Int. J. High Technology Ceramics **4** (1988) 31–39

Hydrothermal Preparation of the Low-expansion NZP Family of Materials

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ABSTRACT

This paper reports on the synthesis of low thermal expansion $NaZr_2(PO_4)_3$ *(NZP) and* $CaZr_4(PO_4)_6$ *(CZP) families of materials and their analogues for each of the alkali and alkaline earth metals by the hydrothermal method. Starting gels were prepared by mixing stoichiometric proportions of alkali and alkaline earth metal chlorides of nitrates with a 0·5* M $ZrOCl_2$ *solution and by titrating this mixture with a stoichiometric amount of 1·0* M H_3PO_4 *while the solution was constantly stirred. The gels were dried to remove the HCl produced during the reaction between* $ZrOCl_2$ *and* H_3PO_4*, and were then heated with water in teflon-lined Parr bombs or gold capsules. In general, the hydrothermal method yielded 100–300 nm sized rhombohedral single crystals of different NZP materials at 175–200°C under saturated steam pressure conditions. The initial pH and the temperature of treatment are the most critical factors in the hydrothermal synthesis of these technologically important low expansion materials.*

INTRODUCTION

The sodium zirconium phosphate ($NaZr_2(PO_4)_3$, NZP family of materials was recently discovered as a new family of near-zero or low thermal expansion materials.[1-3] These materials were also investigated for use as ionic conductors.[4-6] The NZP phase has a versatile three-dimensional structure which incorporates numerous cations in all the available sites.[7] These low thermal expansion materials have a range of uses, such as tiles in

Int. J. High Technology Ceramics 0267-3762/88/$03·50

space structures and catalyst supports in automotive exhaust systems. Thus far these materials have been synthesized mainly by the traditional solid-state method[8] at temperatures around 1000°C. Solution–sol–gel (SSG) processing has also been utilized in the synthesis of these materials.[9] The SSG process also requires high temperatures for their synthesis, although the temperatures are somewhat lower than those for the solid-state method. A few of the NZP phases such as $NH_4Zr_2(PO_4)_3$, $H_3OZr_2(PO_4)_3$ and $NaZr_2(PO_4)_3$ were, however, synthesized at approximately 200°C using the hydrothermal method.[10,11] The above studies suggest that the hydrothermal method may be a low temperature route for the synthesis of ultrafine powders of the NZP family of materials. The synthesis of high surface area powders is obviously important in obtaining good densification at low sintering temperatures. This paper reports the results of a study to synthesize $NaZr_2(PO_4)_3$ (NZP), $CaZr_4(PO_4)_6$ (CZP), and their analogues for each of the alkali and alkaline earth metals by the hydrothermal method.

EXPERIMENTAL

Preparation of the gels

A stoichiometric amount of metal chloride or nitrate was dissolved in 0·5M $ZrOCl_2$ solution and this mixture was titrated with the dropwise addition of a stoichiometric volume of 1·0M H_3PO_4 while the solution was constantly stirred. The addition of phosphoric acid led to immediate gelation or precipitation and the gelation continued until all H_3PO_4 was added. The gel was dried at 70°C in an oven, then ground, rehydrated and redried. This drying removed HCl produced by the reaction of $ZrOCl_2$ and H_3PO_4.

Additional gels of $LiZr_2(PO_4)_3$ and $MgZr_4(PO_4)_6$ were made by first dissolving LiOH and $Mg(OH)_2$ in H_3PO_4 and then adding $ZrOCl_2$ to this mixture. These gels were made with stoichiometric proportions of the three components and with excess Li^+ or Mg^{2+}.

Hydrothermal treatment

Dried gels and water were loaded in teflon-lined Parr acid-digestion bombs and then heated at 175, 200 and 230°C for one to three days in drying ovens. Large batches of up to 20 g were produced using the Parr acid-digestion bombs. Because the Parr acid-digestion bombs cannot be heated above approximately 275°C, additional hydrothermal runs were carried out using gold capsules in cold-seal pressure vessels. The dried gels were loaded with water into gold capsules, sealed[12] and heated in cold-seal vessels for different durations at 300, 350 and 400°C under a confining pressure of 100 MPa. After the hydrothermal treatment, the solid and solution phases were separated by centrifugation. The solid phases were washed free of any soluble salts with deionized water and dried. The solutions were collected for analysis.

