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THE EFFECTS OF THERMAL CYCLING ON THE PHYSICAL AND MECHANICAL PROPERTIES OF [NZP] CERAMICS

T. B. Jackson and S. Y. Limaye
LoTEC, Inc.
Salt Lake City, UT 84119

W. D. Porter
Oak Ridge National Laboratory
Metals and Ceramics Division
Oak Ridge, TN 37831

ABSTRACT

The [NZP] ceramics, sodium zirconium phosphate and its crystal structure analogs, are noted for their very low thermal expansion characteristics. What has not been widely studied is the effect of thermal cycling on physical and mechanical properties. Two [NZP] compositional series were selected ($Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ and $Ca_{1-x}Sr_xZr_4P_6O_{24}$) that exhibit varying bulk thermal expansion from positive to negative and varying degrees of thermal expansion anisotropy. The effect of thermal cycling, to 1250°C, on the bulk thermal expansion and flexural strength of these ceramics will be discussed in relationship to changes in density, thermal expansion anisotropy and microstructure.

INTRODUCTION

Since the discovery of low thermal expansion properties of $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ type ceramics [1] there has been a tremendous amount of work done investigating other related compositions for their low thermal expansion properties [2-5]. Two compositional series have been discovered that have low bulk thermal expansion, varying from positive to negative. Compositions within these series also have varying degrees of thermal expansion anisotropy, and potential high useful temperature ranges [6,7]. These two compositional series are

$Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ and $Ca_{1-x}Sr_xZr_4P_6O_{24}$. In order to successfully incorporate these new materials into industrial applications, where many heating and cooling cycles will be encountered, it is necessary to determine the effect of thermal cycling on the physical and mechanical properties of these ceramics.

There are a number of commercially available low thermal expansion ceramics with high thermal shock resistance available today. The "state-of-the-art" low coefficient of thermal expansion ceramics (fused silica, aluminum titanate, cordierite, etc.) have found many useful industrial applications, but as physical requirements for new products increase, new materials will be needed to be developed to take their place. The disadvantages with the currently used ceramics are their limited useful temperature range (generally below 1200°C) and the inflexibility of tailoring their thermophysical properties to meet specific application requirements. The unique crystal structure of the [NZP] ceramic family allows for the tailoring of the bulk thermal expansion, melting temperature, thermal conductivity and mechanical strength. The tailoring of the physical properties is achieved through the substitution of various ions at different lattice sites in the crystal structure [8]. Within the compositional series investigated in this study, isotropic, low thermal expansion compositions have been identified with upper use temperatures above 1400°C. Since these compositions are isotropic they will have very predictable and stable physical and mechanical properties. The bulk thermal expansion of the anisotropic compositions depend to some degree on grain size and thus processing conditions. The above series of compositions were selected because of their potential for applications in advanced diesel engines as intake and exhaust port liners, as particulate traps and as catalyst supports.

Differences in apparent bulk thermal expansion of some [NZP] compositions have been noticed in the past. Some differences can be ascribed to grain size and the amount of associated microcracking [9], but there are cases where grain size cannot explain the differences. This study takes a systematic look at the bulk thermal expansion of compositions in the above series as a function of the number of thermal cycles to which the specimen has been subjected. Changes in the mechanical strength of the ceramic are determined after thermal cycling and related to changes in the microstructure.

EXPERIMENTAL PROCEDURE

Five compositions in the $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ series (BS series) and three compositions in the $Ca_{1-x}Sr_xZr_4P_6O_{24}$ series (CS series) were prepared by the solid state reaction of constituent oxides. For the BS series x equals 0.00, 0.17, 0.25, 0.375 and 0.50 and will be referred to as BS0, BS17, BS25, BS37.5 and BS50, respectively. The CS series has x equal to 0.25, 0.375 and 0.50 and will be referred to as CS25, CS37.5 and CS50, respectively. Ceramic slips of each composition were prepared using water as the carrier with appropriate binders and dispersants. After ball milling for 24 h, 63.5 mm x 63.5 mm x 9.5 mm tiles were slip cast using plaster of paris molds and then allowed to solidify before removal. After the green tiles were dried they were bisque fired at 1000°C to remove the binders and dispersants. The tiles were then sintered in air with a 10 h isothermal hold time. The sintering temperature was 1625°C for the BS series and 1575°C for the CS series. Finally the tiles were surface ground and sliced into test specimens.

Three expansion test specimens were prepared for each composition. The specimens were ground to a length of 25 mm to match the length of the reference standard (NBS sapphire) used in a Theta dual push-rod dilatometer. The bulk linear thermal expansion was measured from 20°C to 1250°C in the presence of static room air. The heating and cooling rate was 3°C/min., except below 300°C during the cooling cycle where the cooling rate is slowed by heat dissipation from the furnace.

Flexural strength determinations were conducted at room temperature according to ASTM standards (C1161-90) using an Instron model 6027 universal testing machine. Test specimens were the prescribed 3 mm x 4 mm x 50 mm and a 4-point test fixture was used. The inner and outer span was 20 mm and 40 mm, respectively. Typically there were 8 to 10 test specimens for each composition and each test condition. The BS25 and CS25 compositions had 35 to 40 specimens for each test condition.

Thermal cycling of test specimens was achieved by placing the specimens into crucibles made from the BS25 composition. The crucibles were loaded into a furnace where they were heated to 1250°C using a ramp rate of 20°C/min. with an isothermal hold at temperature for 30 minutes, allowing all the specimens to reach thermal equilibrium. The specimens were cooled in the furnace to below 100°C before the next cycle commenced. The furnace atmosphere was room air. Periodically the cycling was interrupted to determine weight loss of selected specimens and to remove a portion of the test specimens which had undergone their prescribed number of thermal cycles.

Fracture surfaces from flexural test specimens were prepared to determine changes in the microstructure of the various compositions, before and after thermal cycling. A Hitachi S-800 Field Emission Scanning Electron Microscope was used for the microstructural evaluations.

