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Synthesis, sintering and thermal expansion of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ – an ultra-low thermal expansion ceramic system

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$Ca_{1-x}Sr_xZr_4P_6O_{24}$ ($0 \leqslant x \leqslant 1.0$) system which belongs to a new large family of low thermal expansion materials known as NZP or CTP, was synthesized by the solid state and the sol–gel methods. The conventional sol–gel method was modified by introducing a seeding step which resulted in significant improvement in the sintering characteristics and the microstructure of the sintered material. Sintering data were compared with those obtained by the powder mixing technique. Thermal expansion of the sintered samples was measured by classical dilatometry and by high-temperature X-ray diffractometry. It was found that $CaZr_4P_6O_{24}$ ($x = 0$) and $SrZr_4P_6O_{24}$ ($x = 1$) phases had opposite anisotropies in their respective axial thermal expansions. This behaviour led to the development of a crystalline solution composition of nearly zero expansion characteristic. Microstructures of the sintered specimens were examined by scanning electron microscopy.

1. Introduction

$Ca_{1-x}Sr_xZr_4P_6O_{24}$ belongs to a very large structural family of new low thermal expansion materials now known as NZP or CTP [1–3], which have extraordinary technological utility in at least three fields: superionic conductors [4, 5], radwaste immobilization [6], and low thermal expansion ceramics. $CaTi_4P_6O_{24}$ (CTP) or $NaZr_2P_3O_{12}$ (NZP) are the parent compositions of this family which allows numerous ionic substitutions at various lattice sites [7] producing a large number of new compounds and crystalline solutions. In 1979, Boilot *et al.* [8] reported the thermal expansion of some phases of $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, a sub-system of the NZP family also known as Nasicon. Since then this family has been intensively studied by us for its near-zero thermal expansion properties [1–3, 9–11].

The interesting properties of CTP materials are mainly attributed to their extraordinary crystal structure, which consists of a strongly bonded but flexible three-dimensional network of PO_4 tetrahedra and ZrO_6 octahedra. These polyhedra are interconnected through corner sharing, and develop a rigid and highly stable hexagonal lattice with structural holes which are partially or fully, depending upon the composition, occupied by calcium, strontium, sodium or any other substituting ion(s). The reasons for the low thermal expansion behaviour of CTP are not yet fully understood; however, it can be attributed to (i) strongly bonded polyhedra, (ii) the presence of structural holes which may absorb some of the thermal vibrations, and (iii) anisotropy in the axial thermal expansions of the lattice. A structural model for thermal expansion based on the rotation of polyhedral network and coupling between octahedra and tetrahedra has been developed by Lenain *et al.* [12]; this model satisfactorily explains the thermal expansion behaviour of alkali analogues of NZP but fails to explain the thermal expansion of other members.

An important and significant aspect of the thermal expansion of these materials is its tailorability. Near-zero expansion materials can be obtained over any desired temperature range by carefully selecting the composition. Recently, Limaye *et al.* [13] have reported the synthesis and the thermal expansion of $MZr_4P_6O_{24}$ (M = Mg, Ca, Sr, Ba) in which they discovered that $CaZr_4P_6O_{24}$ (CZP) and $SrZr_4P_6O_{24}$ (SZP) exhibited the opposite anisotropy in their respective axial thermal expansions, i.e. *a*-axis contracts in CZP and expands in SZP with temperature; on the other hand, the *c*-axis expands in CZP and contracts in SZP. In the present study, an attempt has been made to extend this significant finding to develop a new ceramic with near-zero thermal expansion characteristic by investigating the thermal expansion of the crystalline solution of these two end members. It is expected that because $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$ are isostructural, they would form a continuous crystalline solution. The synthesis was carried out mainly by the sol–gel process, and in order to improve

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the sinterability of the material, this process was modified by adopting a nanocomposite approach or seeding technique which was developed in the last few years by Roy and his co-workers [14–16]. Nanocomposites are defined as a class of di/multi phasic materials where two (or more) phases may differ in composition or in structure with the physical dimensions of the phases lying in the range 1 to 10 nm; this is achieved by introducing submicrometre size seed particles to the sol/solution of the composition to be synthesized. The "seeding" in the solid state provides a lower activation energy path to the nucleation (as in crystal growth) of the thermodynamically (more) stable phase [14]. The main known benefits of this seeding technique as developed today are (1) to improve sinterability of the gel-derived powder, (2) to achieve a fine-grained uniform microstructure in the finished product, and (3) to lower the sintering temperature without a loss in densification.

