

Synthesis, microstructure and thermal expansion studies on $\text{Ca}_{0.5+x}/2\text{Sr}_{0.5+x}/2\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ system prepared by co-precipitation method

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Abstract. We report on the synthesis, microstructure and thermal expansion studies on $\text{Ca}_{0.5+x}/2\text{Sr}_{0.5+x}/2\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ ($x = 0.00$ to 1.00) system which belongs to NZP family of low thermal expansion ceramics. The ceramics synthesized by co-precipitation method at lower calcination and the sintering temperatures were in pure NZP phase up to $x = 0.37$. For $x \geq 0.5$, in addition to NZP phase, ZrSiO_4 and $\text{Ca}_2\text{P}_2\text{O}_7$ form as secondary phases after sintering. The bulk thermal expansion behaviour of the members of this system was studied from 30 to 850°C . The thermal expansion coefficient increases from a negative value to a positive value with the silicon substitution in place of phosphorous and a near zero thermal expansion was observed at $x = 0.75$. The amount of hysteresis between heating and cooling curves increases progressively from $x = 0.00$ to 0.37 and then decreases for $x > 0.37$. The results were analysed on the basis of formation of the silicon based glassy phase and increase in thermal expansion anisotropy with silicon substitution.

Keywords. NZP ceramics; thermal expansion; microcracking; co-precipitation.

1. Introduction

The ceramics belonging to NZP family are extensively studied for their low thermal expansion behaviour along with controlled thermal expansion anisotropy, ionic conductivity, high temperature thermal stability, thermal shock resistance and as a host candidate for radio active waste (Goodenough *et al* 1976; Roy *et al* 1989; Rega *et al* 1992; Petkov and Orlova 2003). These extraordinary properties of the NZP ceramics are mainly due to their unique crystal structure, which has a three dimensional framework structure of ZrO_6 octahedra sharing corners with PO_4 tetrahedra and the structural holes created by this framework are occupied by the Na or any other substitution ions (Roy *et al* 1989; Srikanth *et al* 1991; Breval and Agrawal 1995; Petkov and Orlova 2003). The NZP ceramics, with these useful properties, are the potential candidates for various technological applications such as catalyst supports, automobile engine components, heat exchangers and coatings for space technology (Roy *et al* 1989; Petkov and Orlova 2003). Some of the silica based compositions can be used as a thermal protection system for re-entry vehicles.

Some compositions of the NZP family exhibit anisotropy in their axial thermal expansion behaviour, such as in $\text{CaZr}_4\text{P}_6\text{O}_{24}$ (CZP) and $\text{SrZr}_4\text{P}_6\text{O}_{24}$ (SZP) (Limaye *et al* 1991; Angadi *et al* 2002; Charkraborty *et al* 2005). Due to

this anisotropic thermal expansion behaviour they exhibit large amounts of microcracking when cooling from the sintered state (Srikanth *et al* 1991; Yamai and Ota 1993). The generation of microcracks from such systems was evident from the acoustic emissions detected and the large hysteresis in their bulk thermal expansion behaviour. However, a ceramic system having near zero thermal expansion anisotropy with no microcracking and least hysteresis in thermal expansion behaviour can be synthesized by making a solid solution between two opposing anisotropic ceramics. For example, CZP and SZP exhibit opposing anisotropy in their axial thermal expansion behaviour whereas $x = 0.5$ in $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ is shown to be near zero thermal expansion anisotropy with minimum microcracking and low hysteresis (Srikanth *et al* 1991; Yamai and Ota 1993).

In the NASICON (NA Super Ionic CONductor) compositions, the Si substitution at the P site has successfully produced an applied material. The compositions for $x = 1.3$ to 1.6 in the $\text{Na}_{(1+x)}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ system not only have high cationic conductivity but also have low thermal expansion anisotropy (Boilot *et al* 1979).

