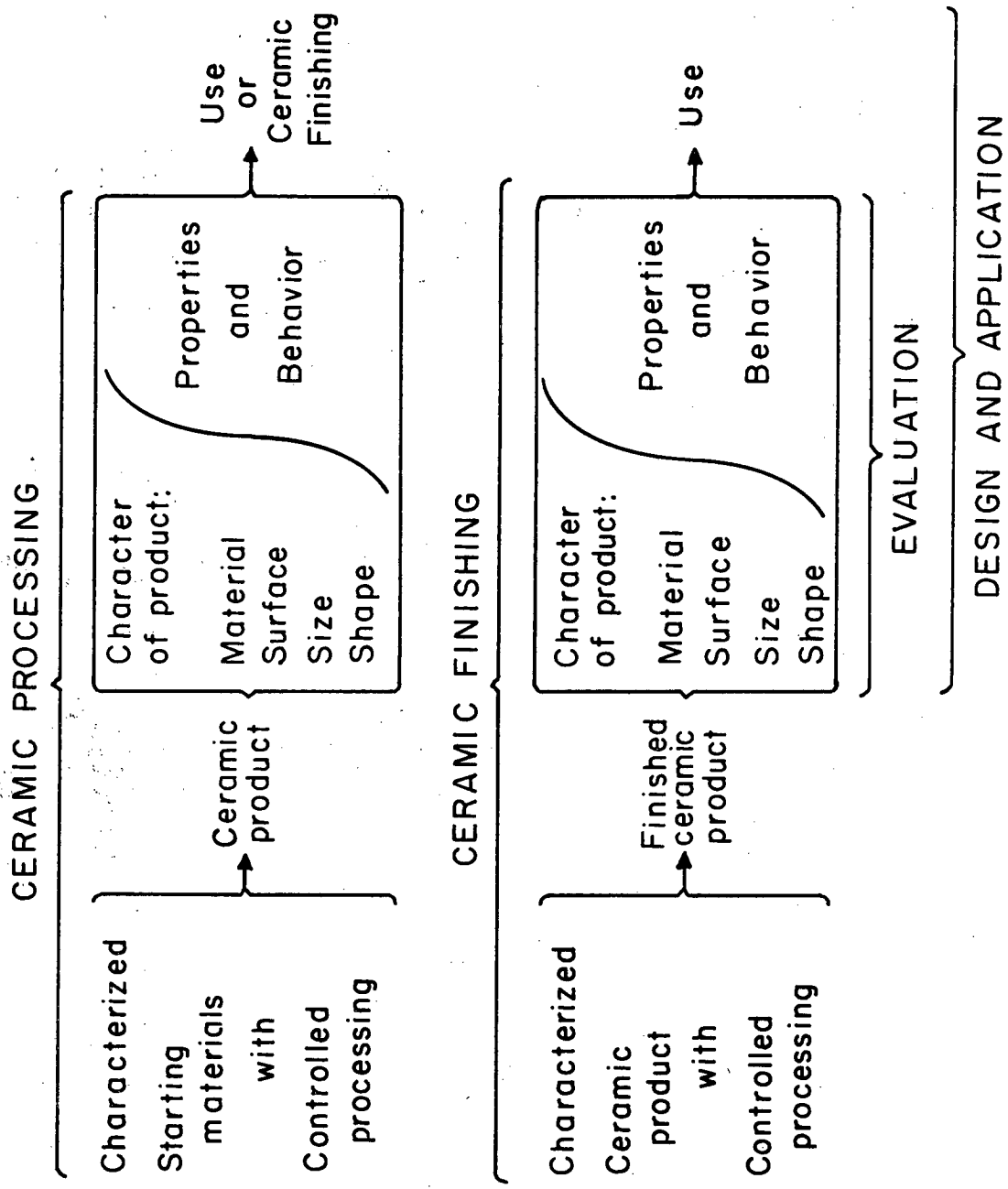
FIGURES

1. Chart showing interrelationship of processing/character/properties/uses.
2. Expanded chart showing interrelationship of fabrication or processing/materials response/character/properties. (Chart is illustrative and not intended to be complete.)
3. Zeta potential of alumina particles vs. pH of suspension. (Curves described in text.)
4. SEM photographs of fractured surfaces of unfired compacts of alumina powder with 50% theoretical density: A) powder treated at isoelectric point, and B) powder with zeta potential of 60 mv.
5. Unfired compacts of mullite powder formed by calcination after ball milling for 0 to 12 hrs.
6. Microstructures of compacts shown in Fig. 5 after firing at 1660°C for 18 hrs.

7. Percent theoretical density vs. time of firing at 1660°C for mullite powders ground for different times.
8. SEM photograph of specimen formed with mullite powder milled for 12 hrs and sintered at 1580°C for 6 hrs.
9. SEM photograph of MgO compact sintered in gas-fired furnace at 1350°C for 6 hrs.
10. SEM photographs of SnO₂ compacts sintered at 1350°C in static air atmosphere: left, 60 minutes; right, 120 minutes.

