THE POTENTIALITIES OF FINE GRAINED CERAMICS FOR OPTICAL AND ACOUSTICAL APPLICATIONS

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We attempt here an evaluation of the potential utility of ceramic materials for optical and acoustical applications, particularly in the realm of micro-electronics. Since so many materials can be prepared as microcrystallites, the ceramic state, in principle, offers the possibility of achieving broad variability of optical and acoustical properties. To name but a few properties which are susceptible to modification: refractive index, electro-optical coefficient, electro-acoustical coefficient, magneto-optical coefficient. In practice, with a few notable exceptions, the vagaries of traditional ceramics processing have greatly limited the exploitation of the potentialities of the ceramic state.

As a minimal requirement for optical and acoustical utility, the ceramics must be of high density to avoid the effects of pore scattering. However, optically birefringent materials and all acoustical materials have the additional requirement of fine grain structure to minimize the effects of uncorrelated grain scattering. We present a simple model for calculating turbidity in ceramics and for estimating the relative importance of various scattering mechanisms.

The recent development of cryochemical methods for preparing microcrystalline powders and of pressure sintering techniques has opened up the possibility of understanding and controlling fabrication methods to the point where a wide range of optical and acoustical materials seem at least feasible. The cryochemical or freeze-dry method yields chemically pure, single phase, ultrafine (10-1000 nm) microcrystallites of myriad materials. The well characterized, cryochemically prepared starting powders lead to greater reproducibility in the densification phase of ceramic preparation. High density materials may be prepared at relatively low temperatures without stoichiometric complications and appreciable grain growth.

I. INTRODUCTION

Although creatures of often poorly understood lore and art, ceramics have a noble history of meeting a variety of important sociotechnological needs. With passing years, techniques have improved and understanding has increased, but the ceramic state remains elusive and ceramic technology, in some respects, under utilized. In this paper, we attempt to give some perspective to the potentialities and actualities of the utilization of ceramic materials in meeting the highly sophisticated requirements of information-communication technology.

At the outset, we must address a fundamental question. With a vast array of materials available in the form of single crystals, films, liquids, glasses, and polymers, why bother with ceramics and their attendant processing uncertainties? The possible reasons for attempting to use a ceramic for a given application are numerous, but may be subsumed under two broad categorizations (Table I).

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185
<table>
<thead>
<tr>
<th>TABLE I. Utilization of ceramic materials in information-communication technology.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1) CERAMICS PROCESSING—A MEANS TO &quot;ENGINEER&quot; MATERIALS</strong></td>
</tr>
<tr>
<td><strong>A. CHEMICAL MODIFICATION TO PRODUCE VARIATIONS IN PHYSICAL PROPERTIES</strong></td>
</tr>
<tr>
<td>OPTICS</td>
</tr>
<tr>
<td>Magneto-optical Coefficients</td>
</tr>
<tr>
<td>Energy Band Gap</td>
</tr>
<tr>
<td>ACoustics</td>
</tr>
<tr>
<td>Electromechanical Coefficients</td>
</tr>
<tr>
<td><strong>GENERAL</strong></td>
</tr>
<tr>
<td>Ferroelectric/Crystallographic Transition Temperatures</td>
</tr>
<tr>
<td><strong>B. ADAPTATIONS IN CONFORMATION OF A GIVEN MATERIAL</strong></td>
</tr>
<tr>
<td>Preforming of Complex Shapes</td>
</tr>
<tr>
<td>Forming Large Scale Components</td>
</tr>
<tr>
<td>Bonding of Dissimilar Materials</td>
</tr>
<tr>
<td><strong>(2) INTRINSIC ATTRIBUTES OF CERAMIC STATE</strong></td>
</tr>
<tr>
<td><strong>A. ISOTROPY OF PHYSICAL PROPERTIES DUE TO RANDOMIZATION</strong></td>
</tr>
<tr>
<td>Isotropic Acoustical and Optical Wave Propagation</td>
</tr>
<tr>
<td>High Magnetic Domain Mobility—&quot;Soft&quot; Magnets</td>
</tr>
<tr>
<td><strong>B. DISCONTINUITY OF PHYSICAL PROPERTIES DUE TO GRANULARITY</strong></td>
</tr>
<tr>
<td>Inhibited Crack Propagation—Fracture Resistance</td>
</tr>
<tr>
<td>Inhibited Optical Breakdown</td>
</tr>
<tr>
<td>Inhibited Acoustical Cavitation</td>
</tr>
<tr>
<td>Inhibited Magnetic Domain Motion—&quot;Hard&quot; Magnets</td>
</tr>
</tbody>
</table>

The first category includes those instances where one would be perfectly happy to have a single crystal of a given material and a given shape, if it were possible to grow one. However, a ceramic might be the only way of approximating the properties of the needed crystal. To give an example, if one wished to modify some property, e.g., index of refraction, by chemical substitution, ceramic processing would be a convenient and, perhaps, the only means of accomplishing the modification. To give a further example under the first category, if one wished to form a component into a complex shape, e.g., a high temperature lamp envelope, again a ceramic might be the only way to obtain in the needed shape a reasonable approximation to the crystalline physical properties.