Breval *et al* (1998) have synthesized $\text{Ca}_{(1+x)/2}\text{Sr}_{(1+x)/2}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ ($x \leq 0.37$) by solid state reaction method, with an intention that silicon substitution in $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ will further lower the thermal expansion and anisotropy and thereby exhibit minimal microcracking. But, their experimental studies revealed that, silicon substitution increases the anisotropy further instead of decreasing. This behaviour

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was attributed to the formation of glassy phase that softens at moderate temperatures. In the solid-state reaction methods, used in the above studies, the temperatures involved for calcination ($>1200\text{ }^{\circ}\text{C}$) and sintering ($1300\text{--}1550\text{ }^{\circ}\text{C}$) are too high and hence it is always associated with higher grain growth. As the microcracking in a ceramic body is related to the grain size, it is necessary to control the size below a certain critical limit (Yamai and Ota 1993). The NZP structure is built up of $(\text{Zr}_2\text{P}_3\text{O}_{12})^{-1}$ anion and monovalent Na^+ cation occupying the trigonal prismatic sites completely. In case of divalent $\text{Ca}^{2+}/\text{Sr}^{2+}$ cations there will be 50% vacancy at the cation sites. In the present case of Si^{4+} substitution at the P^{5+} site, the net charge for $(\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24})$ will be $-(2+2x)$. This additional negative charge is compensated by increasing the cation concentration, as reflected in the general formula, $\text{Ca}_{0.5+x/2}\text{Sr}_{0.5+x/2}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$.

In this study, we synthesized the $\text{Ca}_{0.5+x/2}\text{Sr}_{0.5+x/2}\text{Zr}_4\text{P}_{6-x}\text{Si}_x\text{O}_{24}$ (CSZP, $x = 0.00$ to 1.00) system using co-precipitation method with lower calcination and the sintering temperatures and the effects of silicon substitution on the phase formation, microstructure and bulk thermal expansion are studied in detail.

2. Experimental

The seven compositions of CSZP system ($x = 0.00, 0.10, 0.25, 0.37, 0.50, 0.75$ and 1.00) were synthesized by the co-precipitation method using reagent grade inorganic salts $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and tetraethyl orthosilicate (TEOS). The stoichiometric amounts of $\text{Ca}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ were dissolved in distilled water, then $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was added to this solution, with constant stirring using a magnetic stirrer, till the solution became clear. Known quantity of $\text{NH}_4\text{H}_2\text{PO}_4$ solution was then added drop by drop with continuous stirring, which formed a white curdy precipitate. To this precipitate, TEOS and ammonia solution was added and the stirring was continued for 4 h. It was soaked at room temperature for 12 h and then kept in an oven at $80\text{ }^{\circ}\text{C}$ for 12–24 h. The white solid precipitate (flakes) was then heated to $300\text{ }^{\circ}\text{C}$ for 1 h and ground. The powder was then calcined at $900\text{ }^{\circ}\text{C}$ and then $1000\text{ }^{\circ}\text{C}$ for 24 h with intermediate grinding. The calcined powder was then cold pressed at a pressure of 50 kN after adding a 10% PVA solution. The binder burn out was carried out through a slow heating process up to $550\text{ }^{\circ}\text{C}$. The final sintering of the pellets was carried out at $1250\text{ }^{\circ}\text{C}$ for 24 h.

The phase identification of the samples was carried out by room temperature X-ray diffractometry (XRD) using Scintag X-ray diffractometer with $\text{CuK}\alpha$ (1.5406 \AA) radiation in the 2θ range from 10 to 70° with a scan speed of $0.5^{\circ}/\text{min}$. The lattice parameter refinement was done using linear least squares method. The microstructure of the fractured surface of a sintered sample was examined using a Cambridge stereoscan S360 scanning electron microscope and density was measured using a three-weight method based on the Archimedes principle (Angadi et al 2002). The bulk thermal

expansion measurements were made using a home built push-rod dilatometer from room temperature to $850\text{ }^{\circ}\text{C}$ at a rate $2\text{ }^{\circ}\text{C}/\text{min}$ during heating and cooling cycles (Umarji et al 1997).

3. Results and discussion

3.1 Phase formation

The phase confirmation of all the seven compositions of CSZP system was carried out by comparing their XRD patterns with the standard JCPDS pattern of CZP with No. 33–321. The XRD patterns of the samples calcined at $1000\text{ }^{\circ}\text{C}$ for 24 h are shown in figure 1. From the figure it is clear that the $x = 0.00$ composition shows pure NZP phase at the calcination stage itself. With increase in the silicon substitution there is a formation of the secondary phase of $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ along with NZP phase, however, there is no evidence of the formation of the silicon containing secondary phases. This shows that the substituted silicon has gone into the lattice, forming a solid solution with NZP phase or must be in the X-ray amorphous state. The XRD patterns of the sintered samples at $1250\text{ }^{\circ}\text{C}$ for 24 h are shown in figure 2. The compositions up to $x = 0.37$ show pure NZP phase and the compositions with $x > 0.37$ shows the formation of some secondary phases such as $\text{Ca}_2\text{P}_2\text{O}_7$ and ZrSiO_4 along with the NZP phase. This shows that the $x = 0.37$ is the solubility limit of the solid solution, CSZP and the excess silicon substituted for the compositions $x > 0.37$, is thrown out of the lattice in the form of secondary phases. The absence of ZrSiO_4 phase in the calcined samples may be due to the insufficient temperature required for the crystallization of ZrSiO_4 . The lattice parameters and the unit cell volume