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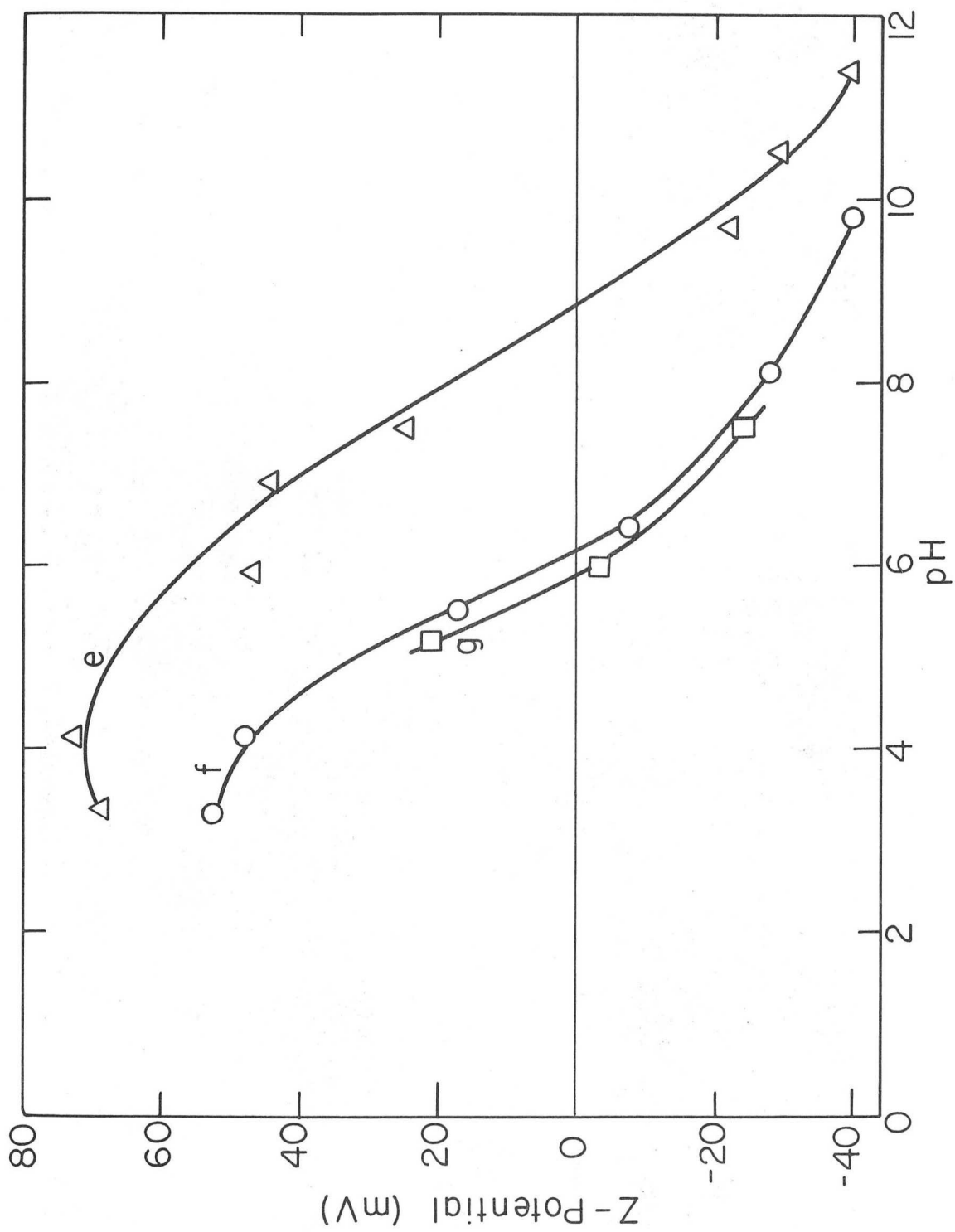