Part (1) of Table I gives additional examples.

The second category includes applications which make use of properties inherent in the finely divided, densely aggregated state of matter—the ceramic state. To give an example, if a given physical phenomenon—say, wave propagation—involves averages over distances large compared to the microstructure of the ceramic the phenomenon becomes isotropic. To give an example at the other end of the relative size scale, some important properties of ceramics, e.g., fracture resistance, involve the pinning of defects by the microstructure.

Part (2) of Table I elaborates further on other types of physical properties which fall within the second category.

In sum, there are a good many reasons for at least considering the possibilities offered by ceramics for a given application. The remaining questions concern the relative performance of current ceramic materials and the prospects for improved performance. In our work at Harvard we have attempted to answer some of these questions.
In the discussion that follows, we emphasize wave propagation—both optical and acoustical—in ceramics. Of course, ceramics are usually turbid, i.e., optically opaque and acoustically lossy. In recent years there have been a number of improvements in ceramic technology which have lead to reduction in turbidity. There has been a lot of fine work on transparent ceramics, much of which has not been reported in the open literature. Although we have drawn heavily on the published reports of others as well as on our own experience we do not attempt an exhaustive review here. Rather, the goal is to provide the basis for understanding and evaluating ceramics.

II. SIMPLE MODEL OF WAVE PROPAGATION IN CERAMICS

In essence, the turbidity of ceramics is a consequence of inhomogeneous wave scattering from void regions, randomly oriented crystallites, inclusions, and other coarse scale imperfections. To achieve useful ceramics, the total effect of all inhomogeneities must be minimized. Unfortunately, it is not possible to simultaneously reduce all scattering sources by any given method of ceramic preparation. In particular, densification with corresponding reduction in pore scattering comes at the expense of enhanced grain growth and, often, of stoichiometric instability. The optimization of the fabrication process requires some means of estimating the relative importance of various scattering mechanisms over a broad range of materials parameters. A complete theory, which would do justice to the subtleties of wave theory and to the details of ceramic microstructure, is unavailable and, doubtless, would be intractable in any case. We sketch here a simple model of ceramic turbidity which provides a general overview of the important factors in ceramic fabrication, particularly the interplay of density and grain size considerations. In spite of the gross simplicity of the model, we shall show that it gives a remarkably good quantitative picture of real ceramic properties.

There has been rather little theoretical work on wave propagation in densely aggregated materials such as ceramics. For good reason, it is a difficult problem. Both optical and acoustical wave fields are vector fields and great care is required to adequately treat wave propagation in a random medium with locally anisotropic responses. However, as a first simplification, we ignore all such complications and assume that the gross features of wave propagation in ceramics are derivable from a scalar Helmholtz equation for an appropriate scalar amplitude function \( \psi (r, \omega) \)

\[
\nabla^2 \psi (r, \omega) + n^2 (r) k^2_0 \psi (r, \omega) = 0 ,
\]

where \( k_0 = \omega/c \) is taken to be the propagation factor in the void regions. The spatial variations in the refractive index \( n (r) \), represent the net effect of all scattering—inhomogeneous and coherent—from material dispersed throughout the void space. We follow the spirit of a mean field approximation by assuming that \( n (r) \) has a well defined average value \( \langle n \rangle \), and that a mean coherent field propagates through the random medium with propagation velocity \( c/\langle n \rangle \) \[1\]. We further assume that turbidity comes about as a result of the scattering of the mean coherent field by deviations from the mean state—defined as \( \langle n \rangle \mu (r) = n (r) - \langle n \rangle \). We emphasize, in this view, it is the deviations from the mean state that scatter, not pores, grains, etc. Finally, we assume that the accumulative effect of the deviations is small—a pragmatic assumption which spans materials likely to have any conceivable utility. Thus, we avoid any discussion of multiple-scattering from the deviations from the mean.
Taken together these assumptions lead us to a quasihuristic expression for the attenuation of the intensity of the coherent beam

\[ \alpha = 4 \langle n \rangle^2 k_0^2 \langle \mu^2 \rangle \int_0^\infty \Gamma (r) \sin^2 (\langle n \rangle k_0 r) \, dr \, , \]  

in terms of the two-point correlation function

\[ \Gamma (r) = \frac{\langle \mu (\rho) \mu (\rho + r) \rangle}{\langle \mu^2 \rangle} = \frac{\langle n (\rho) n (\rho + r) \rangle - \langle n \rangle^2}{\langle n^2 \rangle - \langle n \rangle^2} \, . \]  

