

Sol-gel Synthesis and Properties of Phosphate Ceramics

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Silicon, titanium, zirconium phosphates were synthesized by starting with appropriate chemical precursors in a solution. The synthetic procedure, chemical and physical structures were examined by FT-IR, liquid and solid state NMR, TGA, SEM, XRD, etc. The phosphates were examined for thermal and electrical properties. Advantages of the synthesis technique and the data on unique structures and thermal properties are reported.

Key words: Sol-gel, Phosphates, Crystallinity

I. Introduction

Phosphate ceramic materials have potential applications in many advanced technology areas, such as new laser sources and prosthetic materials. However, due to processing difficulties, the potential of phosphate ceramics have not been fully realized.¹ Several research groups²⁻⁶⁾ have suggested such applications as optical fibers^{7,8)} and as host materials for fast ionic conductors.^{9,10)} All of them used either phosphoric acid or $\text{PO}(\text{OH})_{3-x}(\text{OR})_x$, or $\text{P}(\text{OH})_3$ as the precursor of phosphorus. Some used various phosphorus alkoxides including $\text{P}(\text{OEt})_3$, $(\text{OEt})_2\text{POP}(\text{OEt})_2$, $\text{PO}(\text{OEt})_3$, and could not synthesize homogeneous phosphosilicate compounds successfully due to the big difference in hydrolysis rate of the silicon precursor and phosphorus precursors.⁵⁾

A more direct method is to react P_2O_5 and a metal alkoxide to obtain the phospho-metal oxides sols and gels. By using P_2O_5 directly, our study showed that not only was the reaction process simplified, but also the gelation process and the problem of phosphorus loss upon firing were improved.¹¹⁾

Phosphotitanates are insoluble acid salts which can be obtained with a different layered structure known as γ -structure, $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$. General type $\text{M}^{\text{IV}}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been synthesized by others previously with some difficulty,¹²⁾ e.g., high pressure, high temperature.

$\text{Ti}/\text{Zr}/\text{PO}_4$ (TZP) compound possesses unique properties such as ion exchange and super acidity in catalysis.^{13,14)} Synthesis of TZP with larger specific surface area has been investigated in our laboratory using sol-gel process (SGP).¹⁵⁾

The mechanical and optical properties of crystalline phosphates made by conventional techniques are generally poor due to large grain size and residual porosity, and effective sintering requires very high temperatures and/or pressures. Phosphate ceramics prepared by SGP may improve various properties due to the inherent homogeneity and lower pro-

cessing temperatures. In addition these phosphate ceramics may possess peculiar thermal properties.

II. Experimental Procedure

1. Materials

The chemicals used in this study were obtained from Aldrich Chemical Company, Milwaukee, WI as reagent grade or better. All reaction processes were either carried out in glove box or in an inert gas atmosphere to maintain anhydrous condition.

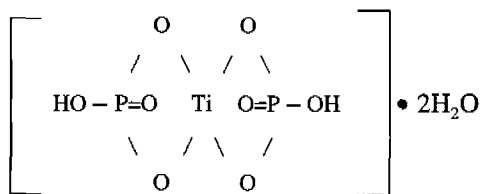
2. Preparation of phosphosilicate sol

Different compositions of phosphosilicates can be prepared by reaction of P_2O_5 and tetraethoxy silane (TEOS). Appropriate amounts of P_2O_5 is dissolved in an appropriate volume of TEOS under an anhydrous condition. The mixture is stirred and refluxed for 12 hours under an inert atmosphere. Completely clear sols can be obtained by adding a small amount of water. The amount of water affects the gelation rates. The homogeneous sols were used to produce uniform films by dipping or spin casting.

3. Preparation of phosphotitanate sols and gels

A titanium alkoxide is treated for partial ligand exchange with 2,4-pentanedione (acetylacetone or acac) to reduce the reactivity of the alkoxide. The premature gelation can then be prevented by dissolving P_2O_5 , as in phosphosilicates, and a homogenous sol is obtained upon refluxing. $\text{PO}(\text{OH})_{3-x}(\text{OR})_x$ could also be used as a source of P by reacting with $\text{Ti}(\text{OEt})_4$.

For synthesis of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (structure formula shown below), the molar ratio of P to Ti was set at 2:1, with anhydrous EtOH as the solvent. The Ti-P sols gelled within 30 min at 23°C. They were aged and dried in an oven for monolithic bulk applications.



