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Composite route to "zero" expansion ceramics

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The use of diphasic or multiphasic composites, involving one negative α phase to control and lower the thermal expansion of a ceramic for substrate, laser mirror and anti-thermal shock applications, was studied. The two phases thermodynamically stable with each other – one with negative α and the second with positive α – were mixed, sintered and characterized for thermal expansion behaviour. The negative-α phase was selected from the [NZP] or [CTP] structural family. Specific systems including $NaZr_2P_3O_{12}$, $CaZr_4P_6O_{24}$ + Nb_2O_5, $GdPO_4$, $ZrSiO_4$, $Mg_3(PO_4)_2$, MgO and ZnO were investigated. Several compositions exhibited a near-zero expansion profile over a wide temperature range.

1. Introduction

What we have named the [CTP] or [NZP] structural family of ceramics has emerged as a major candidate for future ultra-low thermal expansion applications [1, 2]. $CaTi_4P_6O_{24}$ (CTP) and $NaZr_2P_3O_{12}$ (NZP) are the prototypical compositions of this enormous structural family [3]. A sub-family with the structural formula $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ ($0 \leqslant x \leqslant 3$) has been extensively investigated for the last fifteen years [4] due to its potential application in superionic-conducting sulphur batteries, and is sometimes referred to as the Nasicon family. Roy and co-workers [5, 6] have also demonstrated the unique capability of this [CTP] family to immobilize almost all the radionuclides present in typical commercial radioactive waste into a single-phase waste-form.

The thermal expansion of Nasicon members was first noted incidental to fast-ion conductor work by Boilot *et al.* [7] in 1979. No other researcher has made any serious attempt to investigate thermal expansion characteristics of these and related compositions until a systematic effort was initiated in this direction in this laboratory in the last couple of years. The wide range of ionic substitutions at different lattice sites of the [NZP] open network structure and various solid solution schemes have been reported and classified by Alamo and Roy [3]. They also tried to establish a correlation between the lattice parameter changes and rotation of polyhedra in the structure. The effect of various ionic substitutions in [CTP] on the thermal expansion behaviour has been investigated previously by the present authors [2] and it has been shown that this family represents ceramics with a completely controllable thermal expansion for about $+60$ to -30×10^{-6}, including phases exhibiting almost zero expansion in certain temperature ranges.

In an attempt to find alternative routes to utilize the negative thermal expansion of the [CTP] compounds, a diphasic approach was adopted in which the strategy was to mix two thermodynamically compatible ceramic phases – one with negative α and the second one with positive α – and fabricate ceramic compacts (or a composite) by standard ceramic processing techniques. One of these two phases, of course, belongs to the [NZP] family. We selected $NaZr_2P_3O_{12}$ and $CaZr_4P_6O_{24}$ on the basis of their negative coefficients of thermal expansion (-4×10^{-6} and $-1.6 \times 10^{-6}\,\text{deg}^{-1}$ respectively). The second phases included Nb_2O_5, $GdPO_4$, $ZrSiO_4$, $Mg_3(PO_4)_2$, $Zn_3(PO_4)_2$, MgO and ZnO; most of these compounds have low to intermediate values of α. The results of the thermal expansion behaviour with respect to the amount of second phase in a diphasic or multiphasic ceramic are presented in this paper.