RESULTS AND DISCUSSION

Thermal Expansion

As mentioned above, two compositional series were chosen for this study that have varying bulk thermal expansions and degrees of axial thermal expansion anisotropy. Figures 1 and 2 show the relative expansions of the members of the two series. Included in the figures are both the heating and cooling portion of the thermal expansion curve. It can be seen that there are three isotropic compositions, BS17, BS25 and CS50, where the cooling curve lies on top of the heating curve. The other compositions have varying degrees of anisotropy, the magnitude of which can be estimated by the amount of hysteresis. Three specimens of each composition were measured to insure sample to sample consistency. Figures 3 and 4 show the results obtained for the anisotropic CS25 and the isotropic BS25 specimens. There is good sample to sample consistency for all compositions tested.

Initially it was believed that the bulk thermal expansion of many [NZP] type ceramics changed with repeated thermal cycles to temperatures above 500°C. This conclusion was reached when inconsistent expansion measurements were obtained between samples of the same composition or samples measured more than once. Subsequently it was determined that specimens which had undergone identical preparation exhibited identical expansion curves. Identical sample preparation in this case was sintering followed by surface grinding and finally slicing the sintered tiles into test specimens. The slicing and grinding operations saturate the specimen with a water-based coolant which has been determined to promote crack opening in the ceramic [10]. Because of the greater initial crack opening the first expansion curve is lower than subsequent measurements. After the first run in the dilatometer the absorbed water is driven off, allowing microcracks to close. Only a small amount is reabsorbed from the room air upon cooling, partially reopening the microcracks. Thus, the specimen is not restored to its original saturated condition. Subsequent runs in the dilatometer are usually very similar, as shown in Fig. 5. The differences can be explained by differences in room air humidity and the amount of time between heat treatments and dilatometer measurements, Fig. 6. For the highly anisotropic and negative thermal expansion compositions there is evidence that at room temperature continued crack opening occurs at a very slow rate until an equilibrium is reached. Thus, for this class of ceramics extreme care is needed in order to produce accurate and comparable thermal expansion measurements, especially for anisotropic compositions which have a grain size larger than the critical grain size for microcrack formation. The average grain size for all the compositions tested in this study varied from 6 to 12 micrometers. The anisotropic compositions (BS0, BS37.5, BS50, CS25 and CS37.5) have calculated critical grain sizes that are less than 5 micrometers, thus they are subject to microcrack formation.

Compositions which have an isotropic axial thermal expansion (BS17, BS25 and CS50) have little or no thermal expansion hysteresis. This is due to little or no microcrack formation upon cooling from either the sintering temperature or the thermal expansion measurement temperature, in this study 1250°C. The critical grain size for microcrack formation in the isotropic compositions studied is greater than 50 micrometers. These compositions also have bulk linear thermal expansion curves that remain constant after many thermal cycles. Saturation with water from the grinding operation does not affect the initial thermal expansion measurement, Fig. 7 and 8. This is due to the fact that these compositions have little open porosity due to the absence of microcracks and thus have very little absorbed water. This is evident from examining the weight loss of the specimens as a function of the number of thermal cycles, Fig. 9 and 10. The weight has been normalized to the weight after 1 heating cycle to 1250°C. The isotropic compositions (BS25 and CS50) have very little weight change, where as, the anisotropic and thus microcracked compositions (BS0, BS37.5, BS50, CS25 and CS37.5) have large initial weight losses.

Flexural Strength

The flexural strength of these ceramics is dependent on residual porosity, grain size, number and severity of microcracks and processing flaws, with porosity and microcracking being the predominant factors. The isotropic compositions have the highest flexural strength of all the compositions tested due to the absence of microcracking. In the CS series as the anisotropy increased the strength decreased, Fig. 11. The room temperature flexural strength of the anisotropic compositions was not improved due to any crack healing occurring during thermal cycling. It can be assumed that the number of microcracks remained nearly constant and the severity of the cracks, at least at the tensile surface was unchanged, Fig. 11 and 12. Repeated thermal cycles did not have any beneficial or adverse effect on the flexural strength of any of the compositions tested.

Microstructure

Photomicrographs reveal a similar microstructure for all compositions, with generally equiaxed grains. The CS series has a slightly larger grain size than the BS series. The micrographs of the isotropic compositions show transgranular fracture and little evidence of microcracking as expected. After repeated thermal cycles there is no apparent change in the microstructure, Fig. 13 and 14. Thermal cycling to 1250°C does not cause any increase in the average grain size for these compositions. The grain size and the degree of thermal expansion anisotropy determine whether microcracking will occur in anisotropic compositions [11]. In all of the anisotropic compositions fabricated for this study the grain size was sufficiently large so as to be greater than the critical grain size for microcracking to occur. In all anisotropic compositions evidence of microcracking along grain boundaries could be detected, Fig. 15-18. The micrographs of the anisotropic compositions also show both transgranular and intergranular fracture modes.

The most striking feature shown in the micrographs is the presence of voids after thermal cycling. The void formation looks much the same as the voids formed by creep cavitation in other ceramics, but in this case no external stress was applied. The voids or cavities are formed along grain boundaries and faces, Fig. 15-18. In some cases voids could be detected in specimens after just one thermal cycle, but were not found in any of the as sintered specimens. All of the anisotropic compositions had some degree of void formation, with the more anisotropic and negative expansion compositions having the greatest amount. Since the flexural strength does not change with cycling this change in microstructure does not effect the mechanical strength. Strength is still primarily a function of microcrack severity and density.