Similarly the relative intensity of the beam scattered into a unit solid angle in a direction \( \theta \) with respect to the incident beam, i.e., the Rayleigh ratio, is

\[ R (\theta) = \frac{\langle n \rangle^2 k_0^2 \langle \mu^2 \rangle}{4\pi} \frac{1 + \cos^2 \theta}{|\sin \theta/2|} \int_0^\infty \Gamma (r) \sin (\langle n \rangle k_0 r) \, r \, dr \, . \]  

We have taken the medium to be statistically isotropic and homogeneous so the \( \Gamma (r) \) is only a function of the magnitude of the relative distance between the test points. It remains to find some form of \( \Gamma (r) \) that may adequately represent the properties of a real ceramic. If we had but one important inhomogeneity the simple function \( \exp (-r/a) \) would be sufficient for most purposes [2]. For more than one inhomogeneity we could take a series of such functions, but, a priori, it is hard to see how to establish the relationship among the various terms in the series. Computer simulation of the microstructure of the ceramic has been used quite successfully to generate correlation functions which, in turn, have been used to obtain \( \alpha \) and \( R (\theta) \) values [3]. Although rich in detail, the simulations are, however, too costly for survey purposes.

We discuss here a model based on what we call the doubly random Markovian process. Even though the model is very simple, it does not seem to have been applied to wave scattering before, if indeed to any other physical phenomenon. The details of the statistics are discussed in detail elsewhere [4], but Fig. 1 gives the essential parameters of the model. The sketch is of the index variations measured along a test line through the three dimensional aggregation of grains. For specificity, we have taken the grains to have two distinct index values, \( n_a \) and \( n_b \). The parameter \( (w_{12}) \) is the inverse of the mean projected grain size which is always less than the mean grain size, but approaches it in the limit of zero porosity, i.e., \( (w_{12})^{-1} \) tending to zero. \( (w_{12})^{-1} \) in fact is the grain size measured in the intercept method of quantitative microscopy [5]. The lineal porosity \( P_L \) is distinct from the measured volume porosity, but it can be argued stereographically that the two quantities are indistinguishable at high and low densities. The random process thus defined is Markovian in the sense that successive grains have uncorrelated index values. For the doubly random process we find that the correlation function can be expressed as

\[ \Gamma (r) = \{ P_L (\Delta n)^2 + (\delta n)^2 \}^{-1} \{ P_L (\Delta n)^2 \exp [-P_L (w_{12}) r] \}
\]

\[ + (\delta n)^2 \exp [- (w_{12}) r] \} \, , \]  

where \( \Delta n = p_a n_a + p_b n_b - 1 \) and \( \delta n = (p_a p_b)_{1/2} (n_b - n_a) \). Clearly, the first term in the bracket leads to void scattering and the second to birefringent grain scattering. Substituting Eq. (5) into Eq. (2)

\[ \alpha = \frac{k_0 (\Delta n)^2 (1 - P_L)}{\langle n \rangle} \{ P_L G (2 \langle n \rangle q P_L) + b^2 G (2 \langle n \rangle q) \} \, , \]  

(6)
FINE GRAINED CERAMICS

\[ n(r) \]

\[ n_b \]

\[ n_a \]

\[ <n> \]

--- SAMPLING LINE SEGMENT ---

\[ w_{12} = \text{PROBABILITY OF DOWN JUMP/UNIT LENGTH} \]

\[ = (\text{MEAN PROJECTED PARTICLE SIZE})^{-1} \]

\[ w_{21} = \text{PROBABILITY OF UP JUMP/UNIT LENGTH} \]

\[ = (\text{MEAN PROJECTED VOID SIZE})^{-1} \]

\[ P_L = \frac{w_{12}}{w_{12} + w_{21}} = \text{LINEAL POROSITY} \]

\[ P_a = \frac{w_{12}}{w_{12} + w_{21}} = \text{RELATIVE PROBABILITY OF PARTICLE OF TYPE a} \]

\[ P_b = 1 - P_a = \text{RELATIVE PROBABILITY OF PARTICLE OF TYPE b} \]

Fig. 1. Model for doubly random Markovian process defining parameters.

where

\[ G(x) = \frac{x^3}{1 + x^2} \]  

\[ q = k_0 \ (w_{12})^{-1}, \text{ and } b = \frac{5n}{\Delta n}. \]