2. Experimental details

Single phases of $NaZr_2P_3O_{12}$ and $CaZr_4P_6O_{24}$ (called NZP and CZP respectively henceforth) were synthesized by solid-state reactions using oxides as precursors. The stoichiometric amounts of reagent-grade $CaCO_3$, Na_2CO_3 (both Fisher Scientific Co.), ZrO_2 (Alfa Products) and $NH_4H_2PO_4$ (J.T. Baker Chemical Co.) were mixed and homogenized in acetone by hand mixing or ball milling and then air dried. The dry powder was calcined at 200, 600 and finally at 900° C to drive off the volatiles. The calcined powder was consolidated into 1 inch (25 mm) pellets by cold pressing at a pressure of 70 MPa. The pellets were then heat-treated and sintered at 1000° C for 16 h and 1200° C for 2 days to form single phases of NZP and CZP. The phase identification of the sintered material was carried out on a General Electric X-ray diffractometer using a graphite monochromator and Cu*Kα* radiation. These sintered pellets were ground to a fine powder (– 60 mesh). The diphasic compositions were prepared by adding a second component to pre-reacted NZP or CZP; the mixture was pelletized again and heat-treated between 1100 and 1200° C for 24 h. Dilatometric measurements were made on small rectangular bars ($\simeq$ 1.5 cm × 1 cm × 1 cm) cut out from the sintered samples in a Harrop dilatometric analyser. The dilatometer was first calibrated using a fused silica standard and adjusting the heating rate to about $1° \mathrm{min}^{-1}$ in the programmer.

3. Results and discussion

The various systems which were investigated to study the diphasic approach to low thermal expansion are listed in Table I; the sintering temperatures and time are also given. The phase composition of the material after sintering was determined by X-rays and shown in the last column of Table I. It was observed that except for MgO and ZnO, other compounds which were mixed with CZP and NZP do not react and are thermodynamically compatible. MgO and ZnO react with CZP forming their respective phosphates plus free zirconia. The sintered densities of several compositions are presented in Table II. The theoretical densities of CZP and NZP were calculated from their lattice parameters determined from X-ray diffraction patterns. It is to be noted that only $Zn_3(PO_4)_2$ and $Mg_3(PO_4)_2$ promote sinterability and (as a result) densification, due to the low melting points of these phosphates. Other compounds such as Nb_2O_5, $GdPO_4$ and $ZrSiO_4$ do not affect the densification substantially and merely produce poorly sintered specimens. It is expected that if higher sintering temperatures (1400 to 1600° C) were used in these cases, much higher densification could be achieved. It was also determined using an iridium-strip furnace that NZP and CZP melt incongruently at 1800 and 1650 ± 10° C respectively.

A detailed investigation of the influence of MgO and ZnO addition to CZP on its sintering behaviour, thermal expansion characteristics and microstructure has been presented

TABLE I Treatment and properties of systems investigated

System	Firing temperature (° C)	Firing time (h)	Phases present after sintering
CZP + Nb_2O_5	1150	16	CZP + Nb_2O_{5-x}
CZP + $GdPO_4$	1200	16	CZP + $GdPO_4$
CZP + $ZrSiO_4$	1200	16	CZP + $ZrSiO_4$
CZP + $Mg_3(PO_4)_2$	1200	16	CZP + $Mg_3(PO_4)_2$
CZP + $Zn_3(PO_4)_2$	1100	16	CZP + $Zn_3(PO_4)_2$
NZP + Nb_2O_5	1200	16	NZP + Nb_2O_5
NZP + $Zn_3(PO_4)_2$	1100	16	NZP + $Zn_3(PO_4)_2$
NZP + $Mg_3(PO_4)_2$	1200	16	NZP + $Mg_3(PO_4)_2$
CZP + MgO	1200	16	CZP + $Mg_3(PO_4)_2$ + ZrO_2
CZP + ZnO	1100	16	CZP + $Zn_3(PO_4)_2$ + ZrO_2

TABLE II Densities of some of the compositions

Composition	Density ($g cm^{-3}$)
CZP (single phase)	3.12 [8]
NZP (single phase)	3.18 [9]
CZP + 5% $Mg_3(PO_4)_2$	2.975
CZP + 40% $Mg_3(PO_4)_2$	2.83
CZP + 40% $Zn_3(PO_4)_2$	3.04
CZP + 28.6% Nb_2O_5	2.11
CZP + 20% $GdPO_4$	2.15
CZP + 20% $ZrSiO_4$	1.98
NZP + 20% Nb_2O_5	1.94
NZP + 5% $Mg_3(PO_4)_2$	3.05
NZP + 20% $Zn_3(PO_4)_2$	2.99

elsewhere [8]; up to 98% of theoretical densities were achieved by 5% ZnO/MgO additions.

