

Zirconium phosphate protonic conductor obtained by sonocatalytic sol-gel method

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The sol-gel process is an interesting alternative to produce gels, ceramics, glasses, thin films and fibres [1–4] which are difficult to prepare or could not be prepared by conventional methods. This technique is an excellent preparative route to synthesize materials such as zirconium phosphate through hydrolysis and polycondensation reactions of metal alkoxide. We have used the sol-gel method with application of ultrasound in the preparation of α -Zr(HPO₄)₂H₂O gels. This material was initially known as an inorganic ion exchanger and was of interest as a solid state electrolyte for use in fuel cell and alternative energy sources [5, 6]. The electrical transport property of α -Zr(HPO₄)₂H₂O is due to diffusion of protons along the hydrated surface of their microcrystalline structure, and depends essentially on the number of surface ionogenic groups [7], particle dimensions [8] and their hydration [9].

In this work, we discuss the preparation of zirconium phosphate gels obtained by a sonocatalytic route and their characterization by thermal analysis (TG, DTA, DSC), X-ray diffraction (XRD), infrared spectroscopy (IRS) and scanning electron microscopy (SEM). The ionic conductivity of the samples was studied between 50 and 350 °C by a.c. impedance spectroscopy.

Zirconium phosphate gels α -Zr(HPO₄)₂H₂O (denominated as α -ZrP) were prepared by hydrolysis and polycondensation reactions of zirconium propoxide Zr(OC₃H₇)₄ diluted in isopropanol C₃H₇OH, to which phosphoric acid H₃PO₄ and water were added. The volume ratios Zr(OC₃H₇)₄/C₃H₇OH, H₂O/C₃H₇OH and H₂O/H₃PO₄ were equal to 1, 2 and 4, respectively. The technique consists in submitting the solution mixture to the action of ultrasonic irradiation (Sonicator W385 Heat Systems-Ultrasonics, Inc., 20 kHz) [10–13]. After 25 min, the liquid became homogeneous and white. The resulting sols were kept in a closed vessel and left at room temperature until forming gels. The gels were then dried at 50 °C for 1 week.

Thermal analysis (DTA-TG) and (DSC) were performed with a Netzsch STA 409 and a General V4.1C DuPont 2000 instruments, respectively, in an oxygen atmosphere at a heating rate of 10 °C/min.

X-ray powder diffraction patterns were obtained with a Rigaku-Rotaflex Ru 200B diffractometer using monochromatic CuK_α radiation of wavelength 0.15418 nm.

IR spectra were obtained using the KBr disk method with a FTIR Bomem MB-102 operating between 400 and 4000 cm⁻¹ and the SEM analysis was performed with a Zeiss 960 microscope.

Gel pellets of 10 mm in diameter and 1.5–2 mm thick, with bulk densities of about 80% of the theoretical value, were prepared by uniaxial pressing a suitable amount of α -Zr(HPO₄)₂H₂O gels at 60 kN/cm² in order to perform a.c. impedance analysis. The two flat surfaces of the pellet were coated with silver paint and the a.c. measurements of samples were carried out with a Solartron 1260 impedance analyser in the frequency range 10 Hz–10 MHz, at a signal level lower than 1 V using a home-made furnace temperature controller.

The DTA curve shows two superimposed endothermic peaks at 130 °C and 153 °C due to the loss of the hydration water; the third peak at 246 °C can be associated to the formation of a layered pyrophosphate structure of zirconium, and the complete conversion to ZrP₂O₇ was observed between 500 and 750 °C (Fig. 1).

The TG curve (Fig. 1) shows a small difference between the losses of hydration and POH condensation water occurring at about 250 °C. This water loss is the result of condensation of monohydrogen phosphate groups to form the layered pyrophosphate.

The DSC curve (Fig. 2) confirms the DTA thermal analysis and shows two endothermic peaks at 138 °C and 150 °C associated with the hydration water loss

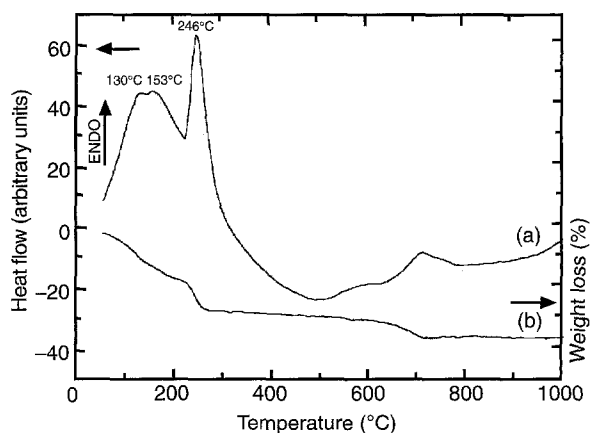


Figure 1 (a) DTA and (b) TG curves for α -Zr(HPO₄)₂H₂O gels at a heating rate of 10 °C/min.