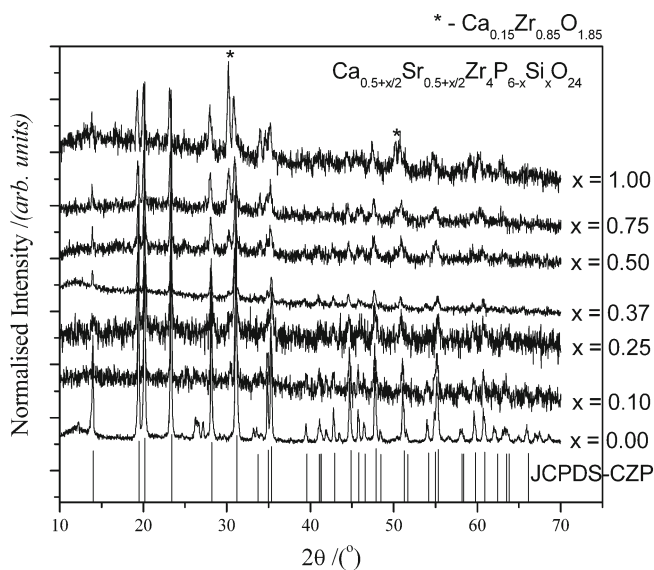


Figure 1. XRD patterns of CSZP ceramics with $x = 0.00$ to 1.00 after calcination at $1000\text{ }^{\circ}\text{C}$ for 24 h.

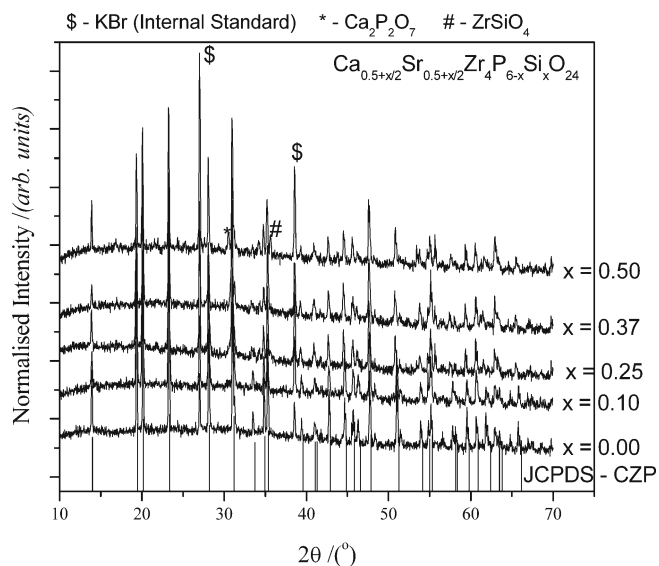


Figure 2. XRD patterns of CSZP ceramics with $x = 0.00$ to 0.50 after sintering at $1250\text{ }^{\circ}\text{C}$ for 24 h.