Similarly, Eq. (4) yields

\[ R(\theta) = \frac{k_0 (\Delta n)^2 (1 - P_L)}{\pi \langle n \rangle} q^2 F(\{\sin \theta/2 \mid q; P_L, b, \langle n \rangle\}) \]  

(7)

where

\[ F(x; P_L, b, \langle n \rangle) = \frac{P_L^3}{[1 + (x \langle n \rangle P_L)^2]^2} + \frac{b^2}{[1 + (x \langle n \rangle)^2]^2} \]  

(8)

We have found that most optical data available to us is remarkably well represented by Equations (6) and (7). As evidence, we consider the fit to a beautiful set of infrared measurements on high density alumina [6]. Samples were collected over a period of several years from a LUCALOX manufacturing facility to establish the precise variations of optical

| POROSITY \( a \) (cm\(^{-1}\)) | CALCULATED \( (w_{12})^{-1} \) FOR TRIAL \( b \) VALUES (\( \mu \)) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0079          | 13.4            | 27              | 26              | 24              | 24              |
| 0.0054          | 8.25            | 37              | 33              | 30              | 28              |
| 0.0029          | 4.18            | 60              | 43              | 32              | 27              |
| 0.0017          | 2.42            | 86              | 36              | 22              | 17              |
| MEAN \( (w_{12})^{-1} \) (\( \mu \)) | 53              | 35              | 27              | 24              | 18              |
| TRIAL \( b \) VALUES | 0.001           | 0.002           | 0.0026          | 0.003           | 0.004           |

--- TABLE II ---

High density alumina—"LUCALOX" absorption coefficients \( (\lambda = 4.5 \mu) \) porosity variation with constant grain size of 27 ± 3 microns.
transmittance with grain size and density. Table II summarizes our attempt to fit the porosity variation at constant grain size. The birefringent parameter $b$, is varied in Eq. (6) to obtain a calculated grain size consistent over the range of data. The best fit value of $b = 0.0026$ is consistent with the optical constants of crystalline $\text{Al}_2\text{O}_3$ and the calculated grain size of 27 $\mu$ is in precise agreement with the measured value! Our calculations of variations with grain size at constant density also fit the measured data very well.

With some confidence that our model represents the state of affairs in real materials, we now use it in a predictive mode to give an overview of what might be expected of various methods of ceramic fabrication. One useful way of looking at the predictions of the model is to use Eq. (6) to generate curves of constant attenuation (precisely $a/k_0 = \text{constant}$) in the density-grain size plane—see Figures 2, 5, and 6. Such diagrams are useful in conceptualizing the effect of sintering on optical and acoustical properties.

Figure 2 shows the optical turbidity map for a typical cubic substance—i.e., $b = 0$. Note that the curves are consistent with Rayleigh scattering ($a \sim \lambda^{-4}$) at low attenuation.

![Image of Figure 2](image_url)

**Fig. 2.** Results of model calculation for material of refractive index of $n_\infty = 2.0$ and zero birefringence. Shown is $k_0 (\omega_1)^{-1}$ vs relative line density with contours of constant attenuation per wavelength ($\lambda$). The right hand axis, which can be interpreted as a projected particle size under certain restrictions as discussed in the text, has been shown when evaluated for a wavelength of 1 $\mu$. 
and with stochastic scattering ($\alpha \sim \lambda^{-2}$) at high attenuation. Clearly, the key to satisfactory optical performance is maximum densification with grain size a secondary concern. Figure 3 shows a photograph of five useful transparent ceramic materials. In each case the samples are of high density, although the densification methods differ. With the exception of PZLT all of the materials are cubic. However, PZLT is a ferroelectric and can be poled so that the orientation of grains becomes correlated, i.e., $P_g$ and, thus, $b$ vanished [10]. It seems clear that transparent cubic materials will become increasingly available with applications limited by other considerations such as impurity levels and intrinsic absorptions.

The situation for finite $b$ materials is considerably more complicated. In view of the complications, do we really need to develop methods for such materials? $b$ is always finite for acoustical wave propagation even in cubic materials, but there are also reasons to be interested in optically birefringent materials. To take but one example, we consider the potentially important magneto-optical materials FeBO$_3$ and YFeO$_3$. Both materials have large birefringences and in single crystal form may vitiate the effect of the magneto-optics. When the birefringence is averaged out in the ceramic the magneto-optics is fully effective. In this case we would be taking advantage of Category (2)A in Table I.