Characterization and analyses of solids and solutions

The solid phases were characterized by powder X-ray diffraction (XRD) using a Picker-Seimens diffractometer with graphite monochromated CuKα radiation and by scanning electron microscopy (SEM) using an ISI-DS 130 instrument with an energy dispersive spectrometry attachment. The solution phases of a few hydrothermal runs were analyzed by atomic emission spectroscopy using a SpectraMetrics SpectraSpan III instrument.

RESULTS AND DISCUSSION

Alkali zirconium phosphates

Scanning electron micrographs of hydrothermally prepared Cs, Rb, K, Na and Li zirconium phosphates are presented in Fig. 1. Cesium zirconium phosphate, $CsZr_2(PO_4)_3$, appears to be a high-temperature phase and crystallized only above 350°C. Figure 1A shows cesium zirconium phosphate crystals which are rhombohedra of 0·8 to 3·0 μm size. Hydrothermal runs at 300°C or below yielded amorphous solids as detected by XRD. Rubidium zirconium phosphate, $RbZr_2(PO_4)_3$, crystallized at 200°C yielding 200 nm sized rhombohedra (Fig. 1B). However, at 175°C, crystallization of $RbZr_2(PO_4)_3$ was partial in three days, yielding anhedral grains of 100 nm along with amorphous solids (Fig. 1C). Potassium zirconium phosphate, $KZr_2(PO_4)_3$, crystallized as 300 nm rhombohedra with some development of stepwise faces (Fig. 1D) at 200°C. At 175°C crystallization of potassium zirconium phosphate appeared complete and yielded 100 nm anhedral grains and aggregates ($\sim$700 nm) of these grains (Fig. 1E). Sodium zirconium phosphate crystallized at 200°C yielding simple 100 nm rhombohedra and ladder-like 500 nm rhombohedra (Fig. 1F). At 175°C crystallization was complete yielding 100 nm anhedral grains and 300 nm subhedral rhombohedra (Fig. 1G). Lithium zirconium phosphate, $LiZr_2(PO_4)_3$ (LiZP), crystallized to rhombohedra of 100–400 nm at 235°C from gels of $LiCl.2ZrOCl_2.3H_3PO_4$. This phase showed the C lattice parameter to be 23·6 Å which is higher than the 22·71 Å reported by the Joint Committee on Powder Diffraction Standards. Analysis of the supernatant indicated that about half of the initially-added Li remained in solution

