Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 106, No. 3, June 1994, p. 757.

Controlled combustion synthesis of Nasicon: A low thermal expansion material

N ARUL DHAS* and K C PATIL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Nasicon (Sodium (Na) Super Ion Conductor), $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ ($x = 0$, 0·5, 1·0, 1·5, 2·0 and 2·5) materials have been prepared by a controlled combustion process involving an aqueous solution containing stoichiometric amounts of sodium nitrate, zirconyl nitrate, diammonium hydrogen phosphate, fumed silica, ammonium perchlorate and carbohydrazide. On rapidly heating the aqueous solution at 400°C, the solution boils and ignites to burn with a flame (temperature $\approx$ 1000°C) and yields the oxide product. Mixtures of metal nitrates and carbohydrazide with ammonium perchlorate are known to be highly explosive. However, the combustion of redox mixtures containing diammonium hydrogen phosphate is controlled. Formation of Nasicon has been confirmed by powder XRD and IR spectroscopy. Lattice parameters ($a = 8{\cdot}8045$ Å and $b = 22{\cdot}8128$ Å for $NaZr_2P_3O_{12}$) refined with a least-squares fit using XRD reflections are in good agreement with the literature (Hong 1976; Clearfield *et al* 1986). The solid combustion products are fine (5–12 μm) and the surface area varies from 8 m^2/g ($NaZr_2P_3O_{12}$) to 30 m^2/g ($Na_{3{\cdot}5}Zr_2P_{0{\cdot}5}Si_{2{\cdot}5}O_{12}$). The powders, pelletized and sintered at 1100–1300°C, 5 h achieved 90–95% of theoretical density. The heat treated (> 1100°C) $Na_3Zr_2PSi_2O_{12}$ material developed a blue colour. This could be due to oxygen deficiency compensated by electrons in the oxygen sites indicating nonstoichiometric nature of $Na_3Zr_2PSi_2O_{12}$ compound (Clearfield *et al* 1986). The 1200°C sintered $NaZr_2P_3O_{12}$ body has a thermal expansion coefficient of $-3{\cdot}4 \times 10^{-6}\,°C^{-1}$ measured between 25 and 500°C. The properties of Nasicon material prepared by the combustion technique are comparable with those prepared by the sol–gel technique.

References

Clearfield A, Subramanian M A, Rudolf P R and Moini A 1986 *Solid State Ionics* **18 & 19** 13

Hong H Y-P 1976 *Mater. Res. Bull.* **11** 173

*For correspondence