In Fig. 4 we show a typical calculation of the relative angular scattering pattern. As $b$ decreases, we note the rapid decline in the forward scattering intensity. The interesting optical properties of poled PZLT can be understood in terms of such variations. Figures 5 and 6 show respectively turbidity diagrams for a strongly birefringent optical material and an ordinary acoustical material. The important point to note is that the grain-orientation grain-size effects become significant at relatively low densities and low attenuations. Thus, in designing a sintering sequence, it is vital that the slope of the grain-growth curve on the turbidity maps be less than the rise in contours of constant
Fig. 4. Angular dependence of relative scattering function evaluated for a material of relative density 99.0% and average index of 2.5. Contours are shown for materials of varying birefringence parameter ($b = 0, 0.01, 0.02$).

attenuation. These limitations place severe restrictions on the type of processing that may be used on finite $b$ materials.

III. PREPARATION OF DENSE FINE GRAIN CERAMICS

In Section II the importance of grain structure and density for wave propagation in ceramic materials has been demonstrated. In ceramics processing powders are compacted and fired at temperatures sufficient to develop useful properties. Assuming there are no solid-state reactions or transformations one can generally say four major changes occur. One, there is an increase in average grain size; two, there is a change in pore shape; three, there is a decrease in pore size; four, the number of pores is lowered. The last two changes give rise to a decrease in porosity. To go into details of all these processes is beyond the scope of this paper and even a single volume, but several important points cannot go without some degree of attention.

During all sintering processes there is some form of material transport. For pressureless sintering these have been most recently enumerated by Ashby [12] and, at previous
times, by a number of other workers [13]. It is generally recognized that for intermediate and final stage densification diffusional processes are dominant and can be divided into boundary or volume diffusion. The driving force that gives rise to densification is the decrease in surface area and, thus, the lowering of the surface free energy. When an external pressure is introduced as an additional driving force, as is the case in hot pressing, account must be taken of plastic flow and stress-enhanced volume diffusion as material transport mechanisms during the final stages of densification. These are much more difficult problems and will only briefly be discussed below. Experiments have verified that the rate of densification is inversely proportional to a power of grain size and proportional to a power of an appropriate diffusion coefficient [14]. The initial particle size of the material and the sintering temperature determine sintering processes which take place by solid-state diffusion and must be closely controlled.

Decreasing initial particle size and using high pressures in final state densification is probably the most effective means of minimizing final grain size. While a number of methods exist for making fine grain (d < 0.1 μ) starting materials, freeze drying methods [15] have several very important advantages. The most prominent advantage
Fig. 6. Result of model calculation for acoustical scattering showing $k_0 (w_{12})^{-1}$ vs relative line density with contours of constant attenuation per wavelength. Values for attenuation and projected particle sizes have been evaluated at 100 MHz and are shown in parentheses and on the right hand scale respectively.

is that very little change in technique is required over an unlimited range of materials of varying crystal structure and control is afforded over particle sizes from very reactive fine grain materials of 50 Å sizes to less reactive micron sizes. The freeze drying process for producing metal or ceramic powders is very simple in concept. It involves the dissolution of salts containing cations of interest, flash freezing of the resulting solution, and sublimation of the solvent, followed by conversion to the desired product. The conversion can be effected by calcining to the appropriate oxide or metal form. Alternatively, conversion may be to a compound, for example, by reacting with a carburizing gas to form a refractory carbide. The initial step of the process, that is, the dissolution of the salt or salts produces a homogeneous solution which is retained during the low temperature quenching process. This essentially locks in the cation distribution which had been present in the liquid solution. The homogeneity of the product is retained during the freeze drying process, since little atomic movement occurs during the low temperature sublimation process. Since most of the frozen solvent molecules are removed by sublimation, the resulting structure is a very open one. The resulting increased surface-to-volume ratio
makes feasible lower calcining temperatures, which in turn leads to a finer particle size after the calcining operation.

A scanning electron micrograph of a typical salt after decomposition is shown in Figure 7 [16]. We see here the open structure of the product is retained through the conversion process as well as the outward geometry of the sprayed droplet. Materials so produced are very fragile and can easily be broken. The resulting shells always show an open partially sintered network of fine grains whose size is dependent on the decomposition time and temperature. Figure 8 shows a transmission electron micrograph of the structure in freeze dried YFeO$_3$. The average grain size is 100 Å. Bright and dark field electron microscopy have verified that the variations in intensity correspond to single crystals. As sintering progresses the individual grains are more easily identifiable.

In evaluating metal salts for use in freeze drying, a number of important points must be kept in mind. Obviously the metal salt must be soluble in a workable solvent. Unfortunately solvents other than water (such as alcohols) must be used for less soluble materials such as barium salts. Certain properties of the salts themselves critically determine their applicability to the freeze drying process. The salt must decompose prior to melting so as not to negate the advantages derivable from the freeze drying process. Also low decomposition temperatures are necessary so as to minimize grain growth.