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Fig. 1

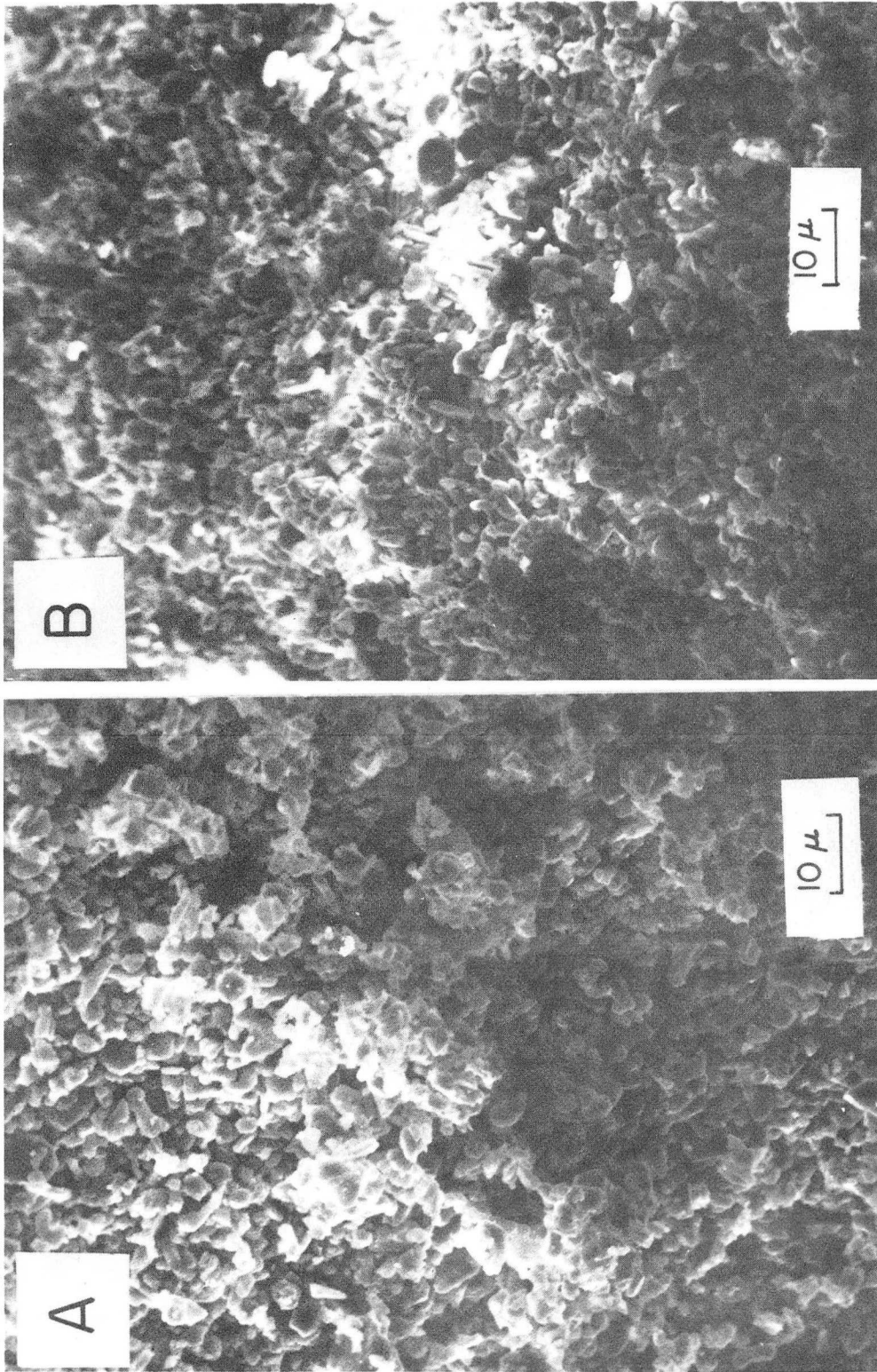
<i>Ceramic Fabrication</i>		<i>Ceramic Processing</i>	<i>Physical Ceramics</i>
<u>PROCESSING STEP</u>	<u>MATERIALS RESPONSE</u>	<u>MATERIAL CHARACTER</u>	<u>PROPERTIES</u>
<i>Starting Materials</i>		Composition Microstructure	Physical behavior Chemical behavior
<i>Formation of Particulates</i>			
Comminution Calcination Precursor salts Freeze-dried salts, etc. Compound formation Direct Conversion	Fracture mechanics of powders Solid state chemistry Thermodynamics Kinetics Mechanisms Nucleation and growth Mass transport	Morphology Size & distribution Composition - Chemical & phase Microstructure - Bulk & surface Defects Impurities	Agglomeration and aggregation Surface energies Surface charges in various media Rheology of particles in fluids
<i>Formation of Assemblies</i>			
Pressureless packing Dry Pressing Extrusion Slip Casting	Stereology -- Packing characteristics of characterized powders Rheology during forming Effect of binders & plasticizers	Composition -- impurities Microstructure -- micro & macro Density gradients Alignment patterns	Mechanical behavior -- Strength Creep resistance
<i>Drying & Pre-firing</i>			
Removal of liquid Removal of organics	Chemical reactions Evolution of fluids	Composition -- residue impurities Microstructure -- micro & macro Strain and density gradients	Mechanical behavior -- Strength Creep resistance
<i>Firing</i>			
Pressure sintering Pressureless sintering Without liquid With liquid Vitrification	Solid state reactions -- phase transformations Microstructure development Mass transport mechanisms Interfacial energies Atom mobilities Grain boundary mobilities	Composition Microstructure Grain size & distribution Pore size & distribution Phase composition & distribution Nature of grain boundaries Defects & flaws Surface structure	Physical properties Mechanical behavior Electrical & magnetic Optical Chemical stability Thermal stability