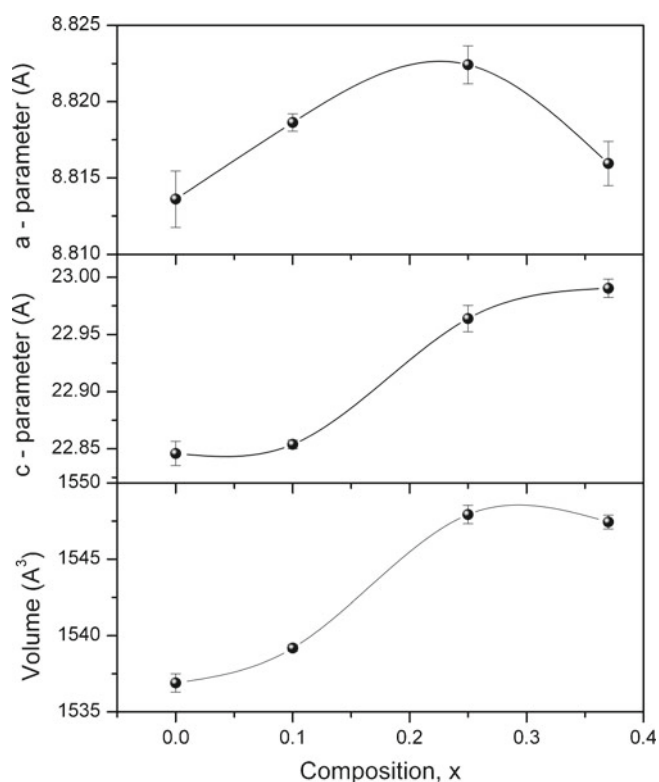


Figure 3. Variation of lattice parameters, a and c and unit cell volume with composition in CSZP system.

calculated for the compositions up to $x = 0.37$ shows an increasing trend with the compositions up to $x = 0.25$ and then starts decreasing, as shown in figure 3. This again confirms the formation of the solid solution up to the composition, $x = 0.37$.

The wet chemical process used in this co-precipitation method must have helped in getting the pure NZP phase for $x < 0.37$ at lower calcination and sintering temperatures compared to the conventional ceramic methods. The higher inter diffusion due to the smaller particle size along with the larger surface area of the co-precipitated product might have helped in the phase formation at lower calcination and sintering temperatures.

3.2 Microstructure

The cross sectional SEM micrographs of the six compositions of CSZP system are shown in figure 4. The $x = 0.00$ composition shows a dense microstructure with few open pores. The average grain size calculated from the linear intercept technique is about $20\text{--}25\text{ }\mu\text{m}$. The microcracks observed in the SEM images are supposed to be generated during cooling of the sample from the sintered state, due to axial thermal expansion anisotropy (Srikanth *et al* 1991). Recently, Breval *et al* (1998) reported that the silicon substitution in place of phosphorous in CSZP system leads to an increase in the thermal expansion anisotropy and also an increased number of counts in the acoustic emission measurements. The generation of microcracks can also be associated with the average grain size of the material (Srikanth *et al* 1991). Microcracks in an anisotropic thermal expansion material will be generated when the grain size is more than a certain critical limit. Microcracking in $x = 0.00$ composition is expected to be minimum because of its low thermal expansion anisotropy. However, few microcracks observed in the micrograph of $x = 0.00$ composition are supposed to be generated due to the larger grain size ($20\text{--}25\text{ }\mu\text{m}$), which is more than the critical limit ($2\text{ }\mu\text{m}$) as estimated by Limaye *et al* (1991).

The micrographs also show a decreasing trend in the average grain size with the increase in silicon substitution. This may be due to the formation of silicon containing liquid phase, which hinders the grain growth. The compositions with $x > 0.37$ show the presence of some clusters in the matrix of CSZP. This can be ascribed to the secondary phases of $\text{Ca}_2\text{P}_2\text{O}_7$ and ZrSiO_4 as seen in the XRD patterns (figure 2). Some of the silicon substituted compositions exhibit needle shaped grains, which may be due to the liquid phase sintering.

3.3 Thermal expansion

The thermal expansion plots for both heating and cooling cycles from room temperature to $850\text{ }^{\circ}\text{C}$ are shown in figure 5. The $x = 0.00$ composition exhibits thermal contraction with temperature for the entire temperature region. With the increase in the silicon substitution the material becomes less contracting and it becomes near zero expanding for the composition $x = 0.75$ and then it is expanding for the composition $x = 1.00$. The average thermal expansion coefficient,