The resultant thermal expansion profile (per cent expansion against temperature curves) of diphasic compositions in various systems are presented in Figs. 1 to 9. $\Delta L/L$ was measured from room temperature to 500° C at a heating rate of $1° min^{-1}$. Addition of 25% Nb_2O_5 or $ZrSiO_4$ substantially improved the thermal expansion behaviour of CZP (Fig. 1). The value of α between room temperature and 400° C is almost zero and at 500° C it is only about -0.2×10^{-6} and -0.5×10^{-6} respectively, which lies in the ultra-low category. In the system CZP + $GdPO_4$ (Fig. 2), a 20% addition of $GdPO_4$ (Curve 3) gives the lowest α values; it has almost zero expansion up to 300° C and then gradually increases to -0.8×10^{-6} at 500° C. An anomaly was noted in that greater amounts of $GdPO_4$ make α more negative (Curve 4). The effect of MgO and ZnO on the thermal expansion of CZP is presented in Figs. 3 and 4; a detailed discussion of these systems has been given by Agrawal and Stubican [8]. The two phases react to produce a three-phase assemblage of CZP + $(Mg/Zn)_3(PO_4)_2$ + ZrO_2. Figs. 5 and 6 illustrate the thermal expansion behaviour of CZP + $Zn_3(PO_4)_2$ and $Mg_3(PO_4)_2$ systems; it is interesting that these Mg/Zn phosphate additions increase the shrinkage of the composite ceramics and demonstrate high densification and good sinterability. Figs. 7, 8 and 9 illustrate the thermal expansion behaviour of NZP + $Zn_3(PO_4)_2$, Nb_2O_5 and $Mg_3(PO_4)_2$ systems respectively. In these systems, the thermal expansion profiles do not change markedly towards the positive direction; only NZP + $Zn_3(PO_4)_2$ compositions (20 and 30%) exhibit lower overall values of α. Even up to a 50% addition of Nb_2O_5 does not greatly alter the α of pure NZP phase. Similar behaviour was observed in NZP + $Mg_3(PO_4)_2$ systems as in the CZP analogue.

In a di/multiphasic ceramic composite, the resulting thermal expansion is not simply an average of thermal expansions of the individual phases but is determined by the manner in which the body constitutents interact with other other. The internal microstructure due to differential thermal expansions of individual phases, intimacy of mixing, strength of the sintered body and interplay of elastic forces influence the thermal expansion of a composite ceramic body [10]. It is considered that in the systems investigated above, interelastic forces are playing a dominant role in controlling the thermal expansion of a diphasic ceramic.

This diphasic approach to tailoring the thermal expansion of a ceramic body opens up an area of new studies and offers a completely new family of materials for ultra-low expansion applications. Various properties can be tailored to desired values to a greater degree by this approach. For example, for RAM materials one could possibly mix a ferrite and a compatible [NZP] member to manipulate magnetic

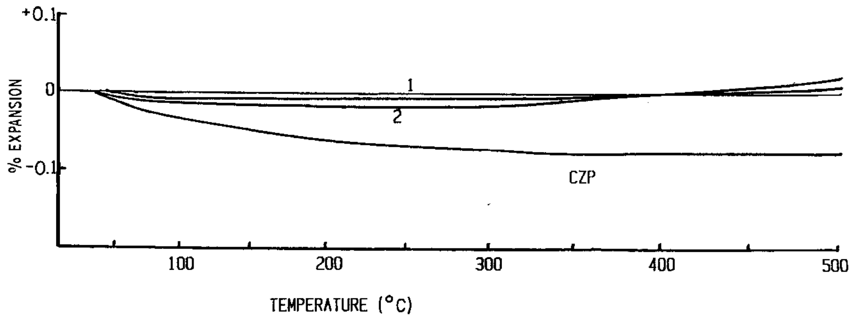

Figure 1 Thermal expansion curves of CZP + Nb_2O_5 and CZP + $ZrSiO_4$. Curve 1, 28.6% Nb_2O_5; Curve 2, 25% $ZrSiO_4$.