Fig. 2



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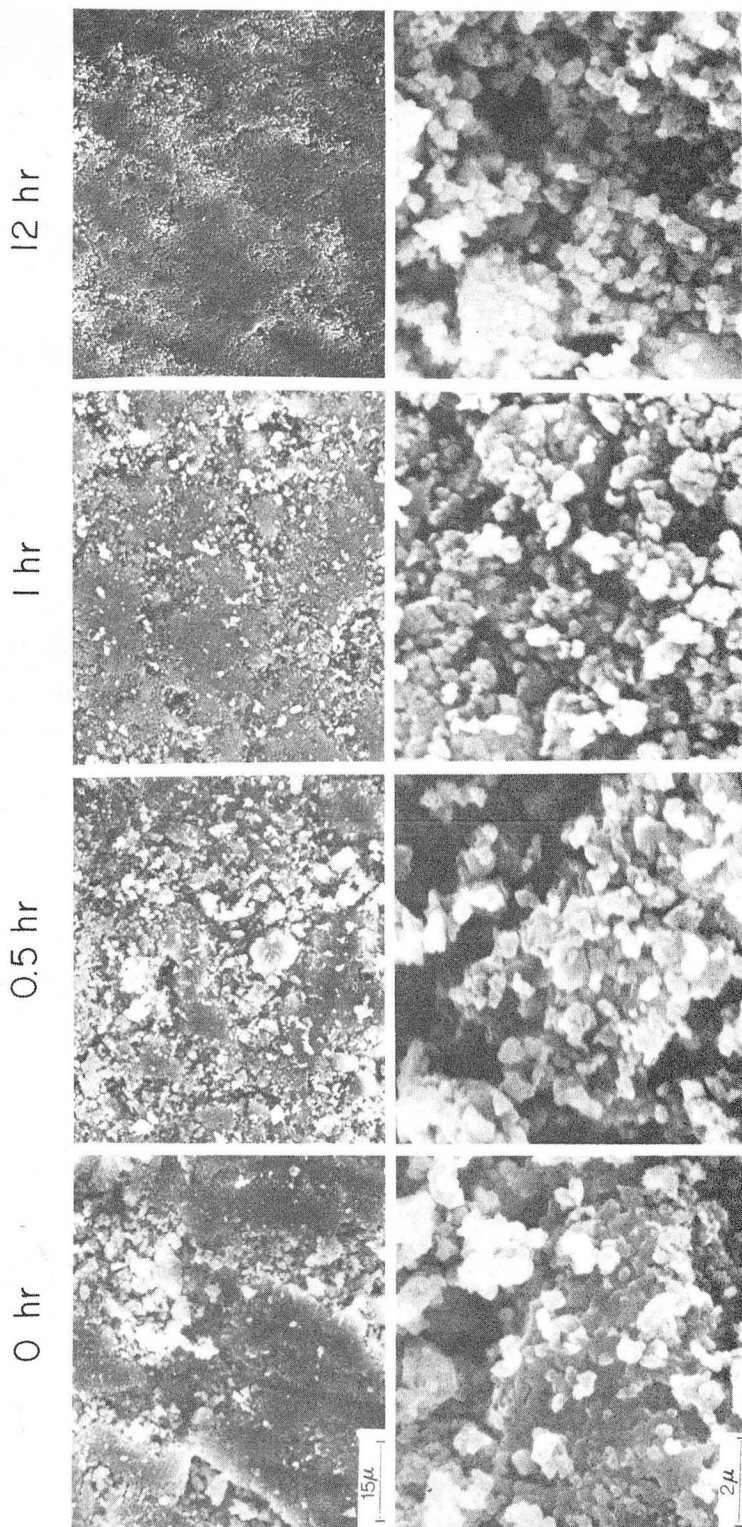
Fig. 3