CONCLUSIONS

Thermal cycling of BS and CS type [NZP] ceramics has little effect on their physical and mechanical properties. The differences in the bulk thermal expansion of microcracked anisotropic compositions are due to differences in the starting conditions of the test specimens, i.e. the amount of microcrack opening due to moisture absorption prior to performing the measurement. Mechanical strength is unaffected and is generally related to the axial anisotropy of the composition and thus the severity of the associated microcracking, for the cases where the grain size is larger than the critical grain size for microcrack formation, as was the case in this study. Thermal cycling to 1250°C does not produce any increase in strength through microcrack healing. At temperatures up to 1250°C these [NZP] compositions are very stable and should perform well in industrial applications. Formation of voids in the anisotropic compositions was unexpected and merits further study.

ACKNOWLEDGMENTS

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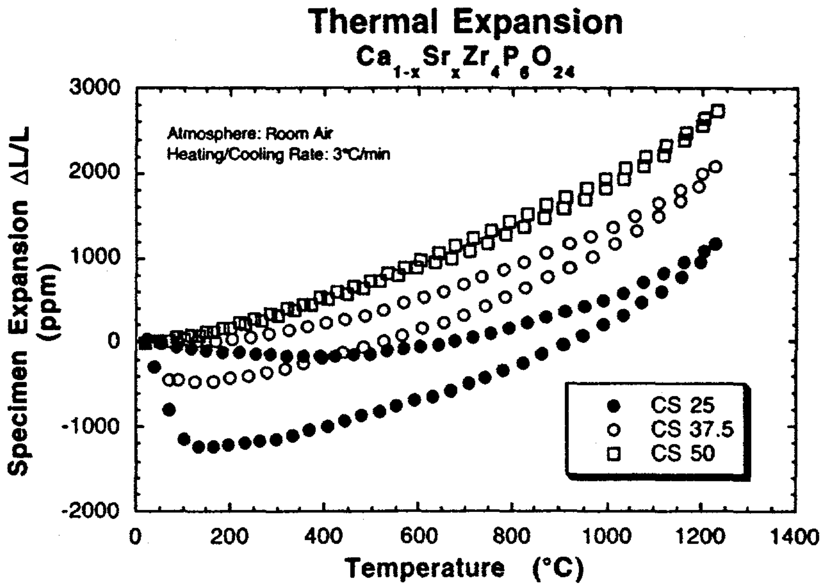


Figure 1. The bulk thermal expansion of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ increases as x increases, while the anisotropy decreases.

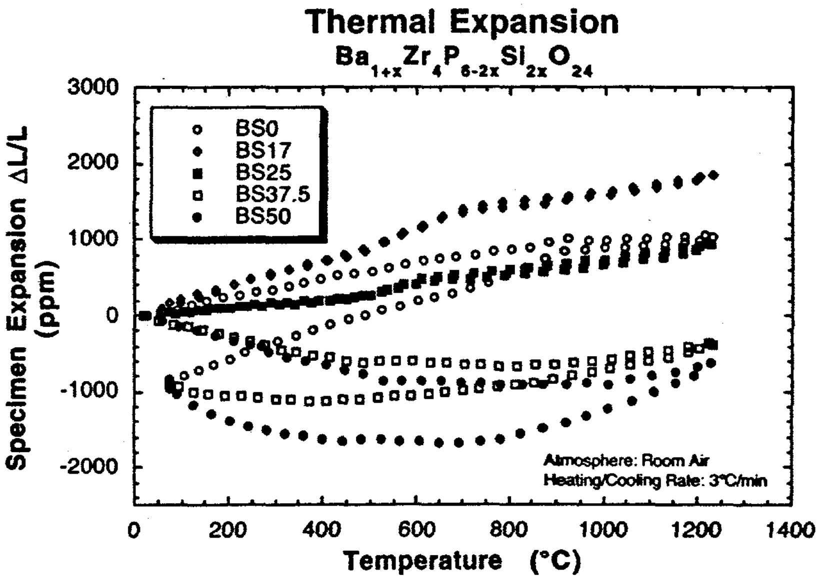


Figure 2. The bulk thermal expansion of $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ varies from positive to negative with increasing x. Minimum thermal expansion anisotropy is between x=0.17 and x=0.25.

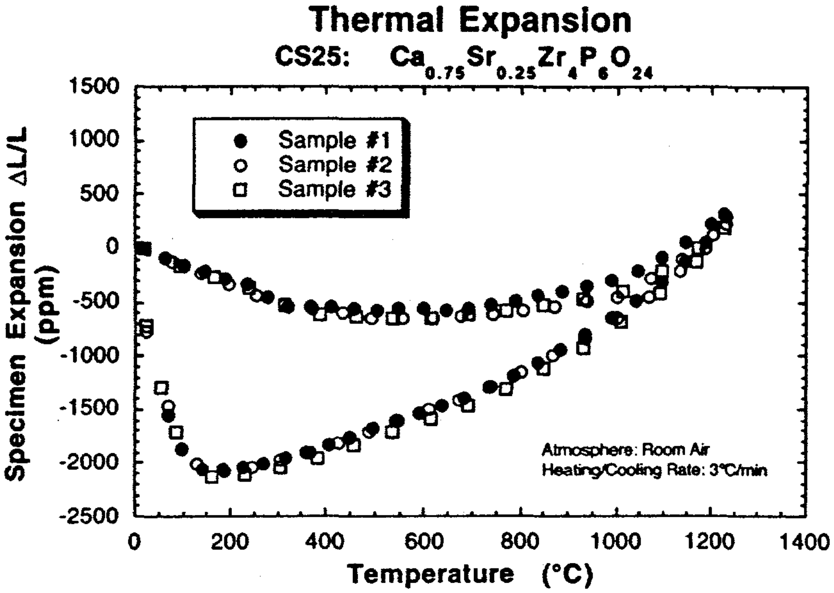


Figure 3. The three thermal expansion curves for the anisotropic CS25 composition, measured in the as sintered and ground condition, indicate good sample to sample consistency.