Table III lists a number of materials we have made in our laboratory together with the salt and solvent used. To illustrate the control over particle size, we have shown in Fig. 9 results of transmission electron micrograph studies and x-ray line broadening studies
Fig. 8. Transmission electron micrograph of fine grains in YFeO₃ made from freeze dried rare earth iron acetates. The average size is 100 Å. Scale: 0.16 μ.

<table>
<thead>
<tr>
<th>FINAL MATERIAL</th>
<th>SALTS</th>
<th>SOLVENTS</th>
<th>DECOMPOSITION</th>
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<tr>
<td>Fe₂O₃</td>
<td>FeSO₄</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe₂(SO₄)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>XH₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>FeSO₄</td>
<td>H₂O</td>
<td>15 hr, 950 °C, H₂</td>
</tr>
<tr>
<td></td>
<td>XH₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>GeI₄</td>
<td>CH₃OH + H₂O</td>
<td>3 hr, 720 °C, H₂</td>
</tr>
<tr>
<td>FeBO₃</td>
<td>Fe(NH₄)₃(C₂O₄) + H₃BO₃</td>
<td>H₂O</td>
<td>1 hr, 400 °C +</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 hr, 835 °C, vac.</td>
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<tr>
<td>LuFeO₃</td>
<td>Lu₂(SO₄)₃ + Fe₂(SO₄)₃</td>
<td>H₂O</td>
<td>30 min, 1100 °C</td>
</tr>
<tr>
<td>YFeO₃</td>
<td>Y(CH₃COO)₃ + Fe(CH₃COO)₂</td>
<td>H₂O</td>
<td>1 hr, 700 °C</td>
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<tr>
<td>YAlO₃</td>
<td>Y₂(SO₄)₃ + Al₂(SO₄)₃</td>
<td>H₂O</td>
<td>3 hr, 875 °C</td>
</tr>
<tr>
<td>Y₃Al₅O₁₂(YAG)</td>
<td>3Y₂(SO₄)₃ + 5Al₂(SO₄)₃</td>
<td>H₂O</td>
<td>10 min, 1383 °C</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Al₂(SO₄)₃</td>
<td>H₂O</td>
<td></td>
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<tr>
<td>ZnAl₂O₄ : Cr</td>
<td>ZnSO₄ + Al₂(SO₄)₃ + 0.1 Cr₂(SO₄)₃</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>TiI₄ + BaI₂</td>
<td>CH₃OH + H₂O</td>
<td>2 hr, 700 °C</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Ba(C₂H₃O₂)₂ + TiO(C₂H₃O₂)₂</td>
<td>CH₃OH + H₂O</td>
<td></td>
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<tr>
<td>KH₂PO₄(KDP)</td>
<td>KH₂PO₄</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>NaNO₂</td>
<td>NaNO₂</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>NbCl₅</td>
<td>C₂H₄OH</td>
<td>20 hr, 1000 °C</td>
</tr>
<tr>
<td>Au + MgO</td>
<td>Au(CH₃CO₂)₂ + Mg(CH₃CO₂)₂</td>
<td>H₂O</td>
<td>30 min, 450 °C</td>
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**TABLE III.** Selected fine grain materials.
on YFeO$_3$ derived from freeze dried yttrium and ferric acetates. The metal acetates were chosen as they satisfied all the conditions mentioned above. Other rare earth salts are objectionable from at least one of the already mentioned points in that they decompose at too high a temperature or melt prior to decomposition.

The subsequent use of these ultra fine grain materials with high pressure hot pressing methods ($P = 30$ kbar $\approx 450,000$ psi) has yielded fine grain ceramics with densities greater than 98% and grain sizes less than one micron. More importantly, consolidation at these high pressures has resulted in a means of preparing high purity, fine grain, fully dense materials without the use of additives often required to promote densification in conventional hot pressing and pressureless sintering. High pressures enable densification in relatively short times at temperatures several hundred degrees below that required for conventional hot pressing. The low temperatures, short times, and high pressures limit normal diffusional processes and hence, fine grain microstructures are obtained. Furthermore, high pressure hot pressing is performed in a closed system which enables one to maintain the stoichiometry of the starting powders; this is important when a material is subject to decomposition by preferential vaporization of one component. The resultant decrease in temperatures afforded by high pressures and the maintenance of a closed sample system would be of use for those materials, such as the chalcogenide spinels, for which the decomposition temperature of the multicomponent system limits the sintering temperature [17].