The layer of $[\text{Ti}(\text{IV})(\text{PO}_4)_2]^{2-}$ is neutralized by exchangeable H^+ with H_2O between the layers in the interlayer distance,⁽²⁾ $d=11.60\text{\AA}$.

4. Characterization of gels and ceramics

Thermal analysis (TGA/DTA) was carried out on Seiko 5200H with $7^\circ\text{C}/\text{min}$ heating rate. X-ray diffraction patterns (XRD) were obtained by using a Philips Model PN3550. Nominal semiquantitative estimation of the crystalline vs. amorphous content in mixed phase samples was calculated by comparing the integrated total diffracted intensity with the integrated background.

For nuclear magnetic resonance spectroscopy (NMR), ^{29}Si and ^{31}P nuclei (both liquid and solid state NMR) were used to identify chemical species formed during the sol-gel process. The solid state NMR experiments were carried out with a Chemagnetic Spectrometer (300 MHz, 89 mm wide-bore Oxford magnet) using a CP-MAS probe at frequencies 120.77 and 59.29 MHz for ^{31}P and ^{29}Si , respectively.

III. Results and Discussion

1. Characterization of sols and gels of PSi and PTi

When gelation time vs. composition was investigated, the amount of water added to a sol was fixed at $\text{H}_2\text{O}/\text{TEOS}=2/1$ in molar ratio. To study the gelation process, the PSi composition was set at 1:1 in molar ratio. The PSi sol gelled faster when the content of phosphorus increased and gelation time was inversely proportional to the amount of water added.

The FT-IR results for PSi sols, without water, showed the existence of P-O-Si bonds at $\sim 1060\text{ cm}^{-1}$ indicating that P_2O_5 reacts with EtO-Si to give rise to P-O-Si-OEt bonds. This reaction stopped at a point depending on the initial ratio of P to Si. If the amount of P was small, most of the EtO-Si bonds of TEOS remained unbroken. Thus the PSi sol took long time to gel. When the amount of P was increased, more EtO-Si bonds were converted to P-O-Si bonds and the gelation time was shortened. When water was added to a PSi sol, some of the unreacted EtO-Si were hydrolyzed hastening the gelation.

The solid state ^{31}P NMR spectrum of the dried PSi gel of 1:1 (Fig. 1a) shows that only one kind of P-O bond existed, while the spectrum of the sample fired at 900°C (Fig. 1b) shows clearly the presence of P-O-Si linkage (-38.3 ppm).⁽¹⁾ In Fig. 2, an interesting result in the ^{29}Si spectrum for a gel dried at 100°C was that not only the tetracoordinated silicon (-104 ppm) but also the presence of hexacoordinated silicon (-212.7 ppm) was observed. Usually hexacoordinated silicon only exists at high temperatures (above 900°C)⁽¹⁾ or in high

pressure synthesized samples.⁽¹⁶⁾ Interest in hexacoordinated silicon has been enhanced by the potential applications based on particular properties of hexacoordinated silicon including its behavior in catalytic reactions.

The dried gels of PSi (2:1) remained amorphous up to 500°C , but crystallized to phase $\text{Si}_3\text{O}(\text{PO}_4)_6$ above that temperature, different from the results reported by Kim *et al.*⁽¹⁷⁾ who observed crystallization occurring at 300°C for phosphosilicate gels. The difference must be caused by the use of different precursors.

Silicon phosphates can be all amorphous, all crystalline, or mixture of the two phases depending on the P to Si composition. The higher the proportion of P, the more crystal-

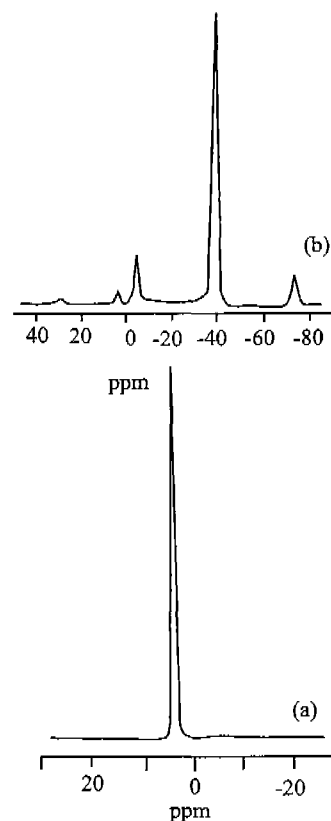


Fig. 1. ^{31}P solid state NMR of PSi (1:1) gel after (a) dried at 100°C and (b) fired at 900°C .