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Fig. 4

73/27 "GEL": GREEN STATE

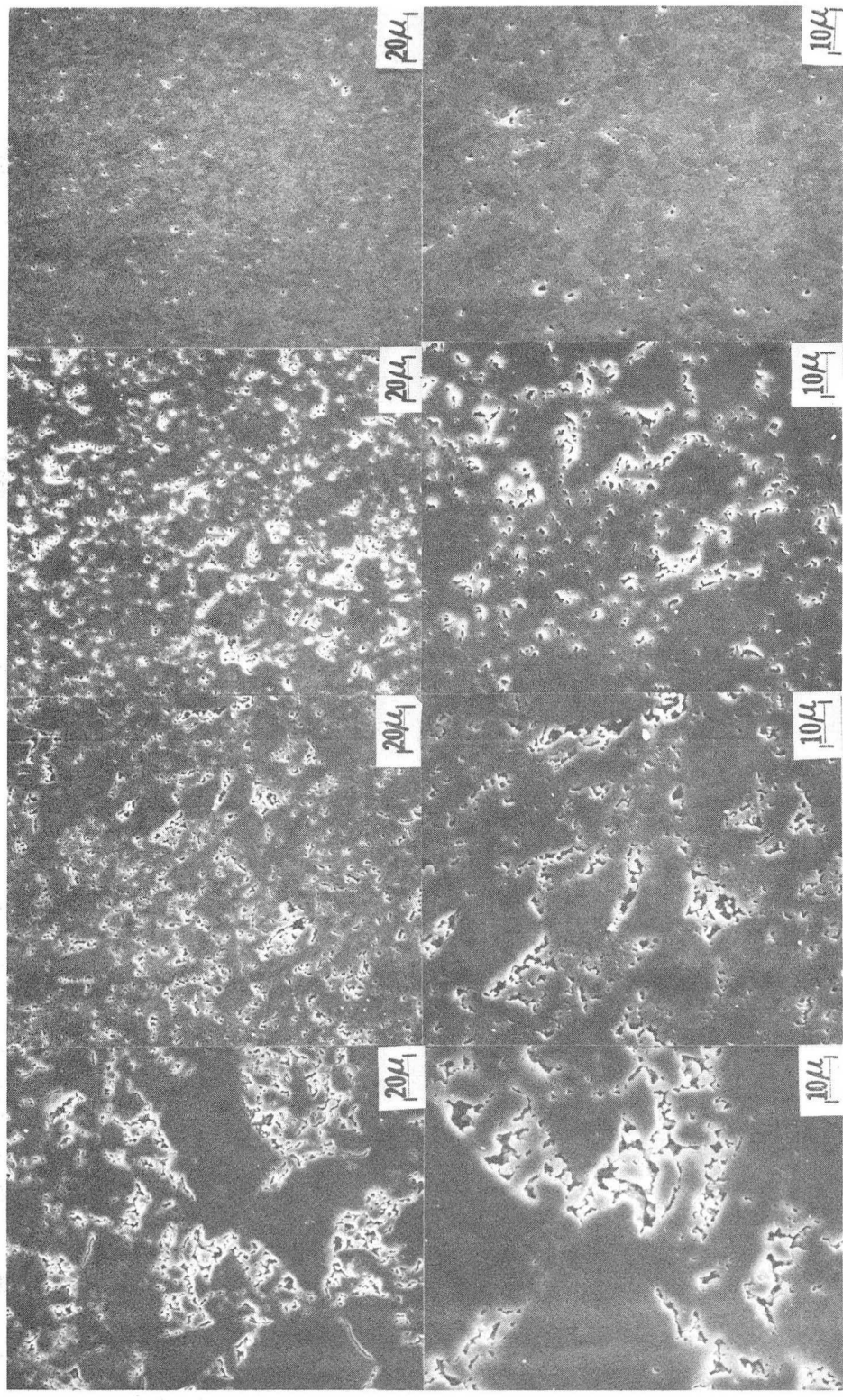