2. Experimental procedure

In the system $Ca_{1-x}Sr_xZr_4P_6O_{24}$ five compositions with $x = 0, 0.25, 0.50, 0.75$ and 1.0 were synthesized both by the solid state or powder method and by the sol–gel process. In addition, some compositions were also prepared by a modified di-phasic sol–gel method using seeds of CZP in order to improve the sinterability and densification of the ceramic.

2.1. Solid state reaction method

In this method $CaCO_3$, $SrCO_3$, ZrO_2 and $NH_4H_2PO_4$ (all Fisher Scientific Co., reagent grade) were used as the starting materials. The proper stoichiometric amounts of the precursor powders of the constituents of the desired composition were mixed and hand ground in acetone to homogenize. The mixture was dried in air at room temperature and then calcined in steps: at 200 °C for 16 h to drive off water and NH_3, at 600 °C for 4 h to remove most of the crystalline water, and finally at 900 °C for 16 h to remove CO_2 from carbonates. The calcined product consisted of dry cake of partially reacted pure oxides; this material was hand crushed in a mortar and pestle to −100 mesh and 15% polyvinyl alcohol (PVA) solution was added to it as a binder. Pellets 2.5 cm diameter were cold pressed from this powder at a pressure of 140 MPa and then sintered at 1300 °C for 48 h.

2.2. Sol–gel method

Aqueous solutions of the inorganic salts such as $Ca(NO_3)_2 . 4H_2O$, $Sr(NO_3)_2$, $NH_4H_2PO_4$–ADP (all Fisher Scientific Co., reagent grade) and $ZrOCl_2 . 8H_2O$ (Aldrich Chemicals) were used as precursors of the synthesis of $Ca_{1-x}Sr_xZr_4P_6O_{24}$. Proper stoichiometric amounts of the precursor solutions for each composition were mixed to form a gel. The sequence of mixing of an individual component is critical to forming a gel of uniform composition and obtaining a single-phase material. The starting solution was calcium nitrate to which strontium nitrate was added followed by zirconyl chloride; all additions were made while the solutions were being magnetically stirred. Finally, the aqueous solution of ADP was added drop by drop under constant stirring conditions. All mixings were carried out at room temperature. At this stage the mixture is a highly viscous slurry which transforms into a semi-transparent gel at 60 °C in about 8 h. The gel was dried at 80 °C for 16 to 24 h to form a weakly cross-linked mass. The dry gel was hand crushed in a mortar and pestle to a powder form followed by calcination at 700 °C for 16 h to drive off the volatiles such as NO_2, NH_3, Cl_2 and H_2O. The calcined product was ground to −325 mesh and PVA was added to it as a binder, and then cold pressed into 2.5 cm diameter discs at 210 MPa pressure. The final sintering of the samples was performed at 1200 °C for 24 h.

2.3. Sol–gel with seeding

Various compositions of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ were synthesized using crystalline seeds of the CZP. These seeds act as nuclei for heterogeneous crystallization of the gel into a fine-grained microstructure. The process flow chart for this method is shown in Fig. 1 and briefly described below.

First, to prepare seeds, single-phase CZP was prepared by the regular sol–gel technique as described above except that in the final heating at 1200 °C calcined "powder" was used instead of a consolidated disc. The resulting prereacted single-phase CZP powder was ground to −325 mesh before mixing with deionized water (1 g CZP/50 ml water) to prepare a colloidal suspension of CZP which was ultrasonified for 2 h to reduce the particle size to submicrometre level. The suspension obtained was allowed to stand undisturbed for 150 h to enable coarser particles to settle down; the supernatant solution was then decanted and retained as the "seed" solution. After this the basic procedure is the same as in the regular sol–gel method above, except that the seed solution was added to the main solution before adding ADP solution. Seed concentrations (0.5 to 1.5% by weight) and sintering temperatures (1000 to 1200 °C) were used as variables to study their effect on densification and sinterability.