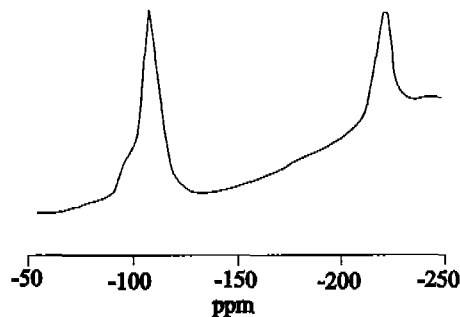


Fig. 2. ^{29}Si solid state NMR of PSi (1:1) gel dried at 100°C .

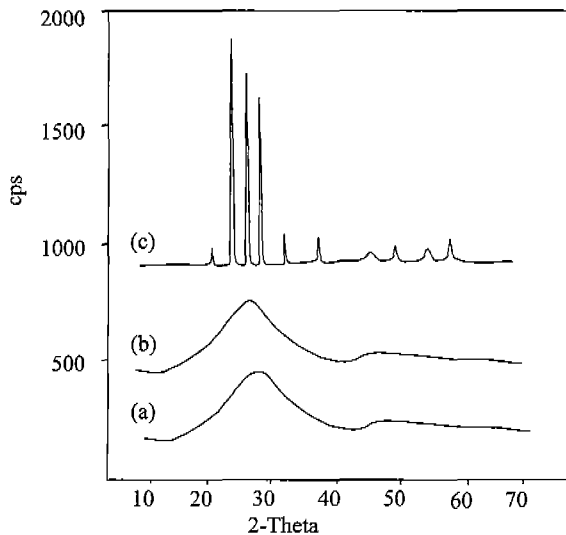


Fig. 3. X-ray diffraction pattern of P-Ti (2:1) gels fired at different temperatures: (a) 300°C, (b) 500°C and (c) 900°C.

line phase one can get. Although both Si and P are glass former, when they are mixed together, they yielded crystalline structure. The usual limit of all amorphous state is about 35 mole % of P. The % crystallinity and thermal conductivity of P-Si for different compositions are given in Table 1.

100% crystalline phase was observed for the mole ratio of P:Si above 1.2:1 and for the ratio below 0.4:1, 100% amorphous phase was obtained. One can get completely amorphous or glass P-Si with maximum P at P:Si ratio of 0.4.

The PTi gels were dried at 100°C and fired at different temperatures in the range of 100-900°C. XRD pattern of PTi gels, in Fig. 3, as a function of firing temperature showed increasing crystallization of the gels with firing temperature. Phosphotitanates with layered structures such as $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ [α -TiP], $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ [γ -TiP] and $\text{Ti}_2\text{O}_3 \cdot (\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been shown to be candidates for ionic conductors, radioactive waste hosts, and low thermal expansion materials.¹⁸⁻²⁰ The layered structure imparts ion-exchange properties and intercalatability of polar organic molecules such as diamines into the layers.^{12,19} The synthesis of these layered phases, however, has been a complicated

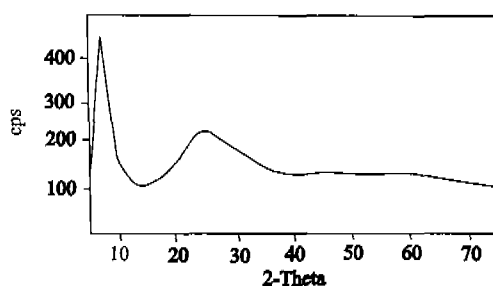


Fig. 4. X-ray diffraction pattern of PTi (2:1) gel dried at 100°C.

