(1) grinding
(2) strain
(3) phase change / polymorphism
(4) $BaTiO_3$
(5) SiO_2

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Effects of Strain Induced by Pressing and Grinding $BaTiO_3$ and SiO_2

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The simple ceramic processes of grinding and pelleting leave residual stresses in common materials such as SiO_2 and $BaTiO_3$. The magnitude of these stresses is easily detected by changes in the temperature of phase transitions; such processes are enough to completely eliminate the phase transitions.

I. Introduction

In a previous paper[1] it has been shown how the change in the temperature of a phase transition may be used as a semiquantitative measure of residual strain (including negative pressure) in systems such as crystals crystallizing in a glassy matrix. It is obvious that if bonding between grains is efficient the same effect will be found in any polycrystalline polyphase system in which no stress-relieving mechanism is operative during the quenching or cooling from high temperatures or high pressures, yet such "pressure-quenching" is exactly what is done in all pelleting operations.

This paper is not intended as an exhaustive account of residual strains in polycrystalline systems but rather as a brief recording of results arising from experimental procedures that are prominent in certain common ceramic processes. Furthermore certain facts regarding residual stress in single-phase polycrystalline systems should be clarified. In a single-component system, a positive stress in one direction must be balanced by a negative stress in another direction so that the total stress in the system is zero. It is assumed **that this condition exists here, particularly in those experiments where grinding is conclusively shown to produce a short-range-order layer and hence a *second phase* for a balancing stress. In pelleting, the surface layers of the specimen must** also be of a different structure, i.e. disordered owing to high shear stresses at the specimen-piston interface.

II. Grinding-Induced Strain

It has been determined that repetitive grinding has a pronounced influence on the transition temperature of a phase. The grinding was effected in a mechanical mullite mortar and pestle. The introduction of any foreign material by this procedure is immaterial as it would tend to dilute the sample only slightly.

Because of the enormous difficulty of determining true particle sizes, no attempt has been made here to determine the size distribution of the samples but only to record the duration of grinding. However, caution was exercised in using only those samples which had been in continuous contact with the pestle. The change in transition temperature was determined by DTA using as a standard the original starting material (325 mesh) or AgI (T_{tr} = 146°C). The precision of a transition temperature measurement was ±0.5°C.

Well-ordered 3C-cristobalite was ground continuously in three experiments for 18, 20, and 24 hours with a resultant increase in transition temperature of 1.2°, 6.3°, and 3.8°C,* respectively. Repeated grinding for 1 week completely removed any trace of a transition. Similarly, quartz ground for 20, 41, and 53 hours produced an increase in transition temperature of 1.0°, 0.6°, and 1.6°C* with complete elimination of the transition after 1 week. X-ray diffraction of the samples showed only minor changes with slight reduction in intensity of the peaks. However, the quartz samples ground for 1 week showed conclusively the existence of large amounts **of amorphouslike material with smaller amounts of crystalline material. Removing the outer skins by dissolving the product of the 20-hour run in dilute HF for 5½ hours altered the transition back to its original temperature. Finally, by grinding the fired $BaTiO_3$ for 35 hours, the ΔT_{tr} is lowered 3°C, i.e. from 129° to 126°C. In all cases the amplitudes of the DTA peaks are reduced but in none of the samples are they noticeably broadened. These data may be explained by the hypothesis of an induced strain generating a layer with**

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* The fact that simple numerical correspondence was not obtained need not be of concern here since many complex variables were not controlled in this preliminary study.