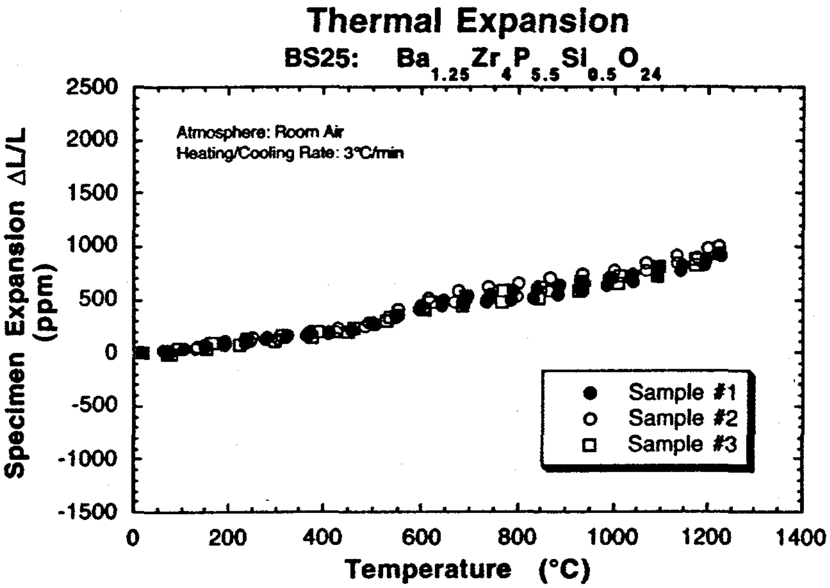


Figure 4. Isotropic BS25 as measured in the sintered and ground condition exhibits excellent reproducibility.

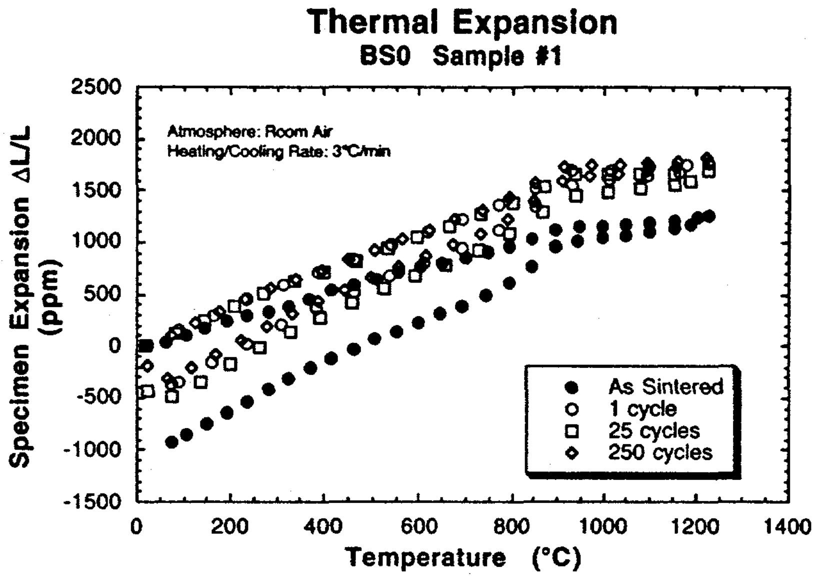


Figure 5. Bulk thermal expansion appears to increase after initial measurement was made in the as sintered and surface ground condition.

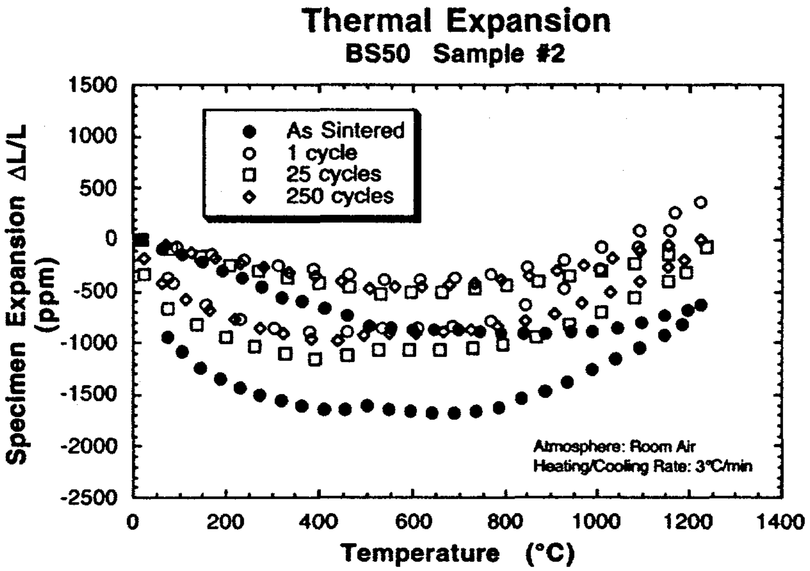


Figure 6. Variation in the bulk thermal expansion of highly anisotropic compositions is due to varying amounts of moisture induced microcracking occurring at room temperature after thermal cycling.

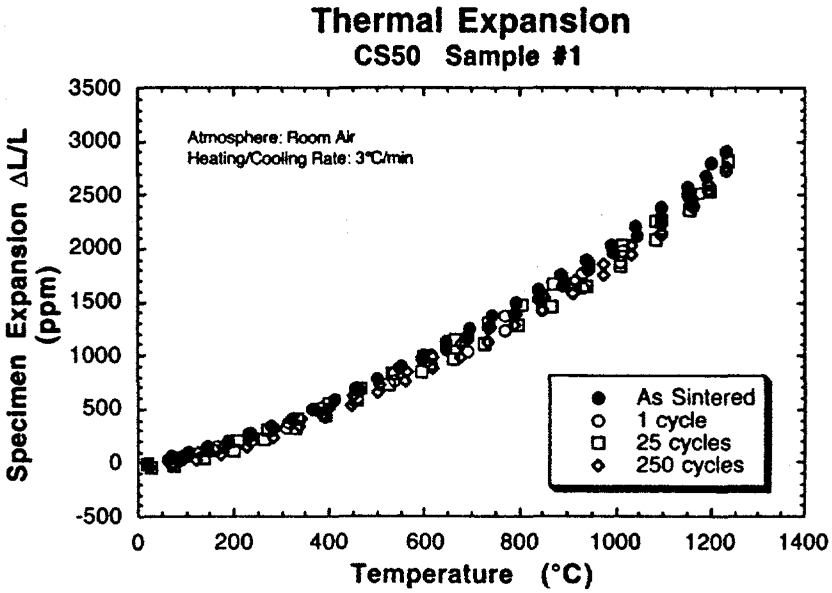


Figure 7. The bulk thermal expansion of isotropic CS50 is constant after repeated thermal cycles to 1250°C.