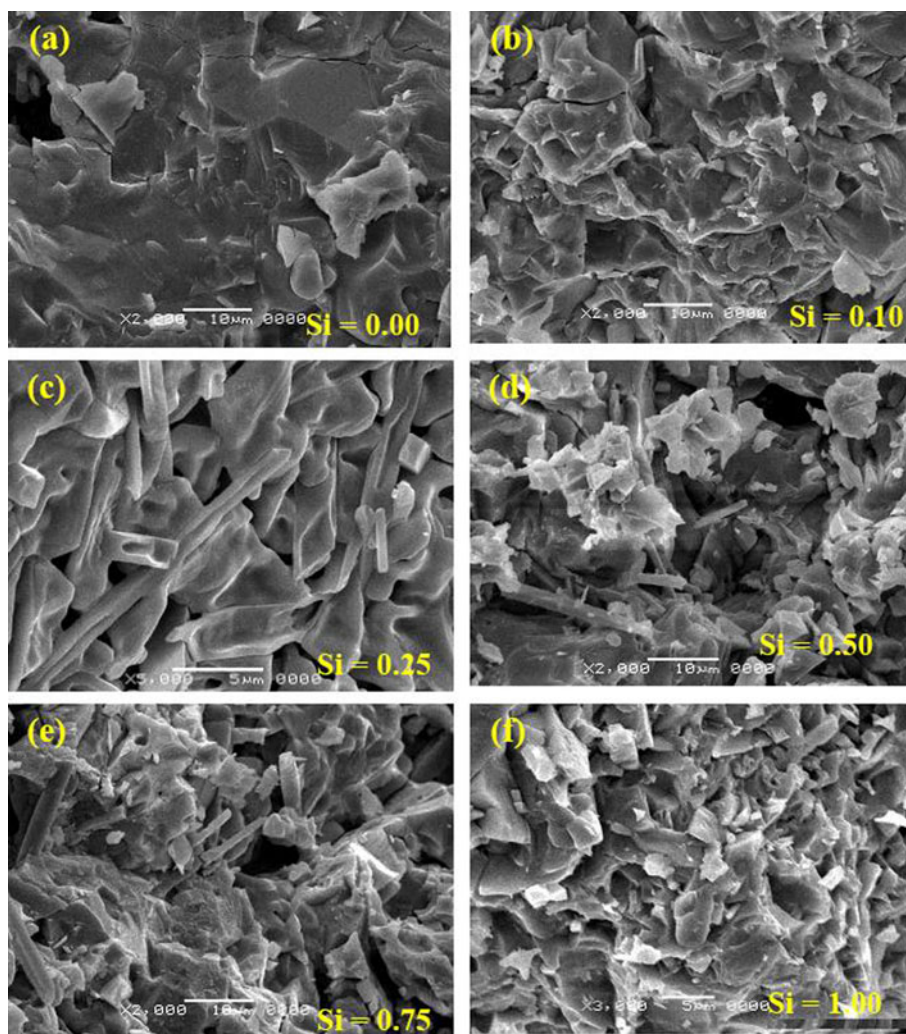


Figure 4. Cross-sectional SEM micrographs of CSZP ceramics for (a) $x = 0.00$, (b) $x = 0.10$, (c) $x = 0.25$, (d) $x = 0.50$, (e) $x = 0.75$ and (f) $x = 1.00$.

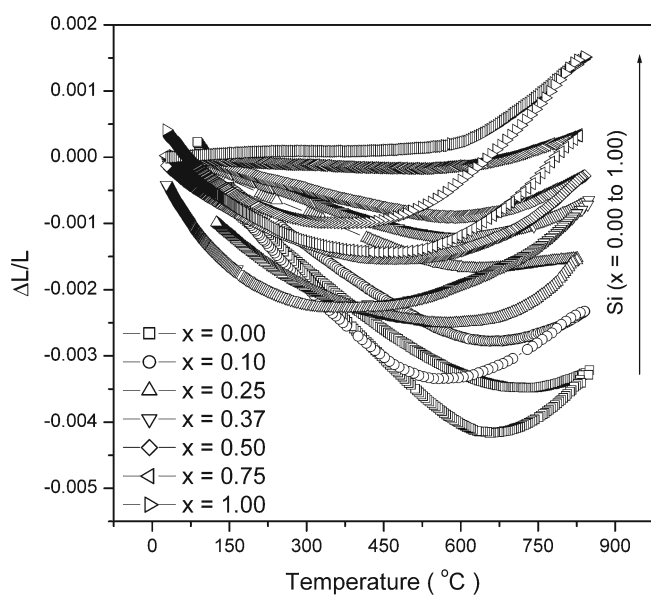


Figure 5. Thermal expansion plots of CSZP ceramics ($x = 0.00$ to 1.00) for both heating and cooling cycles.

