

SOL-GEL DERIVED PHOSPHOSILICATE AND ALUMINOPHOSPHOSILICATE GELS AT LOWER TEMPERATURE

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ABSTRACT: A sol-gel process for producing phosphosilicate (80 P₂O₅- 20 SiO₂) and aluminophosphosilicate (70 P₂O₅- 20 SiO₂-10 Al₂O₃) gels at lower temperatures derived from triethylphosphate (TEP), tetraethoxysilane (TEOS) and aluminum nitrate has been developed. The structural and chemical characteristics of the nanostructures were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Formation of P -O-Si, P -O-P, Si-O-Si, Al-O-Si and P -O-Al bonds was observed from FTIR spectra for the prepared samples after a heat treatment at 300°C. The XRD results show that the crystallinity degree increases with increasing the calcination temperature and Al₂O₃ ions.

KEYWORDS: Phosphosilicate gel, Aluminophosphosilicate gel, Sol gel process, Low temperature, Structure

1. INTRODUCTION: Recent years, the studies of glass-based materials have attracted more and more interest because they can be used in commercial and technological applications. Several kinds of sol-gel derived inorganic and inorganic-organic nano-composites and hybrids have been studied so far aiming to use in different applications such as optoelectronic, window glasses, windshields of automobiles, biosensors [(1)-(4)]. The sol-gel transition involves a number of complex processes of both a chemical and a structural nature. Before the formation of the gel, two basic steps may be distinguished: (i) hydrolysis of the organometallic compound (TEOS) and (ii) polycondensation of ethoxy (≡Si-OEt) and silanol (≡Si-OH) groups to form siloxanes (≡Si-O-Si≡). In the sol-gel process, a large number of hydrolysis catalysts have been employed, for example, HCL, HNO₃, H₂SO₄ and H₃PO₄ [(5)-(7)]. Pure phosphosilicate (P₂O₅-SiO₂) gels and modified with different dopants, which were prepared from alkoxyphosphorus and alkoxy silane by the sol-gel method are promising for optical and solid state proton conductors in the medium temperature range with low humidity [(8), (9)]. Since the phosphosilicate gels consist of thermally stable silica networks and phosphate, which has a strong affinity for adsorbed water molecules, the gels can be expected to show high proton conductivities even at temperatures in the medium temperature range with low humidity. It is well-known that silica is an inert material used as a support in metallic catalysts for petrochemical industry and another applications. The sol-gel process as chemical method is that includes the ability of maintaining high degree of purity and high homogeneity. Samples are prepared at low temperatures, low cost with good control of size, structure, and morphology [(5)-(9)].

In the present work, unmodified and modified P₂O₅-SiO₂ samples with (10 mol%) Al₂O₃ were prepared by the sol-gel method. The objective is to increase Al₂O₃ and textural properties of the P₂O₅-SiO₂ glasses. The prepared samples were thermal treatment at lower temperatures and then were characterized by XRD, SEM and FTIR.

2. EXPERIMENTAL WORK: Preparation of phosphosilicate (80P₂O₅- 20 SiO₂, in mol %) was obtained by hydrolysis and condensation of Triethylphosphate (TEP) (C₂ H₅O)₃ P (O) and tetraethoxysilane (C₂H₅O)₄ Si (TEOS), (TEOS, 99.999%, Sigma-Aldrich). By hydrolysis of triethylphosphate and tetraethoxysilane in ethanol (CH₃CH₂OH) with distilled water (H₂O) under stirring with HCL used as a catalyst. These solutions were stirred at room temperature to increase the solubility of the mixture. The resultant homogeneous solutions of monolith materials were filled in molds or glass vials and aged at the room temperature for one week then dried in oven type GFL 71.5, at about 50°C. For phosphosilicate doped with (10 mol %) Al₂O₃ ions, the same previous procedures were followed after this the Al³⁺ ions

were introduced in the process, by dissolving aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in distilled H_2O to the preceding precursors to get the desired concentration. Densification of gels for phosphosilicate and doped with Al_2O_3 was obtained, by annealing in air for 3h at temperature ranging from 100 up to 500°C, in a muffle furnace with heating rate 5°C/min. X-ray diffraction (XRD) analysis was made using X-ray diffraction (D8–ADVANCE). The measurements were done using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The average crystallite sizes for the samples were calculated using the Debye-Scherrer equation: $D = \frac{0.9\lambda}{B \cos \theta}$, Where λ is the X-ray wavelength (1.54 \AA), θ is the Bragg diffraction angle, and B is full width at half maximum. The particle distribution and the surface morphology with element ration were examined by scanning electron microscopy (SEM), JEOL model JSM 840, Infrared spectra (FTIR) were recorded at room temperature on a JASCO FTIR-460 spectrometer.