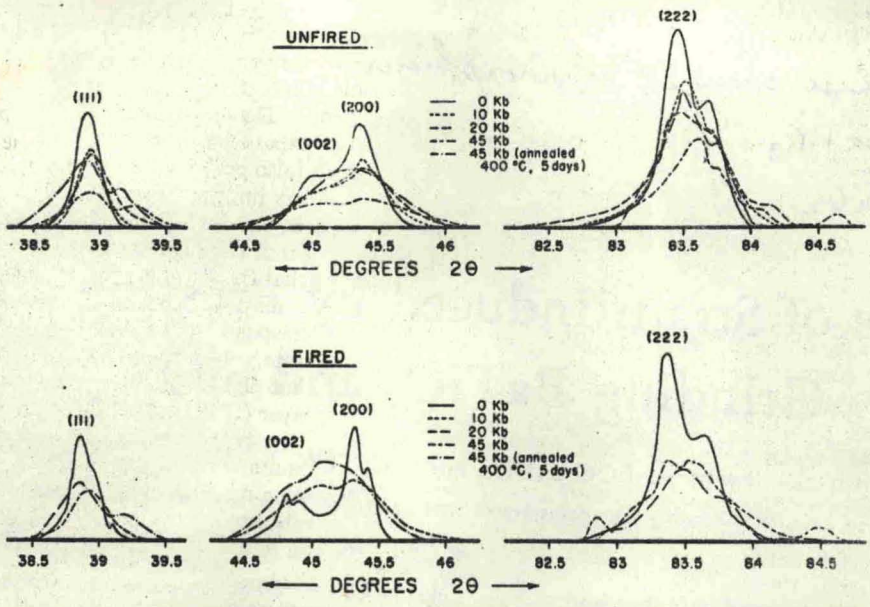


Fig. 1. X-ray patterns of pressed disks of $BaTiO_3$ showing line broadening and *d*-spacing shift as a function of initial pressure.

short-range-order structure and different elastic and thermal properties from the well crystallized phase.

III. Strains Left After Pelleting

(1) *Qualitative Results on NH_4Cl*

To determine if pelleting operations produce measurable effects on polycrystalline, single-component materials, highly compressible NH_4Cl was pelleted (1:13 diameter-to-thickness ratio) at 45 kilobars and the primitive face-centered-cubic transition temperature was determined by DTA. The increase in the absolute temperature and in the hysteresis of transitions is as follows:

$$\alpha NH_4Cl \text{ (loose powder)} \underset{161°C}{\overset{186°C}{\rightleftharpoons}} \beta NH_4Cl$$

$$\alpha NH_4Cl \text{ (pelleted at 45 kilobars)} \underset{149°C}{\overset{192°C}{\rightleftharpoons}} \beta NH_4Cl$$

The 6°C increase in the upward transition temperature can be attributed to the average strain on the individual grains and a value for this can be obtained by making certain assumptions with known elastic parameters.[1] The decrease in the downward transition temperature can also be explained as above; however, the numerical difference between it and the upward transition temperature is probably due to the difference in the high and low crystal structures. Ubbelohde[2] gives as a probable explanation, even for the small hysteresis in the lower NH_4Cl transition ($-32°C \uparrow$ $-30.5°C \downarrow$), the states of strain and surface energy due to the nucleating phase being included in the parent. Here the possibility of strain has clearly been increased after the lower transition by increasing the grain contacts. This increased strain manifests itself in the increased hysteresis.

(2) *DTA and X-Ray Data on Pelleted $BaTiO_3$*

More detailed work was carried out on polycrystalline $BaTiO_3$ (high-purity TAM material*), for which more of the physical constants are known. Disks (33:1 diameter-to-thickness ratio) were pressed at various pressures from 0 to 45 kilobars on as-received and fired $BaTiO_3$. The fired material, before pressing, was held at a temperature of 1350°C for 55 hours and then ground to 325 mesh (44μ); it gave an inexplicably high tetragonal-cubic transition temperature of 129°C. The unfired material (2 to 3μ) gave the usual transition temperature of 120°C. Each disk was carefully mounted on a sample holder for X-ray analysis with every effort to keep the surface of the disk parallel to the surface of the holder; the reflections (111), (222), (002), and (200) were recorded with typical results as shown in Fig. 1. Immediately noticeable is the shift in *d* spacing and the extensive line broadening of each reflection. For this qualitative approach, it may be tentatively assumed that the *d*-spacing shift is mainly a response to elastic stresses whereas the line broadening is a function of both plastic flow and particle size reduction. By annealing the sample, which had been pressed to 45 kilobars, for 5 days at 400°C, the *d*-spacing shift was somewhat reduced, partly confirming the assumption given above.