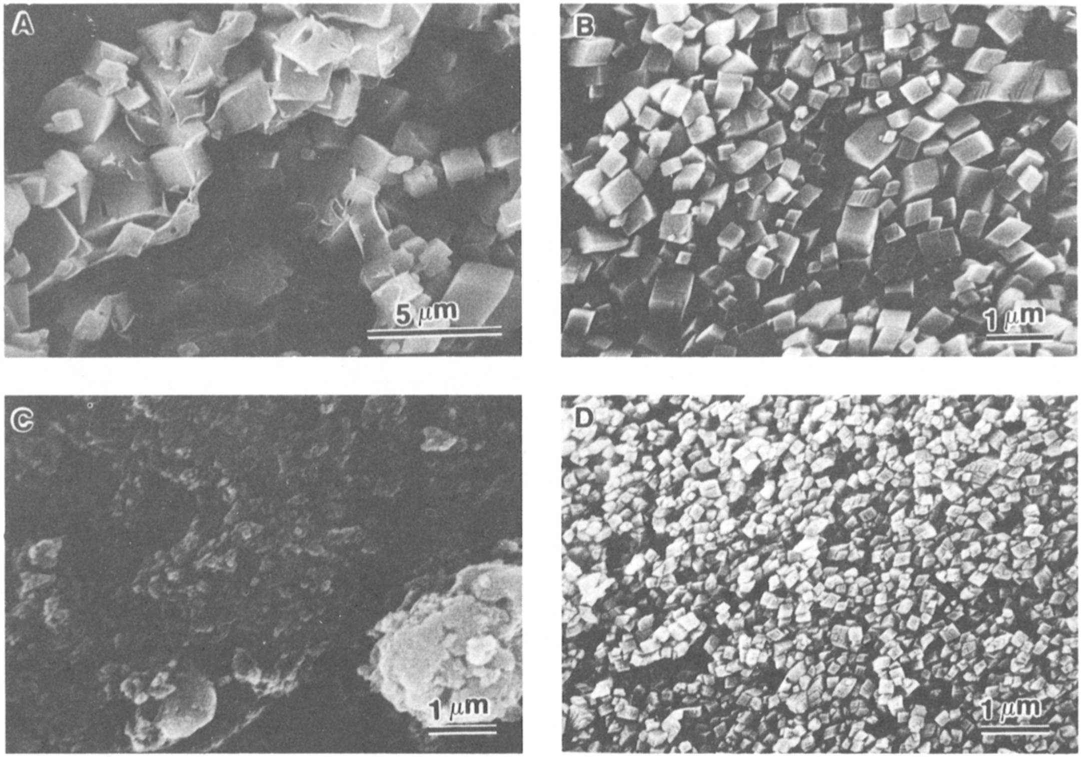

Fig. 1. Scanning electron micrographs of different alkali NZP-phases: (A) $CsZr_2(PO_4)_3$ synthesized at 400°C/three days; (B) $RbZr_2(PO_4)_3$ synthesized at 200°C/three days; (C) as (B) but synthesized at 175°C/three days; (D) $KZr_2(PO_4)_3$ synthesized at 200°C/three days.

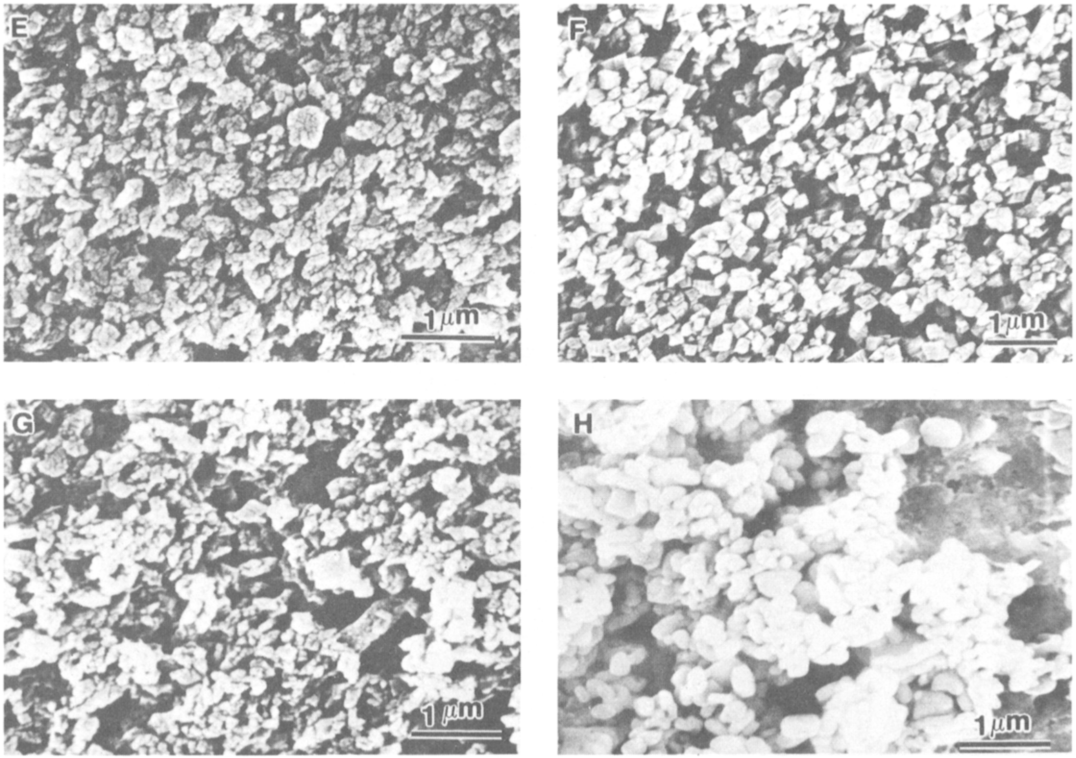

Fig. 1—*contd.* (E) as (D) but synthesized at 175°C/three days; (F) $NaZr_2(PO_4)_3$ synthesized at 200°C/three days; (G) as (F) but synthesized at 175°C/three days; (H) $LiZr_2(PO_4)_3$ synthesized at 350°C/22 h.

which suggested a phase composition of $Li_{0\cdot5}H_{0\cdot5}Zr_2(PO_4)_3$. These gels were too acidic to incorporate only Li^+ in the structure. Therefore, less acidic gels of composition $3LiH_2PO_4 . 2ZrOCl_2$ were used in the synthesis at 350°C for 22 h and these gels yielded a phase (Fig. 1H) with unit cell $a = 8{\cdot}8$ Å and $c = 21{\cdot}7$ Å. This cell is not in accord with the published pattern for LiZP, but it does not fit a trend in alkali NZP phases of decreasing unit cell with decreasing alkali ion radius. Further analysis of this phase showed that it is in fact a new NZP type phase.[13] Calculation of the lattice parameters for the hydrothermally prepared Cs, Rb, K and Na zirconium phosphates agreed with the published values.