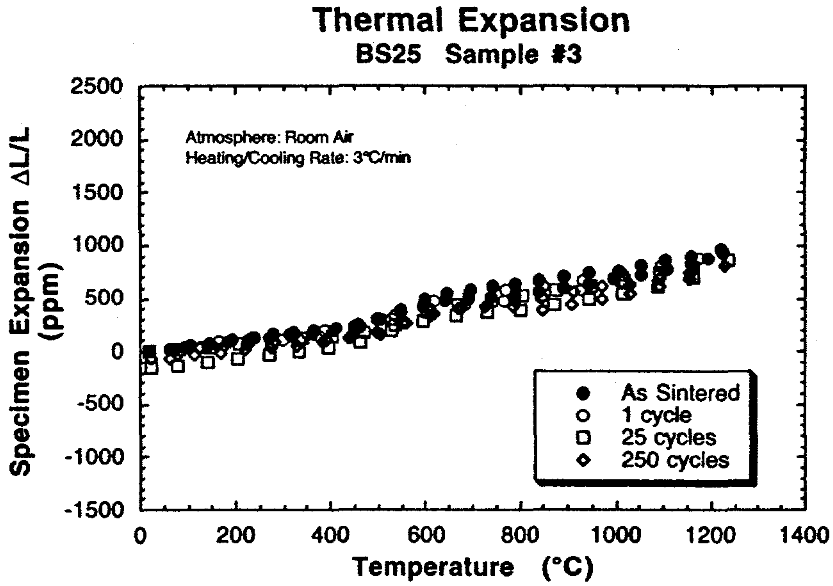
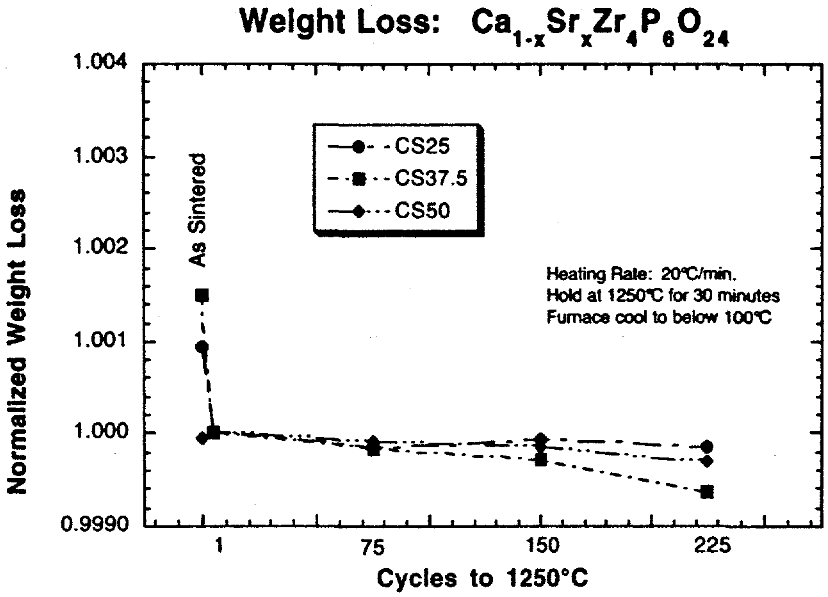
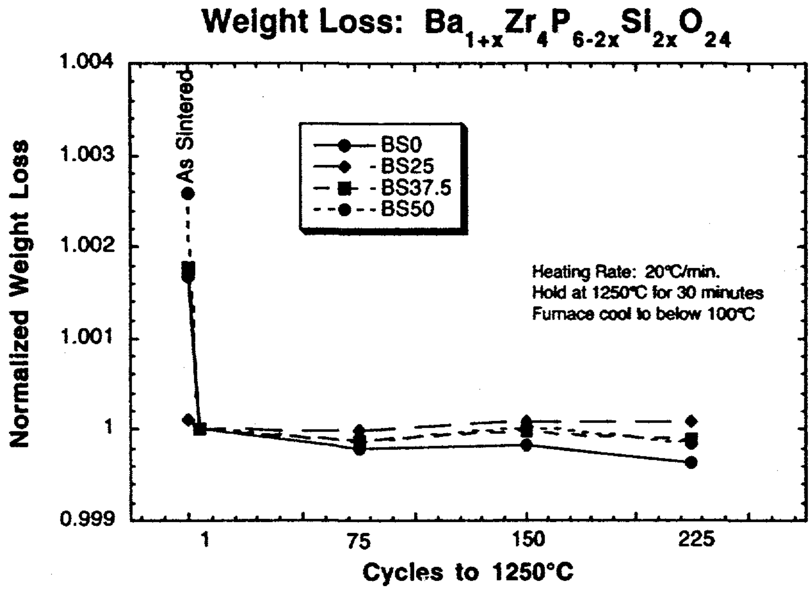


Figure 8. The bulk thermal expansion of isotropic BS25 is constant after repeated thermal cycles to 1250°C.