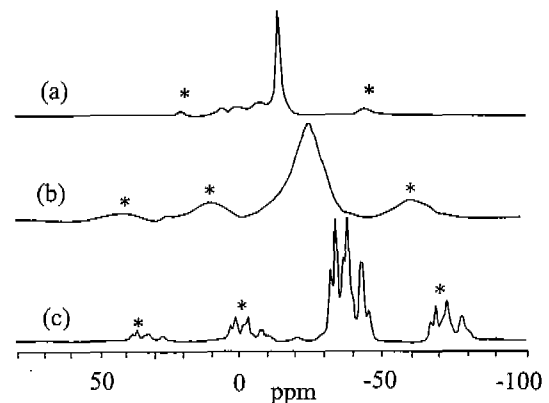


Fig. 5. ³¹P solid state NMR of PTi (2:1) gels fired at different temperatures: (a) 100°C, (b) 500°C and (c) 900°C. * are spin side bands.

process.²⁰⁻²²

The XRD pattern of PTi (2:1) gel dried at 100°C in Fig. 4 matches quite well with that of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS ref. #44-0383), which has a layered structure.^{21,22} To our knowledge, this is the first time this layered material $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ was fabricated through a simple sol-gel method.

The stability of the layered $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ was investigated by firing at different temperatures and by XRD on the fired products. The XRD results showed formation of amorphous materials in the temperature range of 300°C and 900°C, where it crystallized to $\text{Ti}(\text{P}_2\text{O}_7)$. ³¹P NMR spectra were taken in order to investigate the structure of PTi gels and fired samples. Figs 5a-c give ³¹P NMR spectra for PTi gels prepared at 100°C, 500°C, and 900°C. For spectrum (a) with a layered structure, ³¹P NMR spectrum exhibited a large resonance at ~ -14.4 ppm which corresponds to a phosphate bound to two phosphorus or titanium atoms through P-O-P or P-O-Ti bonds. For the layered $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ after being fired at 500°C (Spectrum b), shows a ³¹P NMR spectrum with a broad resonance at -26.6 ppm which suggests the existence of a large amount of amorphous material. This agrees with the XRD data from this sample.

2. Thermal behavior

The crystallinity of sol-gel derived P-Si increased as the proportion of P increased, as shown in Table 1, which also shows increase thermal conductivity as the crystallinity of P-Si increased as expected. Although the samples for the thermal conductivity measurements may be less than 100% dense, the value 0.34 w/m·K is fairly low for a ceramic material when compared with fused silica of ~ 1.4 w/m·K. The dielectric constant of thin film P-Si in Table 1 shows that the dielectric constant increased with increase in the P:Si ratio that is also increase in crystallinity. The film thickness was increased also by the increased proportion of P after 4 cycles of spin coating and firing. Since the precursor for P, P_2O_5 , is 100% retained during firing unlike Si precursor TEOS,

Table 1. % Amorphous, % Crystallinity, Dielectric Constant, and Thermal Conductivity of P:Si Fired at 900°C

P:Si composition	% amorphous	% crystallinity	Dielectric constant @10 ⁶ Herz (film thickness, μm)	Thermal conductivity w/m·K@298K
0.1:1	100	0		
0.2:1			6.7 (1.5)	0.34
0.4:1	100	0		
0.5:1	90	10		
0.8:1	50	50	7.9 (1.7)	
1.2:1	0	100	8.1 (1.9)	0.41

Table 2. Density of Phosphate Gels with Different Compositions Fired at Different Temperatures