From the *d*-spacing change alone, internal stresses of 13,500 psi and 26,325 psi were calculated for the fired and unfired material respectively, pressed at 45 kilobars. Since the change of transition temperature with pressure is $dt/dp = 5.8 \times 10^{-3}$°C per atm,[3] a change of ΔT_t, of $-5.4°$ or $-10.8°$C could be expected depending on whether the material had been fired or not.

The calculations are based on the Clausius-Clapeyron equation and thus a hydrostatic stress system is assumed; however, the values do give an order-of-magnitude estimate. Each pressed disk was run several times in the same DTA apparatus from $-196°$ to 220°C with no observable peaks at the maximum amplification. This surprising result is attributed to the magnitude and distribution of the magnitude of the stresses which tend to "smear" the transition over a large temperature interval. Stresses of the magnitude indicated above could cause changes of 10° to 100°C in the transition temperature, and the distribution of stresses would admit the coexistence of several phases over that particular interval strained to varying degrees.

Of interest is the relative position of the (002) and (200) reflections in both materials. Their position confirms the empirical fact that high-temperature annealing increases the tetragonality of the low-temperature $BaTiO_3$.[4] Large internal stresses, however, reduce the tetragonality in the

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fired phase and tend to leave it unaffected in the smaller-size unfired phase. The line broadening from the pressed disks of $BaTiO_3$ may be assumed to result from both plastic flow and particle size reduction. To confirm this assumption and to specify the nature of the strains present this exploratory approach would have to be extended and refined considerably. From the strong elastic anisotropy it may be concluded that overall strains occurring in individual grains are more influential than internal strains due to lattice imperfections.

Examination of replica electron micrographs seems to indicate almost no size reduction with the unfired material and a slight effect with the fired material. According to Paterson,[5] the line broadening of plastically deformed calcite is due mainly to internal strains which correspond to a stored energy of 10 cal per g. A similar value is not unreasonable in $BaTiO_3$ as well. If it is assumed then that the energy stored in $BaTiO_3$ is equal to or greater than this, and the elastic anisotropy is considered, it is reasonable not to expect a measurable single temperature of transition.

IV. Discussion

Interestingly enough, the effect of grinding on the change of the transition temperature of $BaTiO_3$ is the opposite of the effect of pressing. The lowering of the transition temperature in $BaTiO_3$ caused by the grinding corresponds to an increase in pressure which can be determined from the Clausius-Clapeyron relation. Since this additional pressure may be removed by etching, it may be suspected that it is produced by a compressive stress due to the formation of a disordered surface layer placing the rest of the phase in compression. The surface layer must vary structurally from crystalline tetragonal $BaTiO_3$ and be able to sustain a radial tensile stress of approximately 10,000 psi. The conditions under which such a stress is produced are analogous to situations of mismatch in thermal expansion.[1] Both methods involve stresses derived from the intimate relation of different materials whether or not they are structurally or chemically different. The difference between the stresses created by thermal expansion as performed in the previous study[1] and by grinding (also possibly in pressing) is that in the former case a bulk matrix imposes thermal stresses on the embedded grains whereas in the latter case the stresses are due to a surface layer. From the high stress present in this layer it must be inferred that this layer is coherently bound to the bulk crystallites. It may be concluded, therefore, that this surface layer corresponds to a highly disordered nonequilibrium crystalline state. X-ray and electron diffraction studies[6] have shown that there is a discrepancy in symmetry between a surface layer (thickness of 100 A) and the bulk with the misfit between the two being smaller below the Curie temperature. These results confirm the existence of such a surface layer. In the same manner as for $BaTiO_3$, the ΔT_{tr} for quartz and cristobalite can be explained by a tensile stress through the formation of a short-range-ordered phase on the surface.

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