

## A study of the effect of sol-gel synthesis on ionic conductivity of $\text{MgZr}_4\text{P}_6\text{O}_{24}$

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### Abstract:

Magnesium zirconium phosphate,  $\text{MgZr}_4\text{P}_6\text{O}_{24}$  (MZP) is a magnesium ion conducting material with potential for application as solid electrolyte in high temperature electrochemical sensor. In this work, MZP was synthesised using a simple and economical sol-gel route to produce MZP at a reduced temperature. An insight into the calcination process, and possible phase transformation at higher temperature was obtained using simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC). Phase identification of the synthesised material was studied after calcining the powder at 900°C for 3h using X-ray diffraction (XRD); a single monoclinic phase was observed at that temperature. However, a trace amount of possible minor second phase; zirconium oxide phosphate [ $\text{Zr}_2(\text{PO}_4)_2\text{O}$ ] was formed after heating at temperatures  $T \geq 1000^\circ\text{C}$ . Complex ac-impedance spectroscopy measurement on platinised MZP pellets were carried out in the frequency range 32 MHz – 0.1Hz and temperature range 800 – 30°C to study the electrical properties of MZP solid electrolyte. An ionic conductivity data  $7.23\text{E-}3\Omega^{-1}\text{cm}^{-1}$  was achieved at relatively lower, 725°C. Furthermore, the impedance Cole-Cole plots measured at 764°C and 390°C shows single semi-circles suggesting contribution from only grain interiors (GIs). The ion hopping rate was calculated by fitting the conductance spectra to power law variation,  $\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n$ . The AC-DC conductivities show Arrhenius-type behaviour with activation energies in the range  $0.84 \leq E_a(\text{eV}) \leq 0.87$ . SEM on fractured MZP pellet sintered at 1300°C for 24h revealed a dense microstructure with visible grain boundaries and less porosity is observed in agreement with the relative density of ~99% determined using the Archimedes' principle for the experimental density and the theoretical density calculated from the crystal structure. EDS confirms the presence of Mg, Zr, P, O in appropriate atomic ratio of  $\text{MgZr}_4\text{P}_6\text{O}_{24}$ . Finally, TEM/EDS on MZP particles with crystal size of ~50nm also confirmed MZP as stable at 900°C with no observable second phase,  $\text{Zr}_2(\text{PO}_4)_2\text{O}$ .

**Keywords:** Sol-gel method. Solid electrolyte. Electrochemical sensor. Impedance spectroscopy. Electrical properties. Ac-conductivity. Hopping mechanism

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