3. RESULTS AND DISCUSSION:

3.1. X-RAY DIFFRACTION (XRD) STUDIES: Pure phosphosilicate ($80\text{P}_2\text{O}_5 - 20 \text{SiO}_2$) and doped with (10 mol %) Al_2O_3 were produced by sol gel method. Fig. I shows the XRD pattern of pure and doped phosphosilicate glasses calcined at 100°C for 3 h in air, the samples almost takes amorphous state indicative of the internal disorder and glassy nature of these materials [(8)-(11)]. The two samples are amorphous up to 100°C. However, the thermal treatment at 300°C for 3 h shows that heating at temperatures higher than 100°C is necessary to remove most of the organic solvent and OH groups as in Fig. II. By increasing the calcinations temperature up to 500°C for 3 h the prepared samples becomes higher degree of crystallinity that ascribed to rhombohedral $\text{Si}_5\text{P}_6\text{O}_{25}$ (JCPDS, no.70-2071), tetragonal SiP_2O_7 (JCPDS, no.22-1320) phases corresponding to the formation of phosphosilicate system and hexagonal $\text{Al}_{23}\text{Si}_5\text{P}_{20}\text{O}_{96}$ (JCPDS, no.52-1178) as in Fig. III and the average crystallite size is estimated at ~21 nm from the Scherrer formula. Where the introduction of Al_2O_3 into pure phosphosilicate system results in a distortion of the bonds and increases the content of non-bridge oxygen.

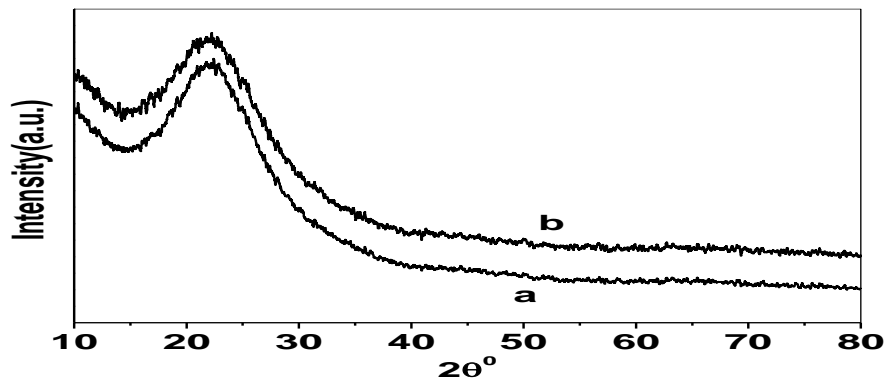


Fig. I. X-ray diffraction patterns of prepared phosphosilicate nanoparticles (a) and (b) doped with (10 mol%) Al_2O_3 calcined at 100°C for 3h.

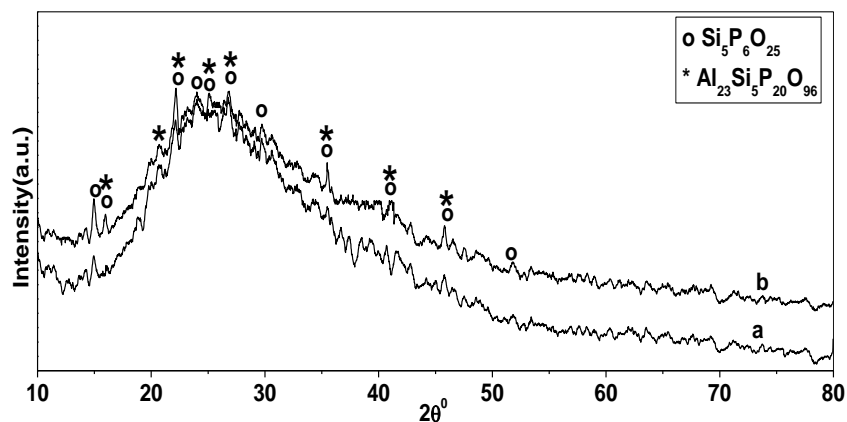


Fig. II. X-ray diffraction patterns of prepared phosphosilicate nanoparticles (a) and (b) doped with (10 mol%) Al_2O_3 calcined at 300°C for 3h.