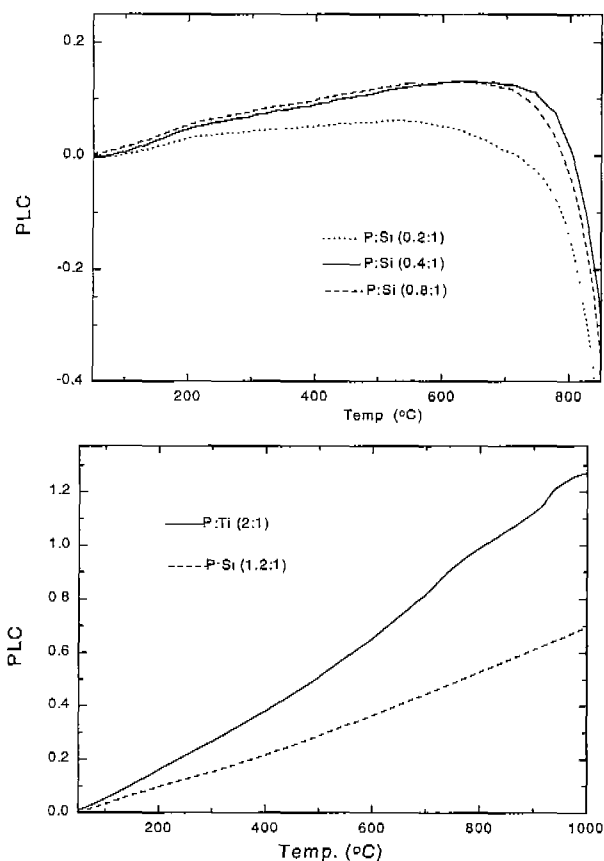
Temperature °C	Density				
	P:Si				P:Ti
	0.2:1	0.4:1	0.8:1	1.2:1	2:1
60	1.54	1.55	1.64	1.72	1.37
400	1.85	1.94	2.01	2.06	1.94
600	1.86	1.95	2.02	2.17	2.02
800	1.86	1.97	2.03	2.12	2.54
900	1.92	1.97	2.01	2.15	2.62
950	1.93	1.97	2.02	2.16	2.62
1000	1.94	1.98	2.03	2.13	2.62

increase of P resulted in denser, i.e., thicker films. These demonstrate a possibility of tailoring dielectric constant and film thickness by varying the P:Si ratio.

For many of the practical applications, sol-gel derived products need to be densified by sintering. Densification would be easier if sintering can be completed before crystallization begins. Table 2 lists the density for different compositions as a function of temperature.

From the results of density measurements, one can find that the maximum density is reached at about 600°C for P:Si gels. If the theoretical density of P:Si (1.2:1), estimated based on the rule of mixture, is 2.25 g/cm³, P:Si (1.2:1) gel was about 92% densified. This means that either the P:Si gels fired had some closed pores or the theoretical density is lower than 2.25 g/cm³. Further study by dilatometry showed that the densification of the P:Si gels is completed at about 700°C.

The density of P:Si gels changed with the variation in the composition. When P:Si molar ratio changed from 0.2:1 to 0.4:1, the density increased slightly. When P:Si mole ratio changed from 0.4:1 to 0.8:1 and 1.2:1, the density obviously increased. This density change with composition variation can be explained by means of phase evolution vs. composition derived from XRD experiment. As the P:Si molar ratio

**Fig. 6.** Thermal expansion of densified phosphate ceramics.

is lower than 0.4:1, only amorphous glass phase exists in P:Si gels. Thus the density did not change much with composition variation. The maximum density of P:Ti (2:1) is reached at ~900°C. This coincides with dilatometry results that the major shrinkage of P:Ti (2:1) occurs at 900°C.

Thermal expansion experiments were carried out on fully densified phosphate ceramics derived from the sol-gel process. Elder *et al.*³⁸ found that the thermal properties of phosphate glasses could be improved by increasing the P₂O₅ content. Thermal expansion diagrams of densified P:Si gels with different compositions and P:Ti (2:1) gel are shown in Fig. 6. The P:Si (0.2:1 and 0.4:1) gels, which are amorphous, exhibited linear thermal expansion up to 700°C, and shrinkage occurred at higher temperatures due to softening. The percentage linear change (PLC) of P:Si glass is very low (<0.1%) in the temperature range of 100-700°C. Fully amorphous P:Si materials exhibited even lower PLC than fused silica. This shows a potential application as low thermal expansion materials and the possibility of tailoring CTE. The PLC increased slightly with the increase of phosphorus content in amorphous P:Si. The thermal expansion character of P:Si (1.2:1), which is crystalline, is quite different from that of P:Si (0.2:1 and 0.4:1), which is amorphous, because the structural difference. Similar to P:Si (1.2:1), P:Ti (2:1) exhibited a linear thermal expansion with higher PLC than P:Si.