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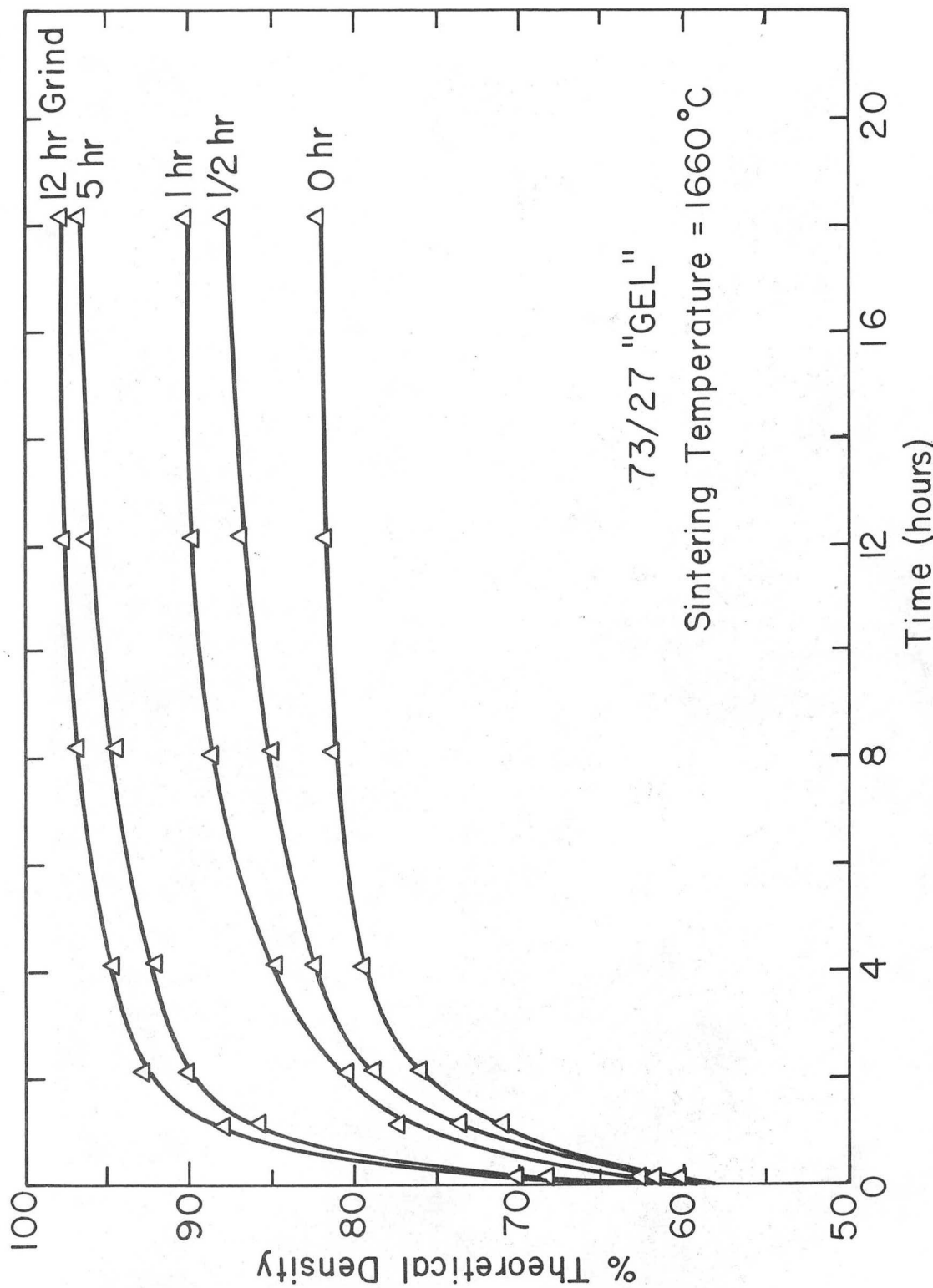
Fig. 5