Weight Loss: $Ca_{1-x}Sr_xZr_4P_6O_{24}$

Heating Rate: 20°C/min.
Hold at 1250°C for 30 minutes
Furnace cool to below 100°C

Figure 9. The weight loss for CS series materials as a function of thermal cycling is less than 0.05 percent after 250 cycles to 1250°C.


Weight Loss: $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$

Heating Rate: 20°C/min.
Hold at 1250°C for 30 minutes
Furnace cool to below 100°C

Figure 10. The weight loss for BS series materials as a function of thermal cycling is less than 0.05 percent after 250 cycles to 1250°C.

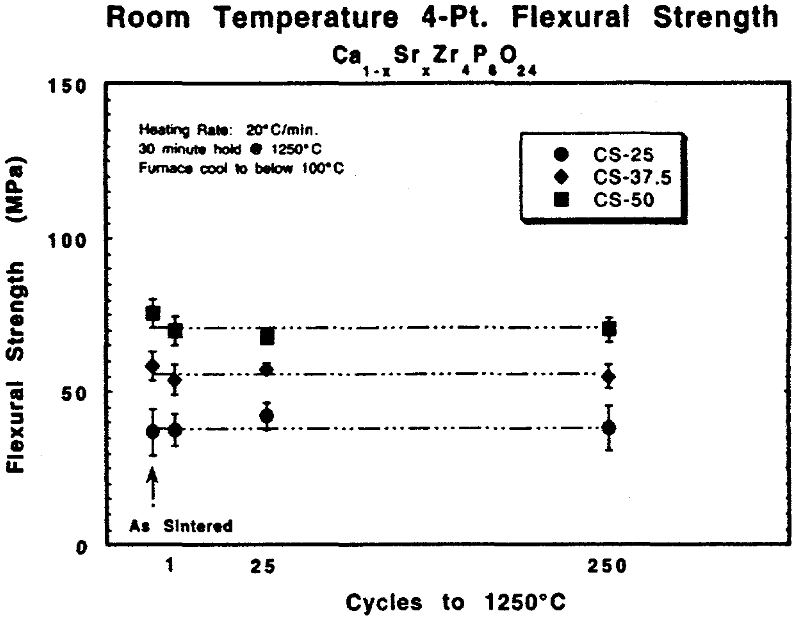


Figure 11. Flexural strength is stable over many thermal cycles and is related to the degree of axial anisotropy.

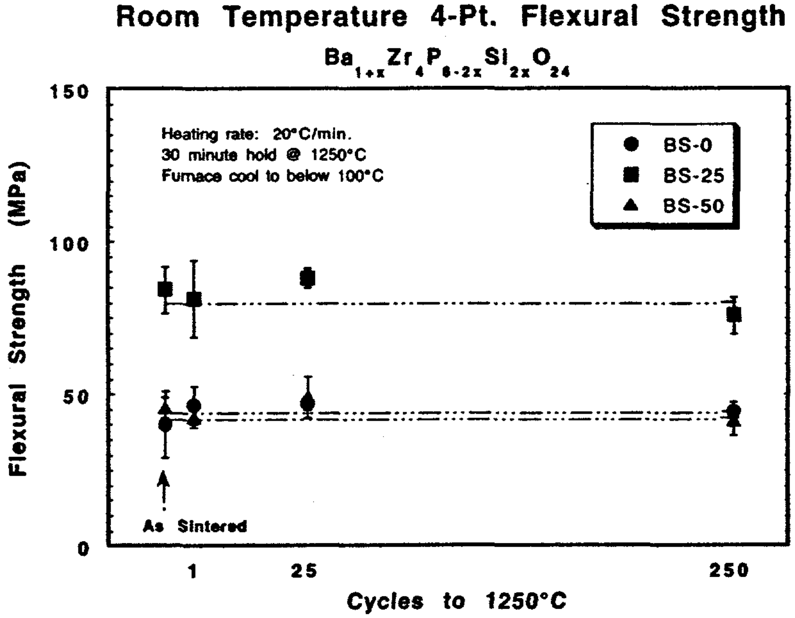


Figure 12. Isotropic BS25 has relatively high strength when compared to positive bulk thermal expansion BS0 and negative bulk thermal expansion BS50.

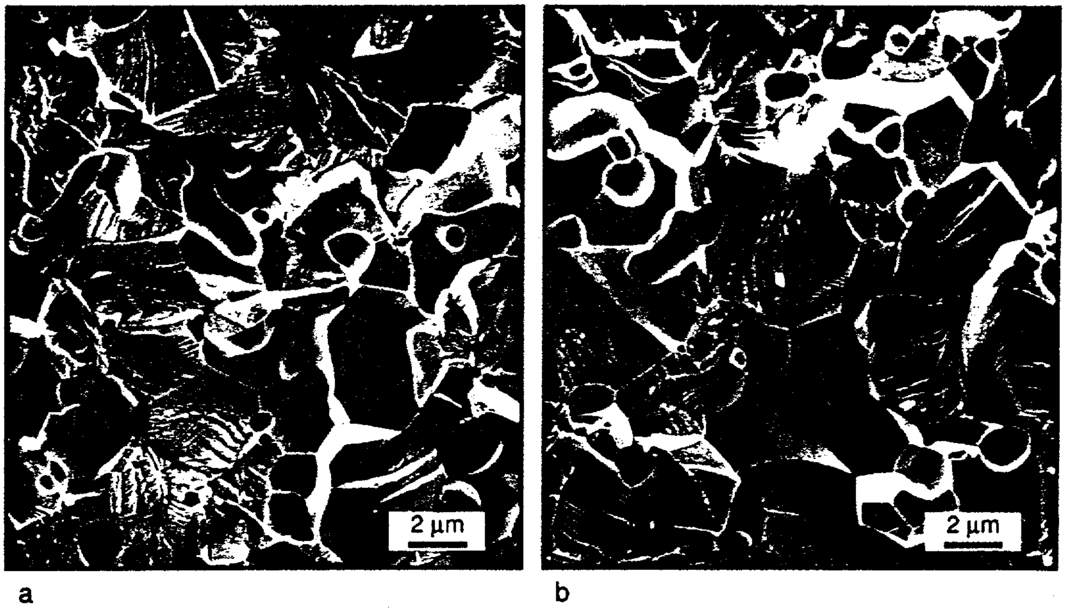


Figure 13. Isotropic CS50 as sintered (a) and after 250 thermal cycles to 1250°C (b).