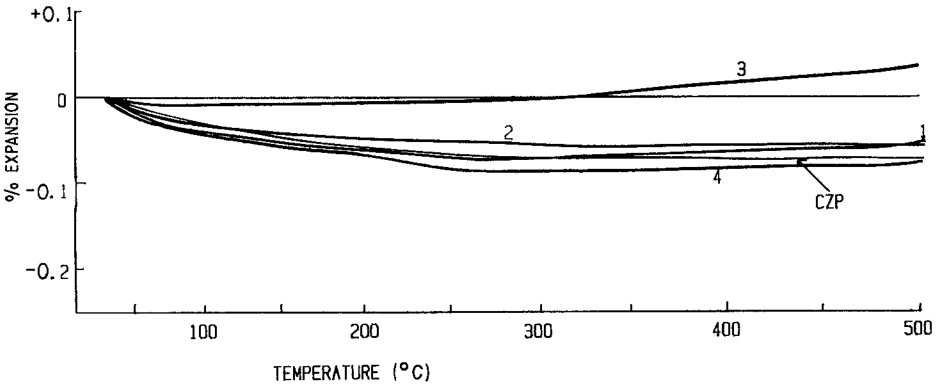

Figure 2 Thermal expansion curves of the CZP + $GdPO_4$ system. $GdPO_4$ contents: Curve 1, 10%; Curve 2, 15%; Curve 3, 20%; Curve 4, 50%.

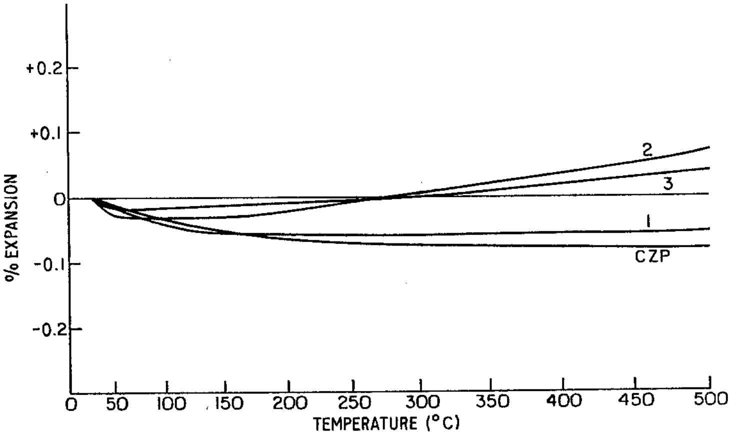

Figure 3 Thermal expansion curves of the CZP + ZnO system. ZnO contents: Curve 1, 10%; Curve 2, 15%; Curve 3, 20%.

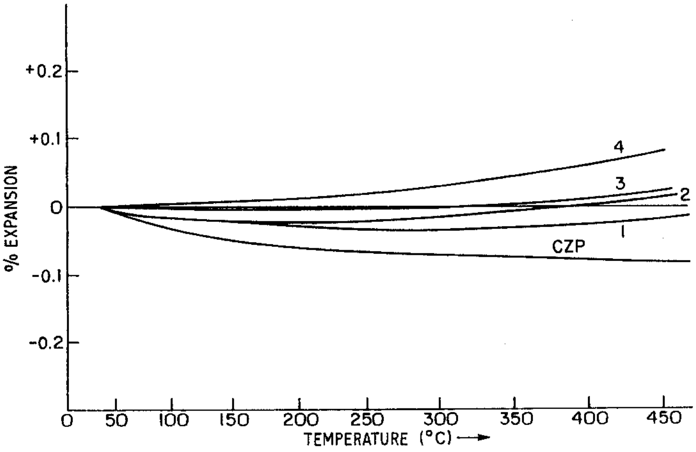

Figure 4 Thermal expansion curves of the CZP + MgO system. MgO contents: Curve 1, 10%; Curve 2, 12%; Curve 3, 14%; Curve 4, 16%.