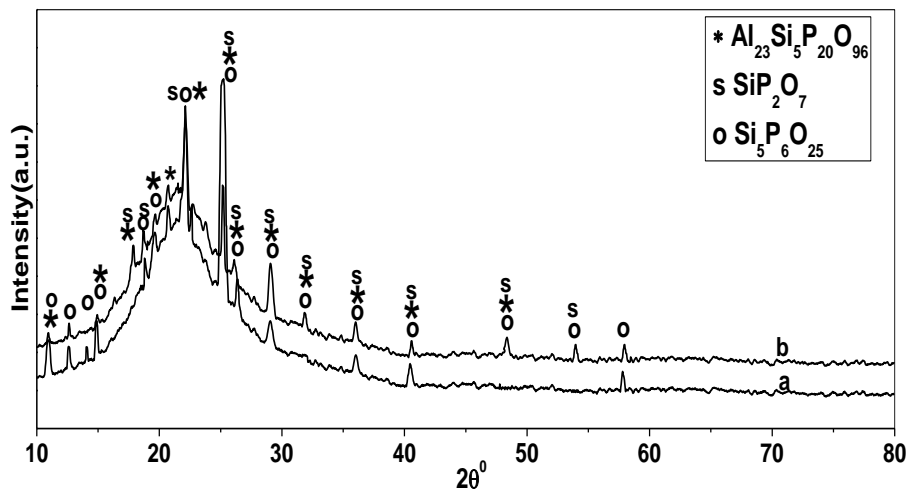


Fig. III. X-ray diffraction patterns of prepared phosphosilicate nanoparticles (a) and (b) doped with (10 mol%) Al_2O_3 calcined at 500°C for 3h.

3.2. SCANNING ELECTRON MICROSCOPY (SEM):

Fig. IV shows SEM image of phosphosilicate sample calcined at 300°C for 3h. From the figure, heterogeneous surfaces consisting of random-sized fine particles and voids among them are shown.

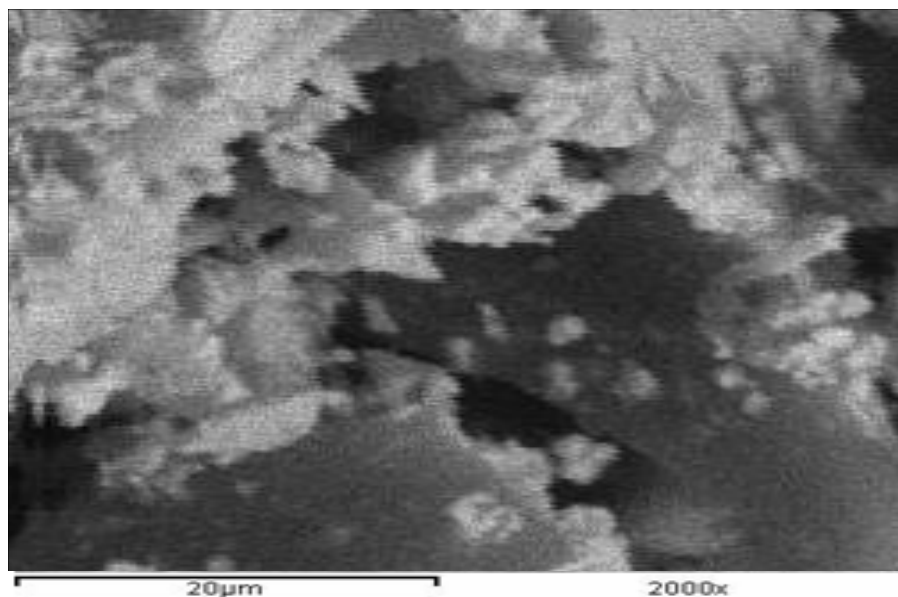


Fig. IV: SEM image of prepared phosphosilicate nanoparticles calcined at 300°C for 3h in air.

3.3. FOURIER TRANSFORMS INFRARED (FTIR) ANALYSIS: Fig.v shows the FTIR absorbance spectra of pure phosphosilicate and doped with (10 mol%) Al_2O_3 calcined at 200°C , in a wide spectral region ($400\text{-}4000\text{ cm}^{-1}$). The broad absorption at 3453 cm^{-1} assigned to the stretching modes of OH groups, indicates that non-bridging oxygens are linked to hydrogens from phosphanol (P–OH), silanol moieties (Si–OH) and (Al–OH) [(8)-(15)]. The two weak absorption bands in the range from 3000 cm^{-1} to 2911 cm^{-1} are related to the -OH and organic groups [(12)-(15)]. These bands were observed in the glass systems containing P_2O_5 and may be explained by the condensation of first P – OH and Si–OH in phosphosilicate and P – OH, Si–OH and Al– OH groups in aluminophosphosilicate (leading to P–O–P, Si–O–Si, P–O–Al,