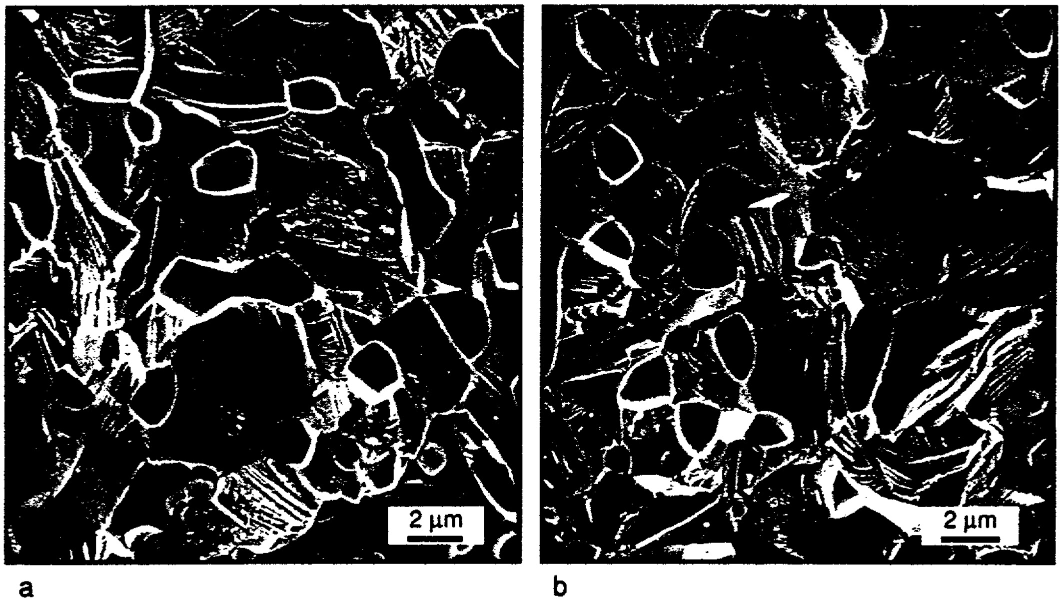


Figure 14. Isotropic BS25 as sintered (a) and after 250 thermal cycles to 1250°C (b).

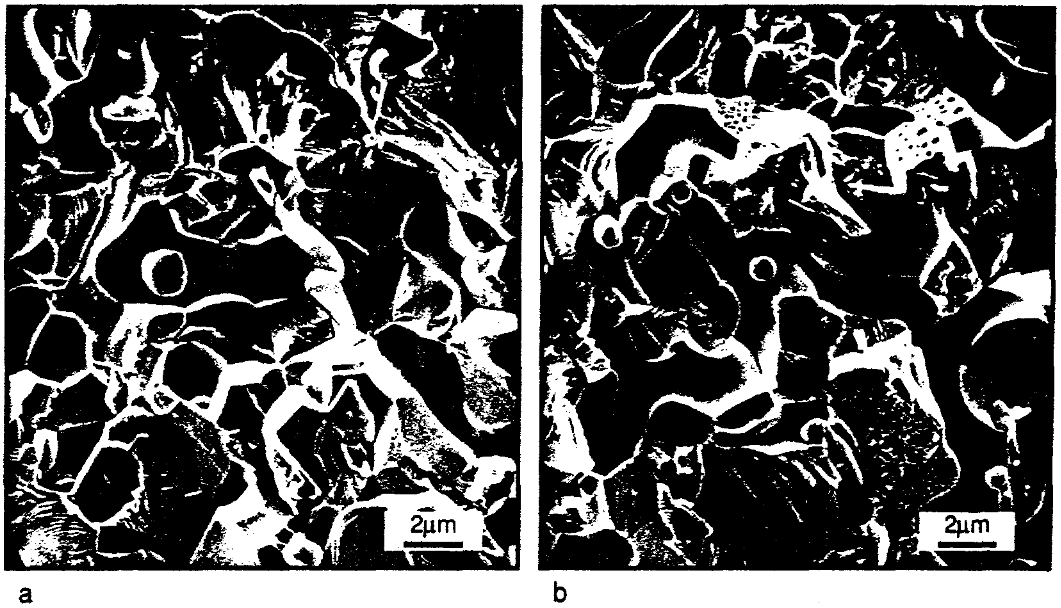


Figure 15. BS0 with positive bulk thermal expansion, as sintered (a) and after 250 thermal cycles to 1250°C (b). Note the cavity formation due to thermal cycling.