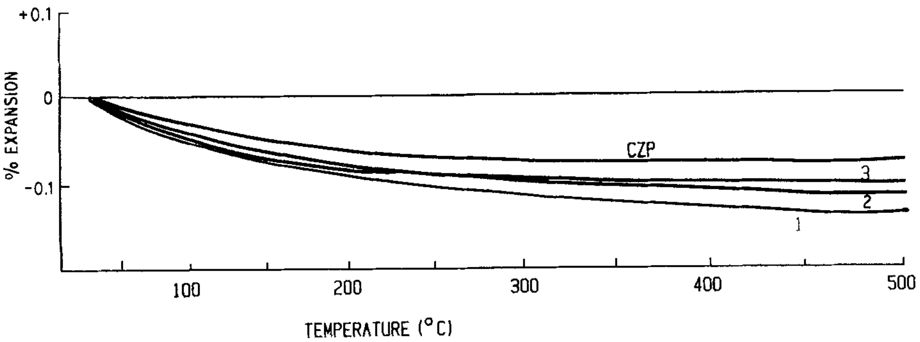

Figure 5 Thermal expansion curves of the CZP + $Zn_3(PO_4)_2$ system. $Zn_3(PO_4)_2$ contents: Curve 1, 15%; Curve 2, 25%; Curve 3, 40%.

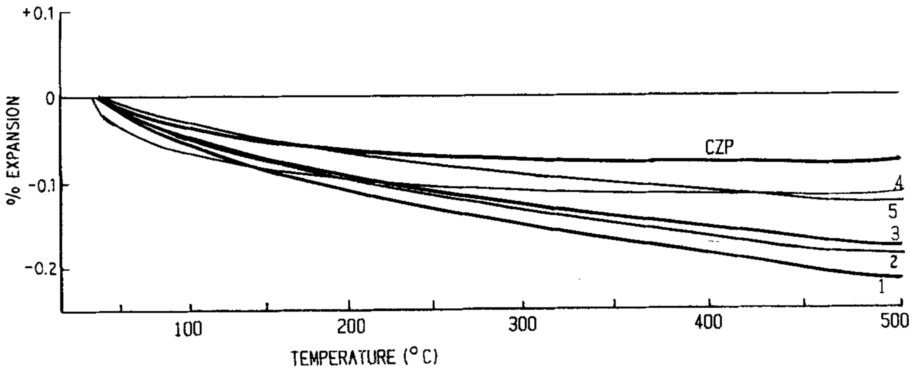

Figure 6 Thermal expansion curves of the CZP + $Mg_3(PO_4)_2$ system. $Mg_3(PO_4)_2$ contents: Curve 1, 5%; Curve 2, 10%; Curve 3, 15%; Curve 4, 40%; Curve 5, 30%.

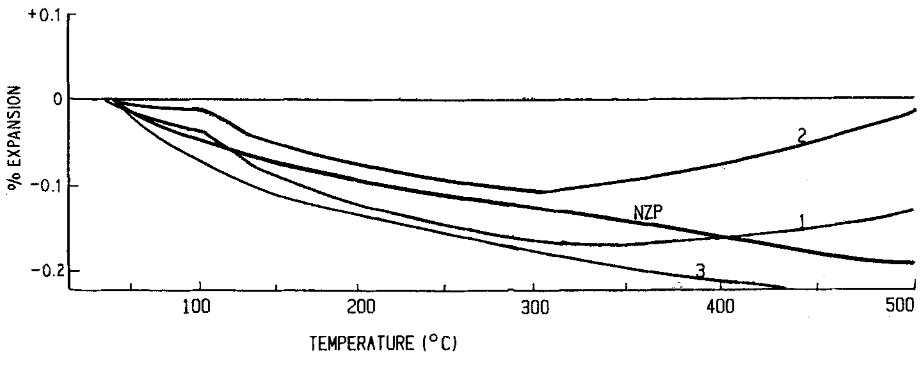

Figure 7 Thermal expansion curves of the NZP + $Zn_3(PO_4)_2$ system. $Zn_3(PO_4)_2$ contents: Curve 1, 20%; Curve 2, 30%; Curve 3, 40%.