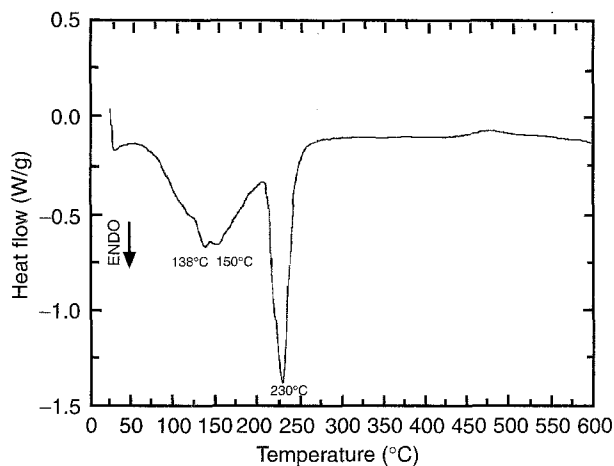


Figure 2 DSC curve of α -Zr(HPO₄)₂H₂O dried gels. The heating rate is 10 °C/min.

and a third at 230 °C with the phase transition to pyrophosphate structure.

At room temperature, the X-ray patterns of α -ZrP gels showed good crystallinity, as can be seen in Fig. 3a. The diffraction patterns present peaks with d values of 0.768, 0.450, 0.358 and 0.264 nm corresponding to the α -structure of monohydrated zirconium phosphate. After heat treatment at 200 °C (Fig. 3b), the crystalline structure of α -Zr-(HPO₄)₂H₂O changes to the layered pyrophosphate structure which is maintained until 700 °C (Fig. 3c, 3d). The X-ray diffractograms of pyrophosphate show peaks which appear at $d=0.499, 0.429, 0.382, 0.347, 0.299, 0.254, 0.187$ and 0.161 nm.

The IR spectra (Fig. 4) show the evolution of Zr(HPO₄)₂H₂O heat treated at different temperatures. According to Clearfield [14] the sharp bands in the region 3150–3590 cm⁻¹ are attributed to symmetric and asymmetric water stretching while the one at 1620 cm⁻¹ is the bending vibration. The bands attributed to water are largely removed upon dehydration at 100 °C. The bands in the region 965–1120 cm⁻¹ represent phosphate vibration and at 1250 cm⁻¹ the deformation of the P–O–H group. The

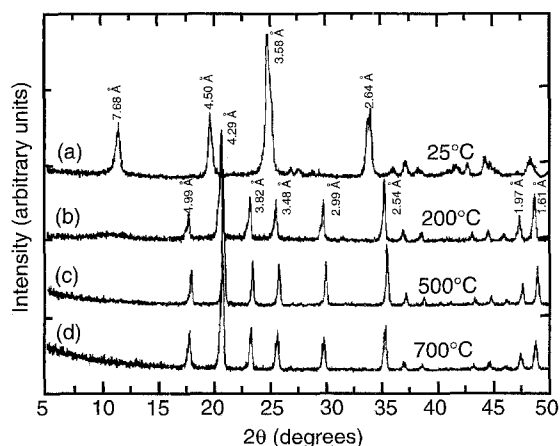


Figure 3 X-ray diffraction patterns of α -ZrP as a function of temperature: (a) 25 °C, (b) 200 °C; (c) 500 °C; (d) 700 °C.

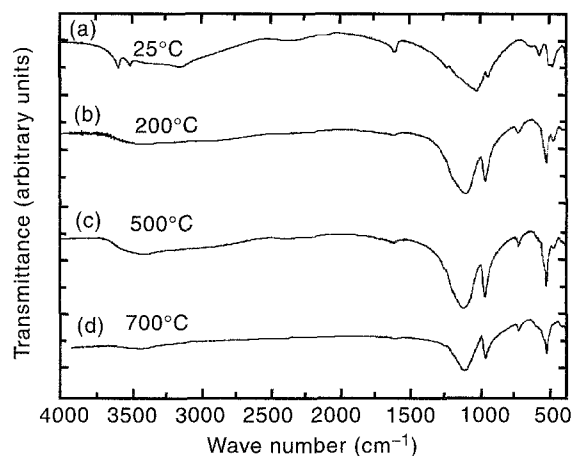


Figure 4 FTIR spectra of α -ZrP heat treated at different temperatures: (a) 25 °C, (b) 200 °C; (c) 500 °C; (d) 700 °C.

crystalline Zr(HPO₄)₂H₂O treated at 200 °C shows four bands at 548 cm⁻¹ attributed to Zr–O group, 747 cm⁻¹ to Zr–O–P group, 977 cm⁻¹ to P–O group and 1131 cm⁻¹ to P–O group, respectively.