Alkaline earth zirconium phosphates

Barium zirconium phosphate, $BaZr_4(PO_4)_6$ (BaZP), crystallized from gels at 200°C. The crystals are 100–800 nm rhombohedra with ladder-like faces (Fig. 2A). Calculated lattice parameters of the hydrothermally prepared phase agreed with published values. It, however, did not crystallize at 175°C. Strontium zirconium phosphate, $SrZr_4(PO_4)_6$ (SrZP), crystallized from gels at 200°C, yielding rhombohedra of 150–250 nm (Fig. 2B). It also crystallized at 175°C after three days. Calculated lattice parameters for the hydrothermally prepared SrZP agreed with the published values. Calcium zirconium phosphate, $CaZr_4(PO_4)_6$ (CaZP), crystallized from gels at 200°C, yielding 150–250 nm rhombohedra with ladder-like faces (Fig. 2C). There was incipient crystallization at 175°C after three days. Calculated lattice parameters of this hydrothermally prepared phase agreed well with the published values. Magnesium zirconium phosphate, $MgZr_4(PO_4)_6$ (MgZP), gels yielded 200 nm rhombohedra along with laths of 200 × 1000 nm (Fig. 2D). Analyses using the energy dispersive spectrometer showed that the Mg was concentrated in the laths and absent from the rhombohedra. This result showed that the rhombohedra are probably $HZr_2(PO_4)_3$ while the laths are probably a layered zirconium phosphate. Single phase MgZP was not obtained even when less acidic gels of composition $2Mg(H_2PO_4)_2 . 2H_3PO_4 . 4ZrOCl_2$ were used under hydrothermal conditions at 200°C. Further studies are in progress to delineate the stability field of MgZP.

pH dependence

The reaction to form the NZP family of materials is highly acidic. For example, with the starting materials used in this research, $NaZr_2(PO_4)_3$ is formed as follows:

$$NaCl + 2ZrOCl_2 + 3H_3PO_4 \rightarrow NaZr_2(PO_4)_3 + 2H_2O + 5HCl \qquad (1)$$