The high pressure hot pressing apparatus in present use is a straight piston cylinder form originally described by Boyd and England [18]. Pressures to 30 kbar (450,000 psi) are easily obtained in a bore of 1 in. diameter. The graphite heater and sample cell
arrangement uses lava and boron nitride as a pressure transmitting medium and allows encapsulated samples of $\frac{3}{4}$" diameter to be routinely made.

Understanding hot-pressing technology rests in the development of physical models which quantitatively describe, in terms of appropriate mechanisms, the rate of densification as a function of processing parameters (temperature, applied pressure, atmosphere, etc.) and physical properties of the material (grain size, self diffusivity, surface energy, amount, and distribution of porosity, etc.). These mechanisms may involve any of the means by which a material can plastically deform [19]. The development of such models has been impeded by the complexity inherent in a real physical system, though some efforts have been directed along these lines in recent years [20]. A general description of the densification process such as that developed for deformation of materials is still unavailable. While advances have recently been made, as exhibited by Ashby [12], in the extensions of the deformation map concept to pressureless sintering maps, the formidable problems associated with changes in microstructure (grain size) and applied pressures have yet to be understood in a way that covers all ranges of pressures (stress) and temperature.

Although constitutive equations for all pressures and temperatures have not been set down, Coble [21] has adopted the well known constitutive equations for diffusional creep to approximate the densification rate during intermediate stage and final stage hot pressing, and concluded that within reasonable limits this approach represents a satisfactory approximation. The models for densification rates are obtained by assuming the flow behavior during densification is the same as observed in fully dense materials and then requiring the applied stress to be a function of porosity, effects due to surface energy, and gases within pores. It has been shown, for the case of volume-diffusion-controlled vacancy diffusion, with pores distributed throughout the grains, that the Coble hypothesis can be reasonably well satisfied [22]. However, more detailed treatments are certainly required.

The essence of Coble’s hypothesis is that for the general creep rate given by a constitutive equation of the form

$$\dot{\varepsilon} = f(\sigma),$$

(other quantities, such as temperature, and grain size are variable parameters) the densification rate in the final stage is obtained by replacing $\dot{\varepsilon}$ by $\dot{\rho}/\rho$ where $\rho$ is the fractional density of the material, and replacing $\sigma$ by an effective stress $\sigma_{\text{eff}}$, given by

$$\sigma_{\text{eff}} = \frac{\sigma}{\rho} + \frac{2\gamma}{R} + P_{\text{INT}}.$$

Here, $\gamma$ is the surface tension of the solid; $R$ an average pore radius; and $P_{\text{INT}}$ the pressure caused by gases contained within pores. The first term is included to represent, in an approximate manner, the amplification of applied stress due to the presence of porosity. For those values of stress and temperature where the predominate deformation mechanism is diffusion controlled (bulk transport-Nabarro Herring or boundary transport-Coble) the constitutive equation is of the form

$$\dot{\varepsilon} = \sigma^n \frac{D}{\rho^m},$$

where: $\dot{\varepsilon}$ is the steady state creep rate; $\sigma$ is the stress; $d$ is the grain size; and $D$ is an applicable diffusion constant. The implications of this are clear for fine grain materials.
For the purposes of this paper, which is an overview of feasibility, we present our results for the densification of YFeO$_3$ [23]. Rare earth orthoferrite, YFeO$_3$, derived from freeze-dried acetates, calcined at 700 °C, was used in the high pressure hot pressing work. The starting materials were processed so that they had average grain sizes of several hundred angstroms. Powders were subsequently encapsulated in platinum and cold pressed to approximately 45% theoretical density before being hot pressed. Figure 10 illustrates the resulting grain size, and density, at a number of different hot pressing temperatures. The pressure used for the presented data was 20 kbar (300,000 psi) and was applied for 15 min. The temperature programming up to the final hot pressure temperature was uniform and never took more than 10 min. Care in releasing pressure and lowering temperature was exercised so as to avoid thermally fracturing the samples. Samples of \( \frac{3}{8} \) dia and \( \frac{1}{4} \) thick were easily obtainable. Densities were measured by standard displacement methods. Grain sizes were obtained from etched surfaces using an optical microscope and when necessary a scanning electron microscope. The right hand histograms show \( d_{\text{max}} - d_{\text{min}} \), the difference (in microns) of the largest and smallest observed grains in the sample. The distribution of grain sizes appeared to be log-normal and thus the average grain size lies near the small end of the \( d_{\text{max}} - d_{\text{min}} \) range.