All the specimens fabricated in the above three methods were characterized for their properties including density, microstructure, phase-composition and thermal expansion. The phase-identification of the sintered and calcined material was carried out by routine powder X-ray diffractometry (XRD) using SCINTAG USA X-ray diffractometer model PAD V and Cu$K\alpha$ radiation. The densities of the sintered samples were determined by either geometrical measurements or by the water immersion technique. The measurements for bulk thermal expansion were made on small rectangular bars ($2 \times 0.5 \times 0.5$ cm^3) cut from the sintered samples, by using a dilatometric analyser (Harrop Laboratories, Columbus, Ohio). High-temperature X-ray diffractometry studies were

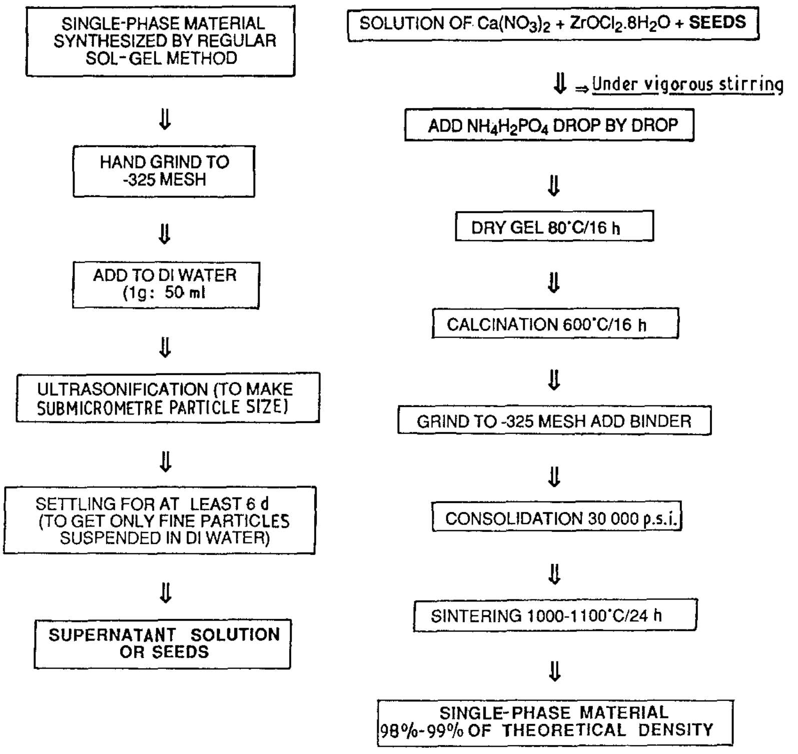


Figure 1 Synthesis of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ ceramics by the "sol–gel with seeding" technique. 10^3 p.s.i. = 6.89 N mm^{-2}.

made on powdered samples to determine axial thermal expansions, and for this purpose an Apple microcomputer was interfaced with the Picker X-ray diffractometer to control the step scanning rate and simultaneously collect diffraction intensity data corresponding to the diffraction angle. These data were further analysed using a least-square curve-fitting program to find accurate peak positions. These peaks were then indexed up to $2\theta = 160°$ and were used to calculate accurate cell dimensions using Cohen's method [17]. To find the errors involved in the determination of the cell parameters, MINITAB program [18] was used. The errors were found to $2\theta < 0.01°$. The thermal expansion measurements were repeated on several samples of the same composition to verify the reproducibility of the data, and it was found that the results were quite reproducible within the limits of the experimental errors. The fracture surfaces of the sintered samples were examined by using a scanning electron microscope equipped with an energy dispersive X-ray (EDX) analyser to study their microstructures, phase compositions, and to determine the grain size.