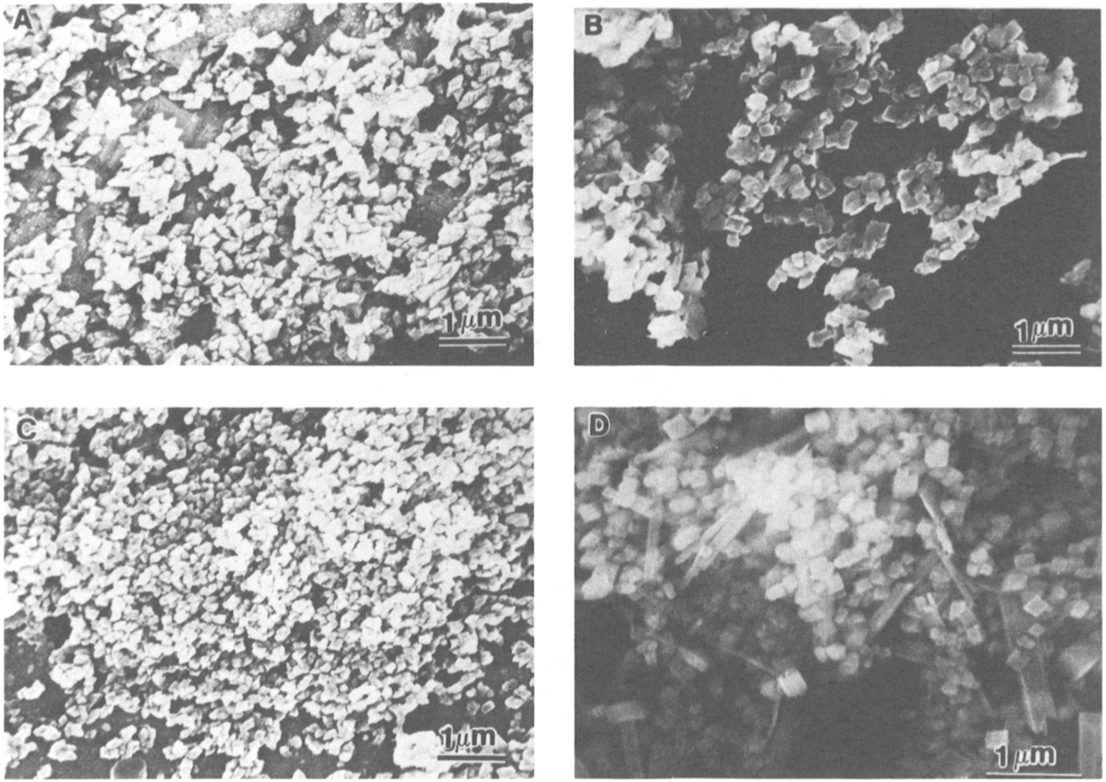

Fig. 2. Scanning electron micrographs of different alkaline earth NZP-phases: (A) $BaZr_4(PO_4)_6$ synthesized at 200°C/three days; (B) $SrZr_4(PO_4)_6$ synthesized at 200°C/three days; (C) $CaZr_4(PO_4)_6$ synthesized at 200°C/three days; (D) Mixed phases resulting from $MgZr_4(PO_4)_6$ composition gels at 200°C/three days.

This reaction leads to a pH < 1, which is too low to form the NZP phase.[14] Therefore, it is necessary to drive off some of the excess HCl by drying the gel before it crystallized hydrothermally. The gels which were dried and rehydrated then registered a pH between 1 and 2 after hydrothermal reaction. These dried and rehydrated gels crystallized to the respective alkali and alkaline earth NZP family of materials, confirming the earlier results of Yamanaka and Tanaka[14] for $NaZr_2(PO_4)_3$. Hydrothermal runs using undried gels produced KZP and RbZP, which suggests that these phases may form at pH lower than 1. However, solution and/or solid phase analyses should be carried out to determine the exact composition. Undried NaZP gels produced a mixture of crystalline NaZP and an unidentified phase. The LiZP and the alkaline earth zirconium phosphates yielded only the above unidentified phase which is a mixture of 400–2000 nm laths and 1000 nm plates (Fig. 3). The synthesis, characterization and identification of this new phase is under investigation. These results clearly show that the hydrothermal synthesis of the NZP family of materials is pH dependent.

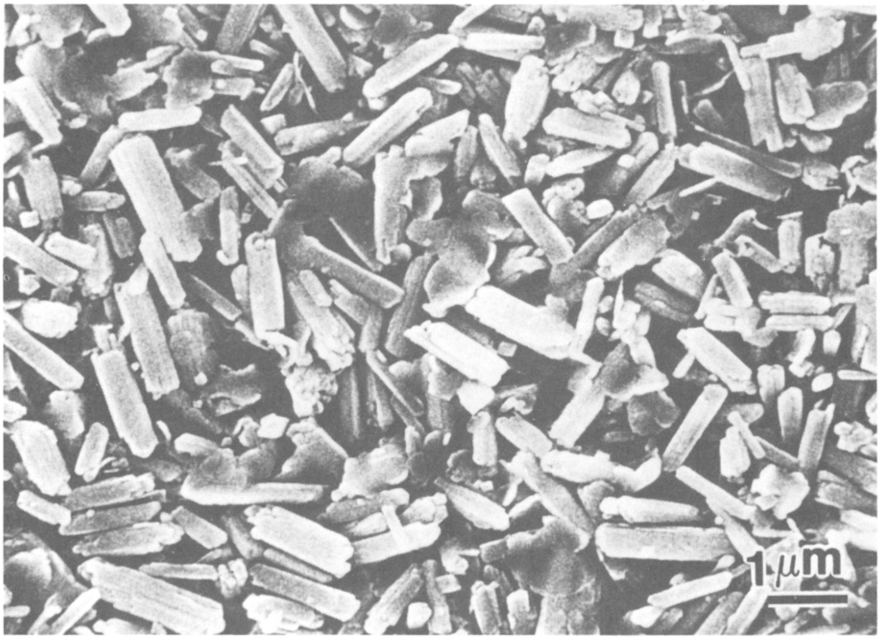

Fig. 3. Scanning electron micrograph of unidentified acidic phase.

CONCLUSION

The hydrothermal method is suitable for the preparation of the ultra-fine NZP-family of materials at approximately 200°C. The formation of these materials is pH-sensitive.

ACKNOWLEDGEMENT

This research was supported by the US Air Force Office of Scientific Research under contract No. F496200-85-C-0069.

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