73/27 "GEL": 1660 °C for 18 hr

0 hr 0.5 hr 1 hr 12 hr

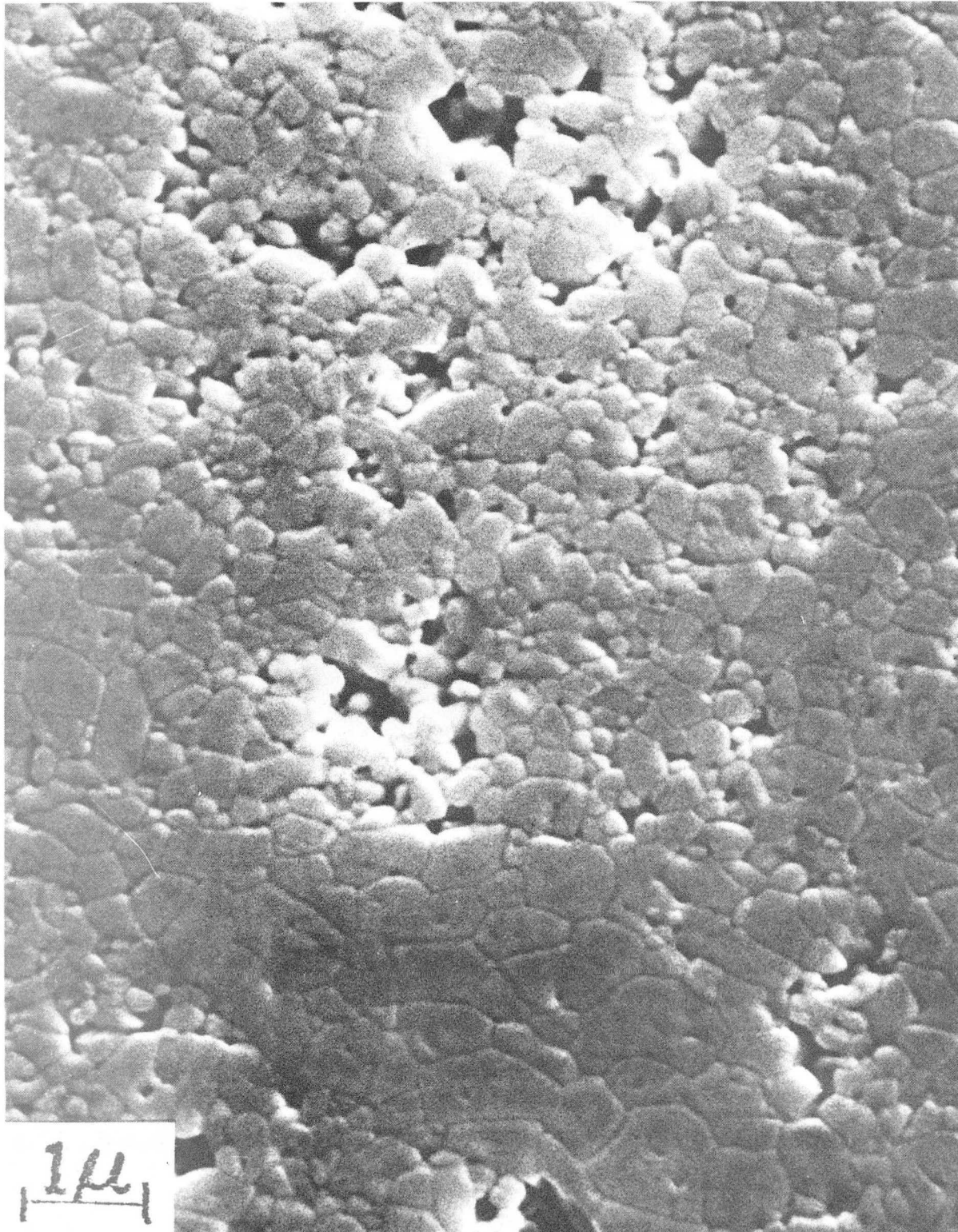


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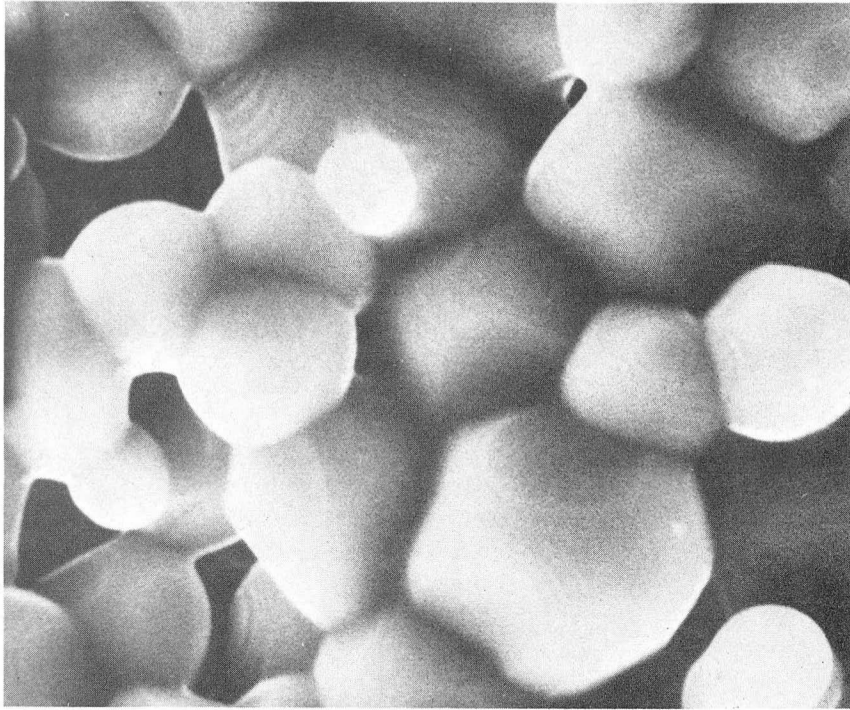
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Fig. 7