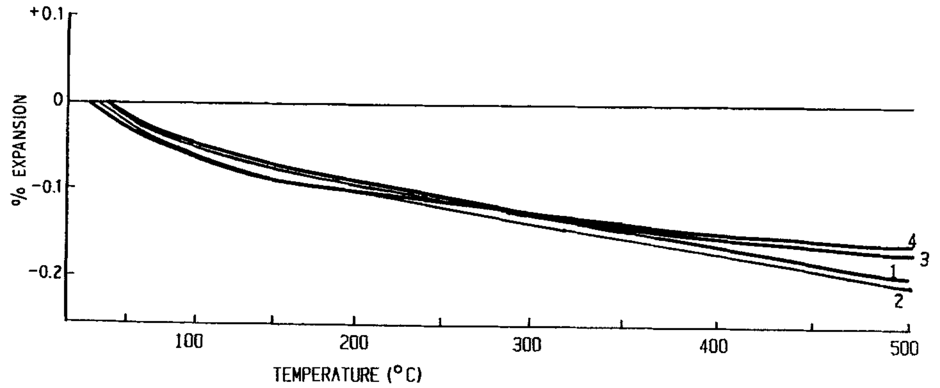

Figure 8 Thermal expansion curves of the NZP + Nb_2O_5 system. Nb_2O_5 contents: Curve 1, zero; Curve 2, 20%; Curve 3, 33%, Curve 4, 50%.

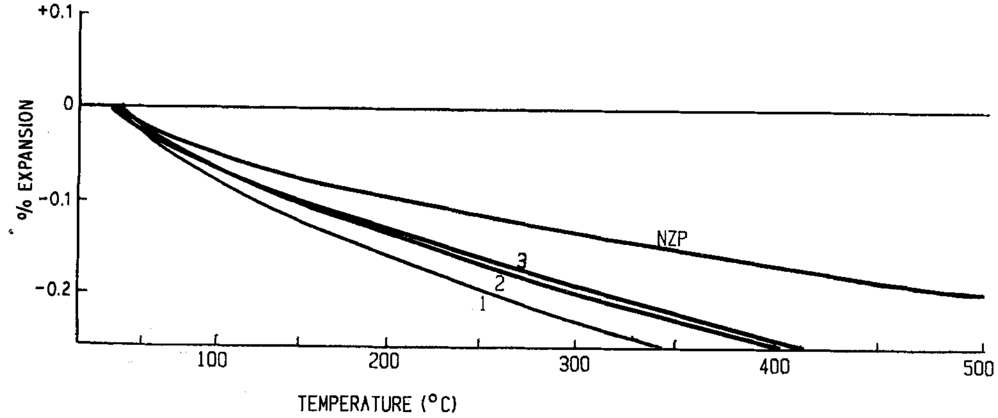

Figure 9 Thermal expansion curves of the NZP + $Mg_3(PO_4)_2$ system. $Mg_3(PO_4)_2$ contents: Curve 1, 5 or 10%; Curve 2, 20%; Curve 3, 30%.

properties in a zero-expansion ceramic composite. In single-phase materials, α can be tailored only by crystal chemical manipulations within the single phase. The diphasic concept permits the selection of both materials – both in terms of α and the quantity of each phase – and any special property which one phase may have.

4. Summary and conclusions

A diphasic approach to the control and improvement of the thermal expansion of a ceramic body was studied; several compositions such as $CaZr_4P_6O_{24}$ + 30% Nb_2O_5, 25% $ZrSiO_4$, 14% MgO, 20% ZnO, 20% $GdPO_4$ and $NaZr_2P_3O_{12}$ + 20% $Zn_3(PO_4)_2$ were found to have near-zero coefficients of thermal expansion in certain temperature ranges and much better thermal expansion profiles that the parent [CZP] phase. In several sintered samples, high densities were achieved by adding a few per cent of magnesium or zinc phosphates to CZP or NZP.

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