3. Results and discussion

3.1. Synthesis, sintering and density

Although the solid state reaction approach is quite simple, and the starting materials are inexpensive and easily available, it was difficult to sinter materials to a high density using this method, and comparatively higher temperatures were required to obtain single-phase material. In this method, after calcination at 900 °C, XRD analysis indicated that the material consisted of zirconium pyrophosphate (ZrP_2O_7) and an amorphous phase of unknown composition. The specimens sintered at 1300 °C consisted of single-phase material and showed a continuous solid solution between CZP and SZP which was evident from the systematic shift in the diffraction peaks. In the case of the sol–gel processes, after calcination at 700 °C the specimens formed single-phase materials. The samples sintered at 1200 and 1000 °C in two methods, respectively, were found to be single phase with improved crystallinity over the calcined product and the solid state reaction product, this was evident from the sharper diffraction peaks in the XRD patterns. Typical sintered densities of CZP, SZP and $x = 0.5$ compositions observed in the specimens prepared by three methods are compared in Table I. In the case of the solid state reaction method, the highest density acheived was around 80% theoretical, while in case of the sol–gel processes densities as high as 99% were achieved even at temperatures 100 to 200 °C lower than in the former; another significant point is the lowering of the sintering time also (at least 48 h were required to obtain single phase in the case of the solid state reaction method while in the sol–gel sintering only 24 h was enough). It should be noted that the seeding approach has lowered the sintering temperature from 1200 to 1100 °C without any significant change in the density of the sintered product, and at 1200 °C the densities have further improved in comparison with the conventional sol–gel technique.

An attempt was made to study the effect of seed concentration and sintering temperatures on density and grain size of $Ca_{0.75}Sr_{0.25}Zr_4P_6O_{24}$ ($x = 0.25$) as a representative case for the CSZP system. The data listed in Tables II and III show that by increasing the seed concentration from 0.5 to 1.5% the density does not change substantially; however, by increasing the sintering temperature from 1000 to 1200 °C the density increases substantially from about 82% to >99%. The optimum sintering temperature and seed concentration were found to be 1200 °C and 1%, respectively, for the composition $x = 0.25$. A similar observation

TABLE I Density data (g cm^{-3}) of the $Ca_{1-x}Sr_xZr_4P_6O_{24}$ system obtained by different processing methods

Composition	Solid state reaction (1300 °C)	Sol–gel (1200 °C)	Sol–gel with seeds	
			(1100 °C)	(1200 °C)
$CaZr_4P_6O_{24}$	2.64 (82.5%)	3.145 (98.3%)	3.15 (98.4%)	3.165 (98.9%)
$SrZr_4P_6O_{24}$	2.61 (78.6%)	3.25 (97.6%)	3.24 (97.3%)	3.29 (98.8%)
$Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$	2.62 (80.1%)	3.21 (98.8%)	3.215 (98.5%)	3.24 (99%)

was found in the case of grain size, i.e. change in seed concentration has no effect on the grain size but temperature helps in grain growth, the average grain size increases from 0.25 to 2 μm when the sintering temperature changes from 1000 to 1200 °C.

3.2. Microstructure

The microstructures of the fracture surfaces of the sintered specimens obtained by the sol–gel and the sol–gel with seeding methods are illustrated in Fig. 2a to c. It can be observed in these micrographs that, in general, microstructure is quite uniform and there is very little porosity in the samples. In the case of the sintered specimen prepared by the seeding technique, there are still fewer pores of less than 1 μm in size, and only closed porosity is observed. The average particle size ranges between 2 and 5 μm. Fig. 2c shows the as-sintered surface of a specimen fabricated by the seeding method, which indicates how intimately the grains fill up all space with hardly any porosity left on the surface.

3.3. Thermal expansion

The thermal expansion data obtained by the classical dilatometry and by the high-temperature X-ray diffractometry have been plotted in Figs 3 and 4, respectively, the average coefficients of thermal expansion (α) are presented in Table IV, they were measured from 25 to 500 °C. The values of CZP and SZP are in good agreement with those reported by Limaye *et al.* [13]. The high-temperature X-ray data clearly indicate anisotropy in axial thermal expansions as reported by other researchers, and in the solid solution composition $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$ there is almost no expansion or contraction along either the *a*- or *c*-axis, which means no anisotropy and theoretically the bulk thermal expansion of the ceramic of composition $x = 0.5$ should be near zero. This is, however, not reflected in its dilatometric curve where it has $\alpha = 1.4 \times 10^{-6}\,°C^{-1}$ between 25 and 500 °C . The difference between the dilatometric data and the X-ray data which were obtained on a powdered sample, can be explained by a constraint effect. In a powdered sample of a crystalline material, the individual crystals are free to expand in any manner without any constraint and in a sintered ceramic body the individual grains are bonded/linked during sintering reactions and thus a constraint is placed upon an individual grain by the grains surrounding it. This may alter the thermal expansion on macroscopic level.