The electron microscopy micrographs (Fig. 5a, 5b) show the resultant morphology of α -ZrP xerogels heat treated at 150 °C for 2 h. The structure of the gel is formed by uniform aggregates of particles with average size of about 150 nm. When the samples are heat treated at 400 °C for 2 h, no change was observed (Fig. 5c, 5d).

The a.c. conductivity measurements were performed as a function of temperature in the range 50–350 °C (Fig. 6) in air. The conductivity of the α -Zr(HPO₄)₂H₂O increases from a value of $2.75 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 50 °C to $4.25 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 180 °C. For temperatures higher than 180 °C, conductivity decreases as a result of the dehydration of the sample and formation of pyrophosphate ZrP₂O₇ in accordance with the X-ray analysis, which shows a conversion to zirconium pyrophosphate at temperature 200 °C. We believe that the dehydration process is responsible for the loss in conductivity.

α -zirconium phosphate with surface proton conductor can be easily obtained using a solution of organo-metallic precursors and phosphoric acid with the application of ultrasonic treatment; the material can be converted upon heat treatment to a pyrophosphate form. The investigation of the a.c. conductivity of the samples performed over the range 50–350 °C indicates that the protonic conductivity of samples increases with temperature up to a value $4.25 \times 10^{-4} \text{S cm}^{-1}$ and then decreases. α -Zr(HPO₄)₂H₂O has the highest protonic conductivity at 180 °C.

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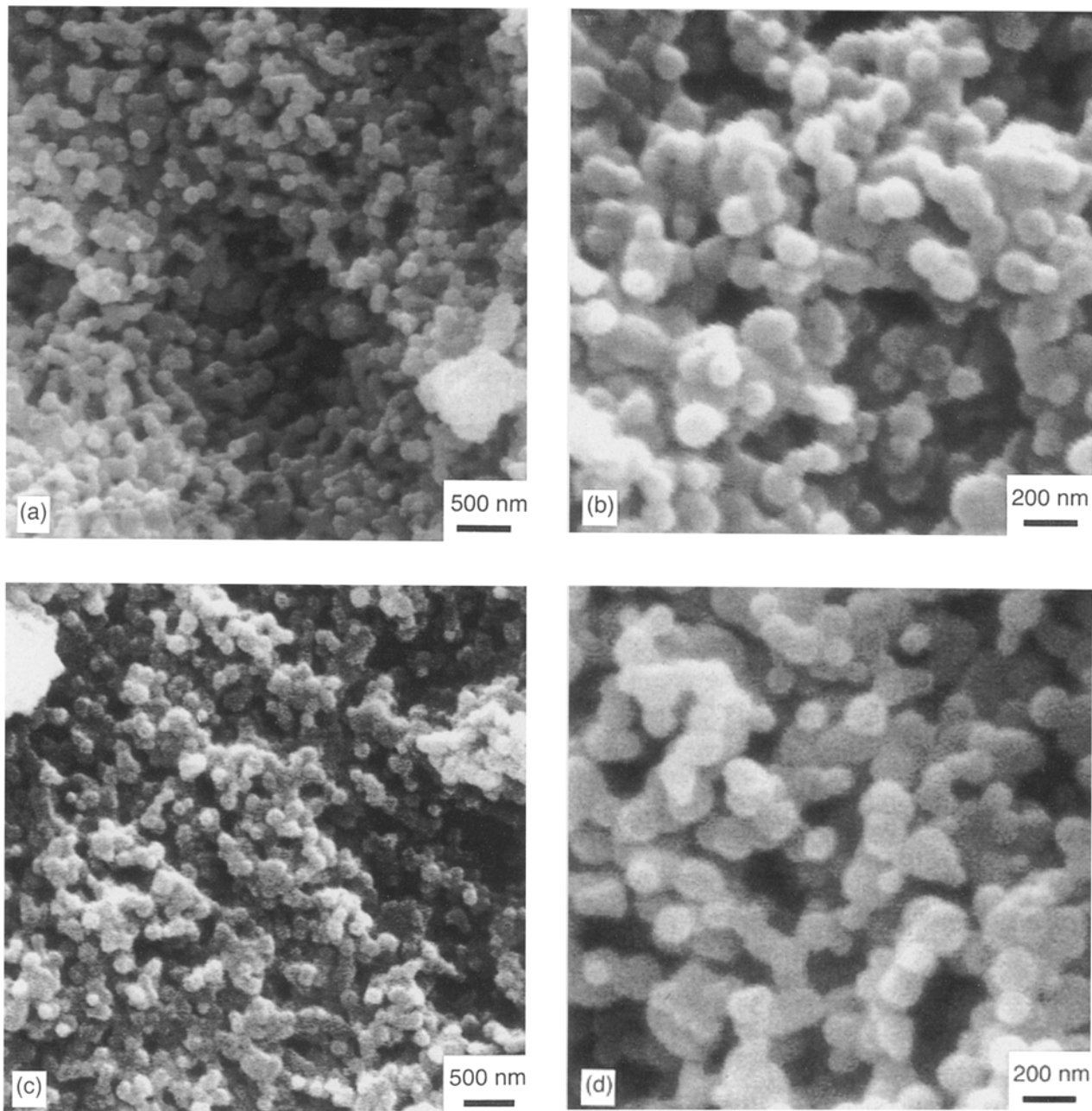