and Si–O–Al links) and the inorganic part becomes sufficiently rigid to form a real trap for the remaining OH groups, preventing their evacuation [(14)-(16)]. Hydroxyl groups generally exist as phosphanols and silanols covering the surface of the phosphate- silica and phosphate- silica-aluminum skeletons of the prepared samples[(14)-(16)].The absorption band at around 1635 cm^{-1} is due to the deformation modes of δ (H–O–H), attributed to bending vibration of crystalline water as interstitial molecules, which could come from KBr in the pellets and the adsorbed water [(17), (18)]. The shoulder at 1221 cm^{-1} may be attributed to P–O and/or P= O stretching vibration, because these bands occur in the fingerprint region ($1320\text{--}1200\text{ cm}^{-1}$), they cannot be used without some other indication that P is present, because C–O and O–H groups can also absorb strongly in these ranges. The band located at 1091 cm^{-1} is attributed to the vibration of Si–O–Al and P–O–Al bands for the nano-structure aluminophosphosilicate[(19), (20)].The characteristic vibration bands assigned to the P–O–P or/and P–O–Si bonds were not identified because they overlap with the characteristic band of the silica or phosphate matrix. Silica may exist inside the phosphorus clusters or at the interfaces between P_2O_5 clusters and the SiO_2 matrix in the form of P clusters or P–O–Si bonds, beside the Si–O–Al and P–O–Al bands distributed in the phosphosilicate matrix[(18)-(20)].The vibration at 962 cm^{-1} and 802 cm^{-1} can be due to stretching vibrations of terminal P–O–, Si–O– and Si–O–P surrounded by P cation in pure phosphosilicate system or corresponding to Si–O–Al, P–O–Al and single or double bonds of P–O in the $[\text{PO}_4]^{3-}$ group in aluminophosphosilicate matrix absorbed on the phosphosilicate surface, respectively [(8), (21)]. The absorption band 466 cm^{-1} is associated with P–O–Si and Si–O–Si tetrahedral bending vibrations [(8), (22)]. The phosphate-based glasses reveal major resonances at wave numbers of 557 , 802 , 962 and 1100 cm^{-1} , which were associated with the P–O bonds in the phosphate network [(8), (22)].

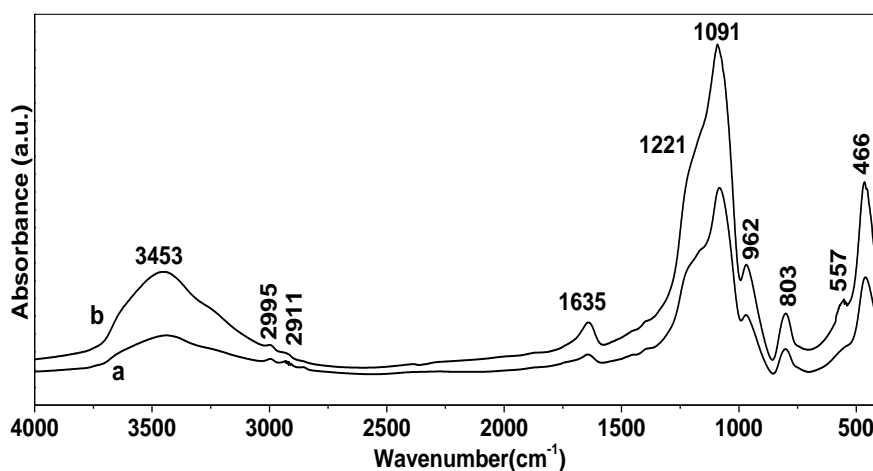


Fig. V: FTIR absorbance spectra of (a) pure phosphosilicate and (b) doped with (10 mol %) Al_2O_3 calcined at 200°C .

4. CONCLUSION: In conclusion, pure and doped phosphosilicate gels ($80\text{ P}_2\text{O}_5:20\text{ SiO}_2$) and ($70\text{ P}_2\text{O}_5:20\text{ SiO}_2:10\text{ Al}_2\text{O}_3$) has been successfully prepared by the sol-gel technique. Also this glasses has shown significant enhancement in the crystallinity with increasing the calcinations temperature, as verified by the formation of phosphosilicate and aluminophosphosilicate phases at their surfaces confirmed by XRD, SEM and FTIR analyses.

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