Infrared measurements are presented in Fig. 11 for several of the hot pressed samples. The absorption coefficients were computed from transmission and reflection measurements on a Perkins-Elmer Model 567 infrared spectrometer from 2.5-50 \( \mu \). In the region of low intrinsic absorption for the single crystal (from 2.5-8 \( \mu \)), the scattering absorption coefficients behave qualitatively as expected; the absorption declines as the wavelength increases. At constant grain size, the higher density sample has lower absorption. Even though GHP 38 is slightly less dense than GHP 29, it is less absorbing because

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Fig. 10. Structural results - grain size and density in percent - for freeze-dried YFeO$_3$ at pressures of 20 kbar (300,000 psi) and times of 15 min for varying temperatures. The samples at 1050 °C were mechanically unstable so that no meaningful densities could be measured.
Fig. 11. Optical transmission properties of several hot pressed YFeO$_3$ samples in the infrared. The density and average grain size for the samples are: GHP 28, $\rho = 96.7\%$, $d = 2.3$ $\mu$; GHP 29, $\rho = 98.5\%$, $d = 2.4$ $\mu$; GHP 38, $\rho = 98.0\%$, $d = 1$ $\mu$. The cold pressed sample has a density of about 40% with average grain size of 0.03 $\mu$. The strong bands are tentatively identified as adsorbed H$_2$O.

It has a smaller grain size. Finally, it is interesting to note that in the region of lattice absorption above 8 $\mu$, the samples with finer grain size (GHP 38 and the cold pressed powder) are relatively more transparent than materials with larger grain size. This enhancement in transmission continues to 50 $\mu$ and may be due to retardation effects in finite size crystalline materials as discussed by Lucas [24] and several other workers [25].

Density and grain structure are of particular importance when one is attempting to enhance optical, thermal, electrical, magnetic, or mechanical properties in ceramic materials. To fully utilize any of these properties more work is needed in finding, and optimizing, high pressure sintering schedules, as previously described for pressureless sintering by Ashby [12]. The optimization of pressureless sintering schedules can lead to higher density, finer grain materials as has been shown by Huckabee and Pamlour [26]. They found it was possible to obtain densities in excess of 99% with grain sizes of 0.75-1 $\mu$ by use of a rate controlled sintering program and commercially available powders. With ultra fine grain freeze dried materials and high pressures one should be able to make substantive improvements.

IV. DISCUSSION

In spite of considerable advancement in the ceramic art, the prospects of wide application in micro-electronics seem modest. Through pressureless sintering, with careful
control of sintering schedules and the use of appropriate additives, one may obtain, in large size and specified shapes, high density samples of a number of materials. However, resultant large grain size and impurity effects seem to limit the utility of these materials in sophisticated optical applications. For example, it is conjectured that the presence of ThO₂ additives in high density Y₂O₃ lead to small but extended fluctuations in the refractive index, thereby reducing lasing efficiency [27]. In principle, pressure sintering bypasses some of these difficulties, but does, in turn, introduce practical problems in obtaining samples of adequate size for some applications. However, these problems are not fundamental and have been mitigated by the development of continuous hot pressing techniques [28, 29] and large bore pressure dies [30]. In the same regard, it is our view that the subject of ceramic extrusion or forging needs further investigation [31, 32].

The key issue is that our understanding of pressure sintering is not sufficient to allow us to exploit it fully. In particular, it has not been possible to obtain high density materials with grain sizes of less than 0.5 μ and to fully eliminate residual entrapped gases. By trial and error improvements will continue, but a more complete modeling of pressure sintering is essential to the design of optimum sintering programs. Short of the development of such a methodology the scope of ceramics applications will be limited.

We end with a word about acoustical materials. As discussed above there have been some successful applications of ceramics in optical technology, but, to our knowledge, ceramics have had no applications in surface wave acoustics. Indeed, the discussion of section two makes clear the difficulties of making use of ceramics in acoustics—see Figure 6. Due to elastic anisotropy, the grain size effect is of first order importance even in cubic materials. Except for a single set of measurements on PZT (hot pressed lead zirconate titanate with iron additives) [33], to our knowledge the acoustical properties of truly fine grain materials have not been studied. Recently we have made some preliminary measurements on YFeO₃ samples at 20 and 60 MHz. As might be expected from Fig. 6, samples with submicron grain structure show relatively low attenuation (order of 10 dB/cm). Thus for acoustical materials the statements above on pressure sintering apply with even greater importance.

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REFERENCES


[7] YTTRALUX is the General Electric trade name for sintered Y2O3. This sample was obtained through the courtesy of C. Greskovich and is 89% Y2O3 + 10% ThO2 + 1% Nd.

[8] This PZLT is hot pressed La doped Pb, ZrTiO3 and was obtained from the Sandia Laboratories through the courtesy of R. Barkowski.

[9] IRTRAN-V is the Kodak trade name for hot pressed MgO and is commercially available from Kodak.