Figure 5 SEM observation of morphology of xerogels zirconia phosphate heat treated at 150 °C during 2 h (a-b) and 400 °C during 2 h (c-d).

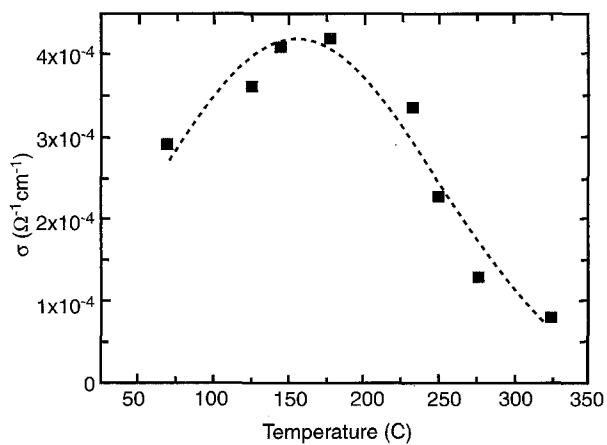


Figure 6 α values versus temperature for α -ZrP.

References

1. L. L. HENCH and G. ORCEL, in "Better ceramics through chemistry II," edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (MRS Vol. 73, Pittsburgh, 1986) p.35.
2. M. TOKI, S. MIYASHITA, T. TAKENCHI, S. KANBE and A. KOCHI, *J. Non-Cryst. Solids* **100** (1988) 479.
3. S. SAKKA and K. KAMIYA, *ibid.* **42** (1980) 403.
4. H. DISLICH, in "Sol-gel technology for thin films, fibers, preforms, electronics and specialty shapes," edited by L. C. Klein (Noyes, Park Ridge, NJ, 1988), p. 50.
5. R. P. HAMLIN and E. J. SZYMALAK, *Electrochem. Technol.* **4** (1966) 172.
6. C. BERGER and M. P. STRIER, *J. Electrochem. Soc.* **115** (1968) 230.
7. G. ALBERTI, M. CASCIOLA, U. COSTANTINO and M. LEONARDI, *Solid State Ionics* **14** (1984) 289.
8. E. KROGH ANDERSEN, I. G. KROGH ANDERSEN, C. KNAKKERGDARD MOLLER, K. E. SIMONSEN and E. SKOU, *ibid.* **7** (1982), 301.

9. S. YDE ANDERSEN, J. S. LUNDSGAARD, J. MALLING and J. JENSEN, *ibid.* **13** (1984) 81.
10. M. ATIK and M. A. AEGERTER, *J. Non Cryst. Solids* **147 & 148** (1992) 813.
11. P. DE LIMA NETO, M. ATIK, L. AVACA and M. A. AEGERTER, *J. of Sol-Gel Sci. Technol.* **1** (1994) 177.
12. M. ATIK, C. R'KHA and J. ZARZYCKI, *J. Mater. Sci. Lett.* **13** (1994) 266.
13. M. ATIK and J. ZARZYCKI, *ibid.* **13** (1994) 1301.
14. A. CLEARFIELD, "Inorganic ion exchange materials" (CRC Press, Florida, 1982).