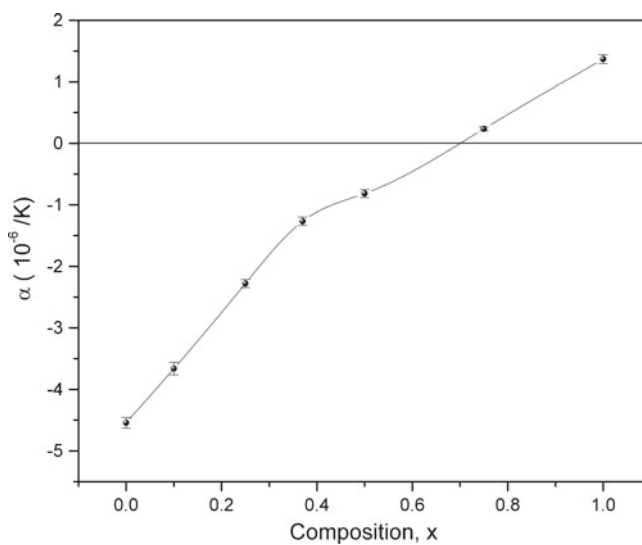


Figure 6. Variation of thermal expansion coefficient, α , with composition in CSZP system ($x = 0.00$ to 1.00).

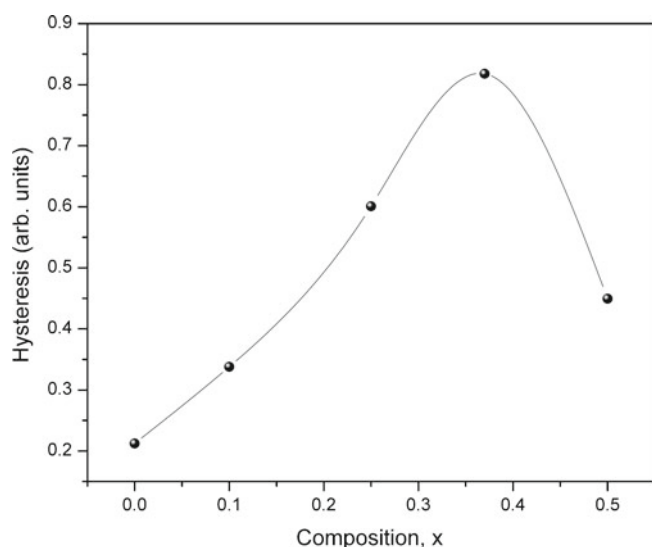


Figure 7. Variation of amount of hysteresis in thermal expansion curves with composition for CSZP system ($x = 0.00$ to 0.37).

α , calculated from these plots is plotted as a function of composition in figure 6. The figure shows a continuous increase in α with silicon substitution changing from negative value to positive value. The linear change in the value of α from $x = 0.00$ to 0.37 may be due to the substituted Si going into the lattice in place of P. The formation of secondary phases, $\text{Ca}_2\text{P}_2\text{O}_7$ and ZrSiO_4 , influences the change in α for the composition, $x > 0.37$. The α of these compositions will be an average of the three phases present in the material.

The area under the thermal expansion curves, which represents the amount of hysteresis between heating and cooling cycles, is plotted as a function of composition in figure 7. The amount of hysteresis is minimum for $x = 0.00$ composition and it increases with the silicon substitution up to $x = 0.37$ and then starts decreasing for $x > 0.37$. The hysteresis in thermal expansion is due to the presence of microcracks in the material. As discussed earlier, the generation of microcracks is dependent on the thermal expansion anisotropy and the average grain size. The $x = 0.00$ composition having less thermal expansion anisotropy but with grain size above the critical limit exhibits few microcracks, as seen in the SEM, and hence hysteresis in thermal expansion. The silicon substitution leads to an increase in thermal expansion anisotropy with the grain size above critical limit and hence to the generation of more microcracks, which in turn leads to the increase in the amount of hysteresis in thermal expansion. However, acoustic emission results of Breval *et al* (1998) shows highest

counts for $x = 0.10$ composition representing more microcracks. The decrease in the amount of hysteresis for compositions $x > 0.37$ in our samples may be due to the presence of secondary phases, which influences the thermal expansion anisotropy and grain size. Further, smaller grain size observed for $x > 0.37$ may be within the critical limit for microcrack to occur.

4. Conclusions

The co-precipitation method, which is being wet-chemical method, helped in decreasing the calcination and the sintering temperature for getting the pure NZP phase in CSZP system for $x < 0.37$. The smaller particle size and the larger surface area of the co-precipitated product might have increased the inter-diffusion of the cations during calcination stages. The continuous increase in unit cell volume and TEC for the compositions up to $x = 0.37$ shows the substitution of silicon for phosphorous in CSZP system. The increase in thermal expansion anisotropy, which in turn leading to generation of microcracks, is responsible for the increase in the hysteresis in thermal expansion of CSZP system up to $x = 0.37$.

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