TABLE II Effect of seed concentration and sintering temperature on density for $Ca_{0.75}Sr_{0.25}Zr_4P_6O_{24}$ (% theoretical density)

Seed concentration (%)	Sintering temperature (°C)		
	1000	1100	1200
0.5	81.66	96.8	98.45
1.0	82.9	96.2	98.8
1.5	82.3	96.5	98.9

TABLE III Effect of seed concentration and sintering temperature on grain size (μm) of $Ca_{0.75}Sr_{0.25}Zr_4P_6O_{24}$

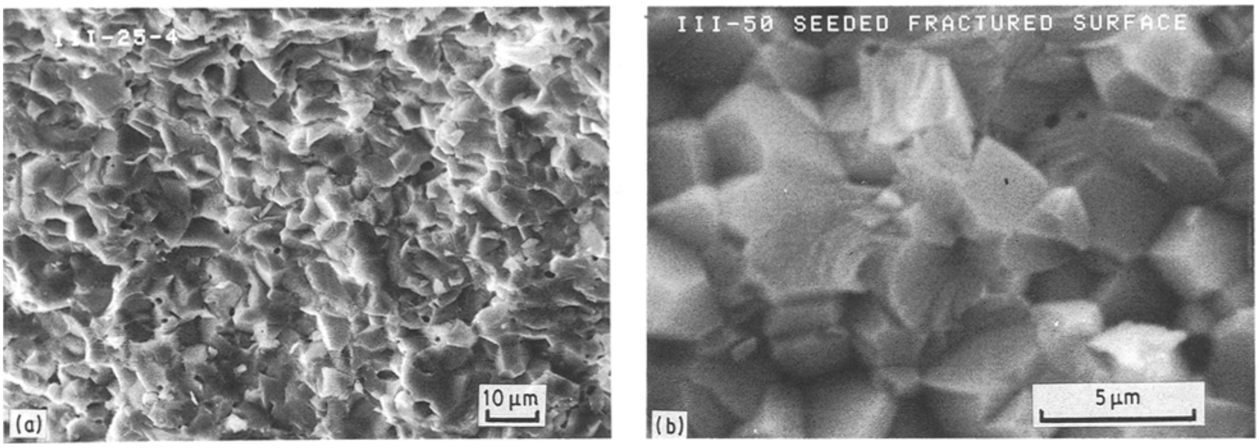
Seed concentration (%)	Sintering temperature (°C)		
	1000	1100	1200
0.5	0.25	1.0	2.0
1.0	0.25	1.0	2.0
1.5	0.25	1.0	2.0

4. Conclusion

Highly dense ceramics in the $Ca_{1-x}Sr_xZr_4P_6O_{24}$ system were fabricated by traditional ceramic processing techniques such as powder mixing and the sol–gel methods. Sintering temperature was lowered by 100 to 200 °C by adopting a nanocomposite approach in which 1% seeds of $CaZr_4P_6O_{24}$ were used in the regular sol–gel synthesis to lower the activation energy of crystallization by introducing isostructural nuclei in the system. Microstructure studies of the sintered samples indicate that uniformity and homogeneity were remarkably improved by introducing the seeding step. Some selected crystalline solution compositions exhibited near-zero average thermal

TABLE IV Average coefficient of thermal expansion, α of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ between 25 and 500 °C

Composition (*x*)	$\alpha(10^6\,°C^{-1})$ (by dilatometery)	$\alpha_a(10^6\,°C^{-1})$ (by high-temperature X-ray diffractometry)	$\alpha_c(10^6\,°C^{-1})$
0	−2.11	−5.1	9.9
0.25	0.6		
0.50	1.4	−0.7	1.1
0.75	2.5		
1.0	3.2	3.6	−1.2