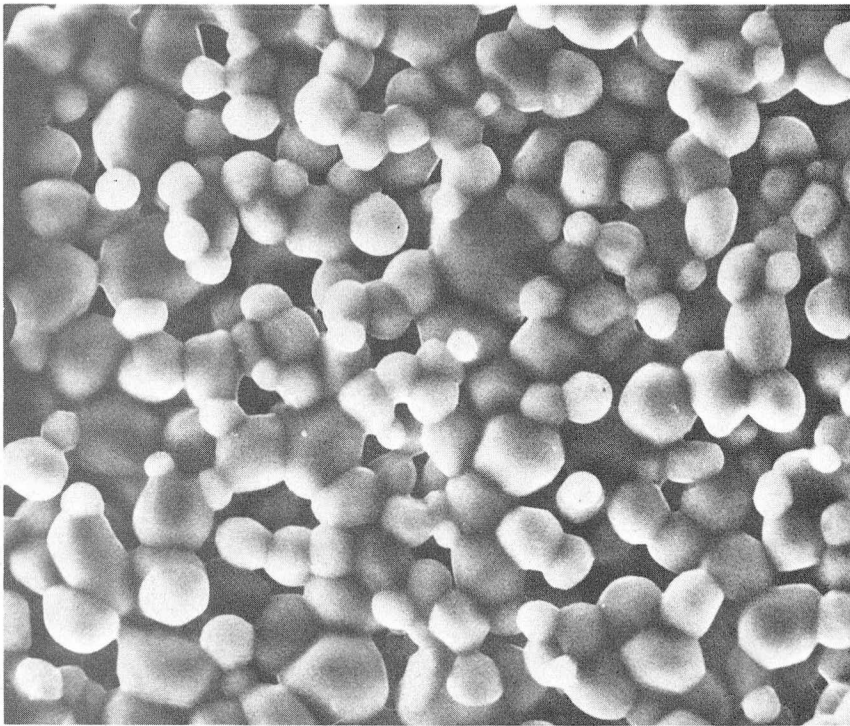


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Fig. 8

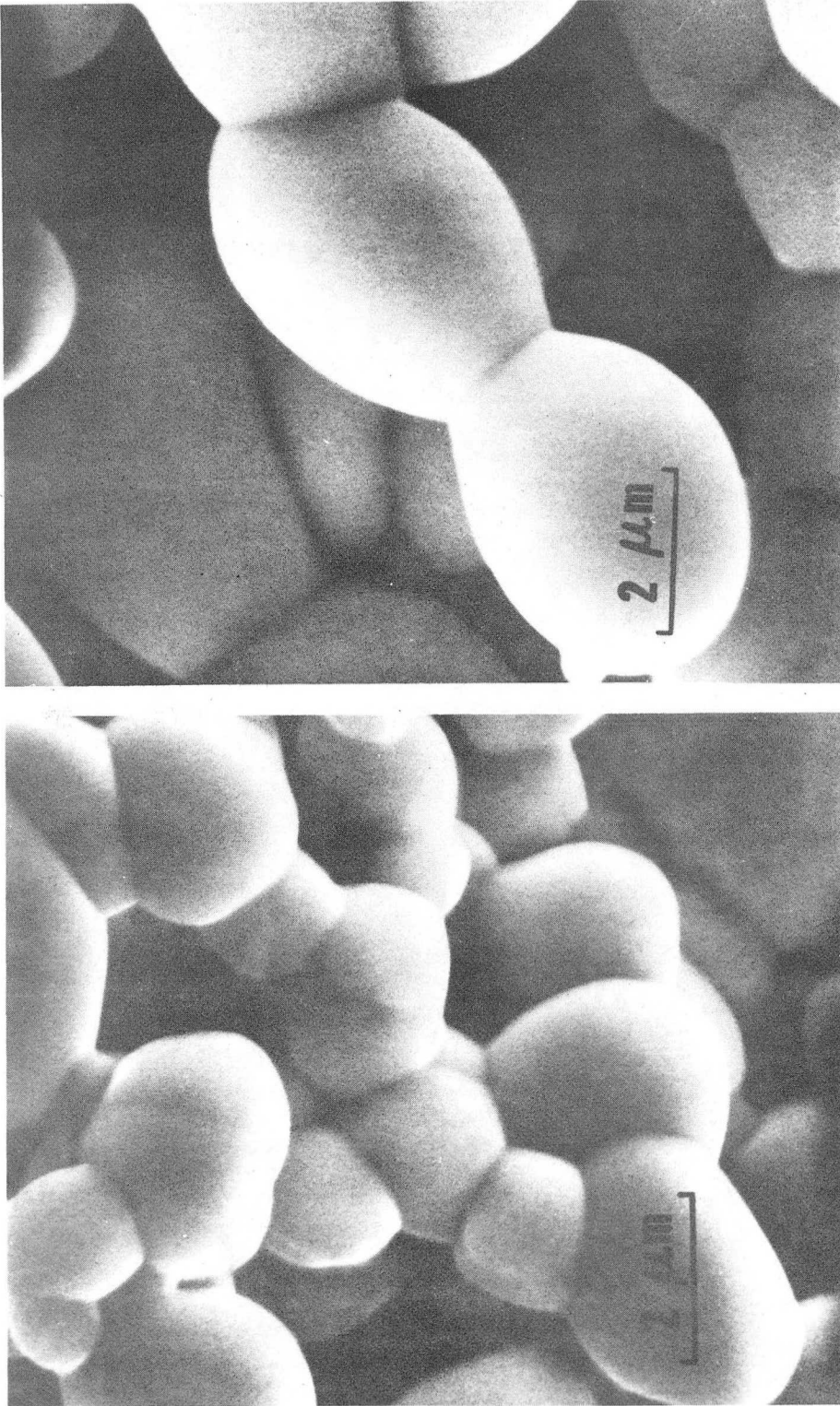


2 μm
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5 μm

Fig. 9



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Fig. 10

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