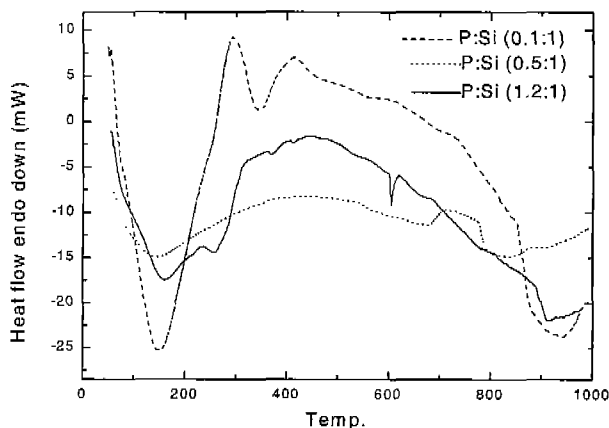


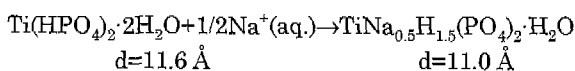
Fig. 7. DTA of P:Si gels dried at 100°C.

DTA in DSC mode of P:Si gels with different compositions dried at 100°C were plotted in Fig. 7. All samples showed a broad endothermic peak at temperatures below 300°C. This corresponds to the dehydration and evaporation of residual organic solvents. Chemically bonded organic groups were burnt out at higher temperatures, giving rise to an exothermic peak at 300-500°C. Comparing the DTA curves of P:Si gels for different compositions, one can notice the different behavior of phase evolution upon firing. P:Si gel with composition of 1.2:1 showed clearly a crystallization peak at about 600°C. This is identical with the result derived from XRD experiment. DTA curve of P:Si (0.5:1) has a broad crystallization peak at 700°C. This also agrees with XRD results that P:Si (0.5:1) consists of both crystal and amorphous phases. The P:Si gel with composition of 0.1:1 showed no crystallization peaks since it is all amorphous.

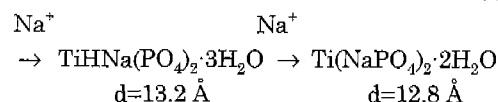
4. Some Potential Applications

Phosphotitanates

Example 1. Ion Exchange Properties of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$,

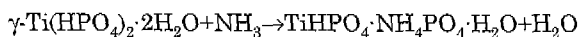


$$d=11.6 \text{ \AA} \qquad d=11.0 \text{ \AA}$$



$$d=13.2 \text{ \AA} \qquad d=12.8 \text{ \AA}$$

Example 2. Intercalation of Organics, e.g., alkanols and alkylamine,



Example 3. Large layer spacing (d) permit larger cations, e.g., Ca^{2+} and Sr^{2+} selectively. As $\gamma\text{-TiP}$ loses the reversible water, d value decreased from 11.6 to 9.4 Å which is more difficult to accommodate larger ions. The $\gamma\text{-TiP}$ also exchange Cs^+ in aq. solution.

Example 4. Since the exchange rate constant for K^+ is 4 times that of Na^+ , Na^+/K^+ separation is possible.

Example 5. Ion exchange membrane sheets can be fabri-

cated for fast separation of cations.

Example 6. Other potential applications:

- Water softening
- Chromatography
- Membrane & solid electrolytes
- Catalysis, e.g., surface acidity & alcohol dehydration, metal support

IV. Conclusions

The reaction steps of P_2O_5 and TEOS investigated through liquid state NMR and solid state NMR showed that hexacoordinated silicon exists in dried P:Si gels. Weight loss during P:Si gel preparation using P_2O_5 was less than that from alkyl phosphate precursors. The layered phosphate $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared through the sol-gel technique for the first time. As compared with H_3PO_4 and $\text{PO}(\text{OH})_{3-x}(\text{OR})_x$, P_2O_5 was a better precursor for preparation of phosphosilicate sols and gels.

Phosphosilicates remained amorphous up to the compositions of P:Si=0.4:1 mole ratio, and begin to crystallize to $\text{Si}_5\text{O}(\text{PO}_4)_6$ at higher phosphorus contents. No devitrification was found when P:Si glass was fired up to 900°C. The sintering property of P:Si and P:Ti, investigated by density measurement and dilatometry, exhibited densification at about 800°C. The thermal expansion property of phosphate ceramics showed that the P:Ti (2:1) and crystal phase of P:Si exhibited linear percentage of linear expansion (PLC). The P:Si glass showed low thermal expansion compared with the crystalline phases. Within the compositions of P:Si amorphous phase, the thermal expansion increased slightly with increasing amount of phosphorus. The fully amorphous P:Si exhibited lower coefficient of thermal expansion than fused silica.

Acknowledgments

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