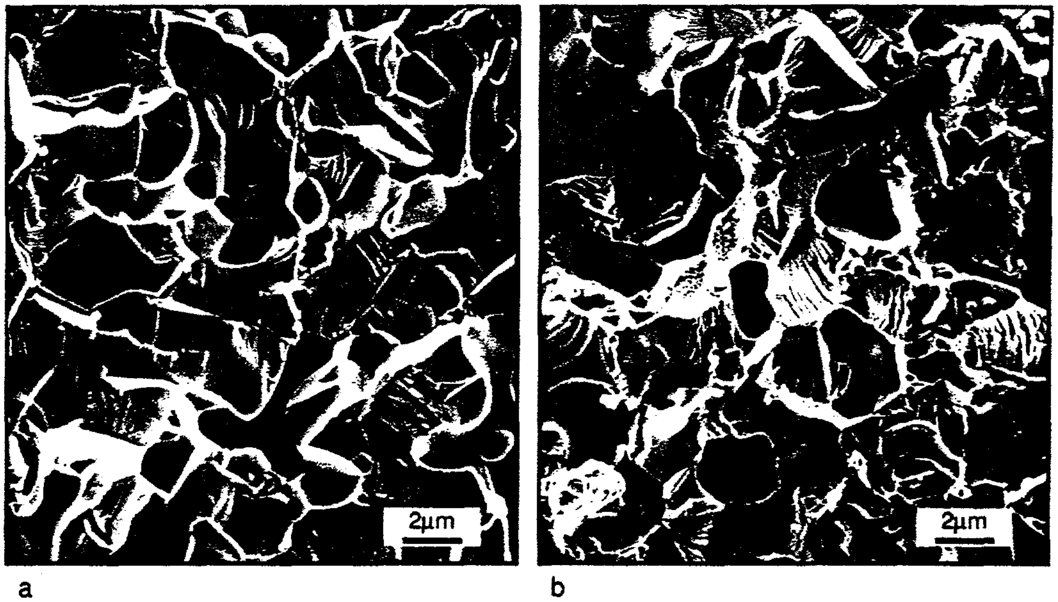


Figure 16. BS50 with negative bulk thermal expansion, as sintered (a) and after 250 thermal cycles to 1250°C (b). Note the cavity formation due to thermal cycling.

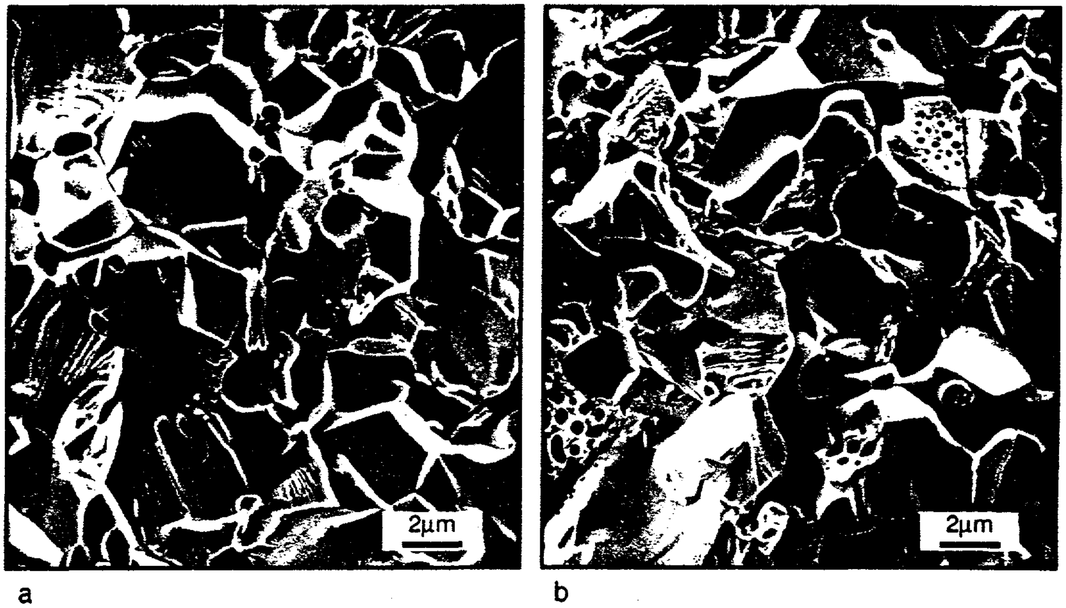


Figure 17. Anisotropic CS25 as sintered (a) and after 250 thermal cycles to 1250°C (b). Note the microcracks in both the as sintered and thermal cycled material.

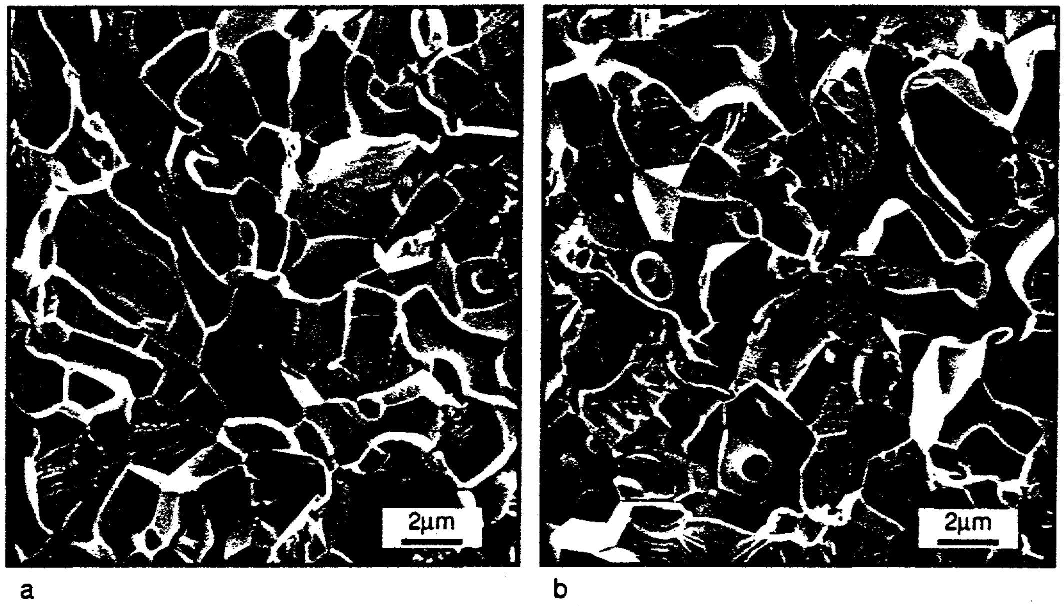


Figure 18. Slightly anisotropic CS37.5 as sintered (a) and after 250 thermal cycles to 1250°C (b). Note the small amount of cavity formation after 250 thermal cycles.