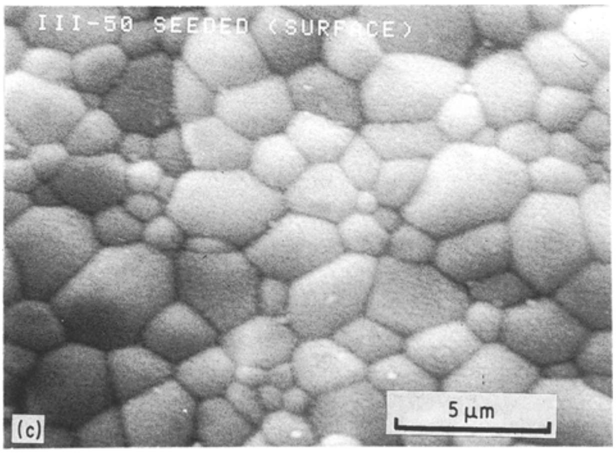


Figure 2 Microstructure of $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$ sintered samples: (a) sol–gel method, (b) sol–gel with seeding method, and (c) as-sintered surface by seeding method.

expansions. Composition $x = 0.5$ showed almost no anisotropy in its axial thermal expansions.

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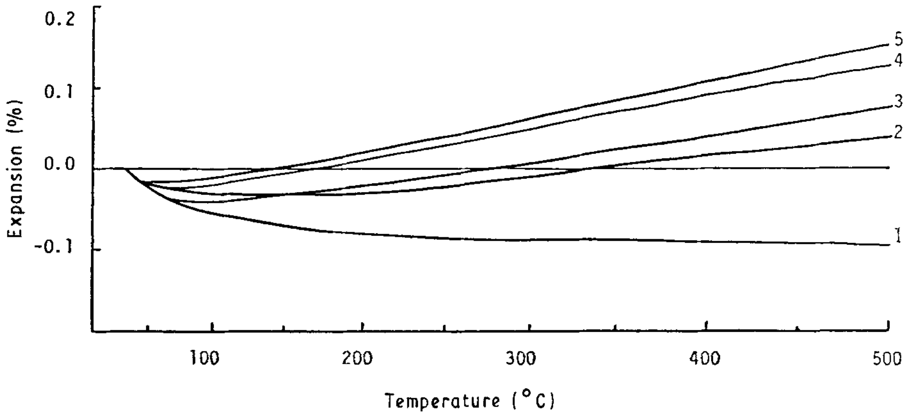

Figure 3 Bulk thermal expansion of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ ceramics by dilatometry. x = (1) 0, (2) 0.25, (3) 0.50, (4) 0.75, (5) 1.00.

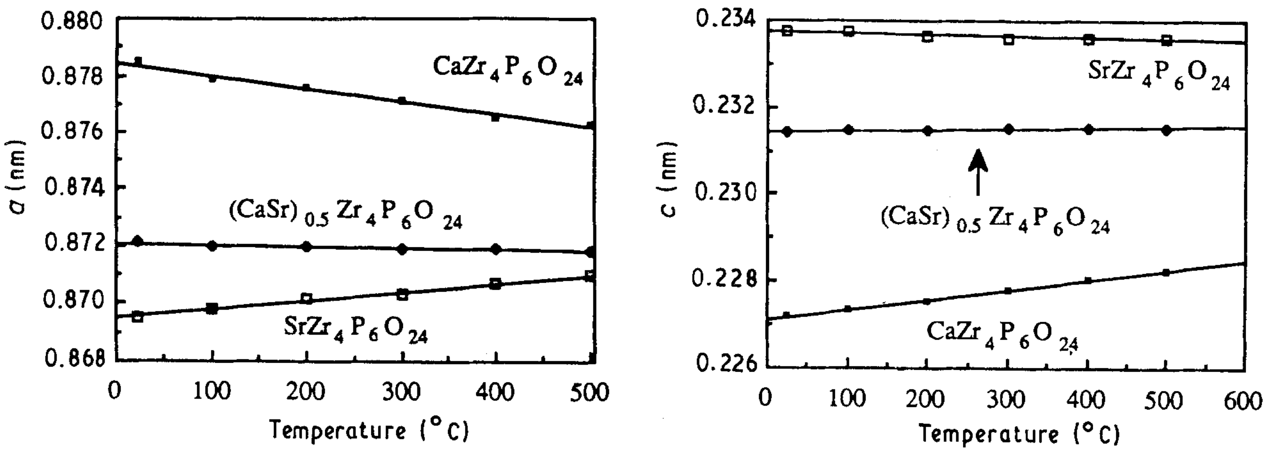

Figure 4 Lattice thermal expansion of $Ca_{1-x}Sr_xZr_4P_6O_{24}$ determined by high-temperature powder X-ray diffractometry.

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