Hydrothermal synthesis and characterization of $(NH_4)Ce(PO_4)_2{\cdot}H_2O$

Yaohua Xu, Shouhua Feng, Wenqin Pang and Guangsheng Pang

Key Laboratory of Inorganic Hydrothermal Synthesis, Department of Chemistry, Jilin University, Changchun 130023, P.R. China

A new monohydrated ammonium cerium phosphate $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ is hydrothermally synthesized from the system NH_3–CeO_2–P_2O_5–H_2O and characterized by powder X-ray diffraction, differential thermal analysis–thermogravimetric analysis, elemental chemical analysis, IR, Raman and impedance spectroscopy.

Most solids that show proton conduction at room temperature are hydrates[1–3] in which the proton conductivity is limited to a restricted temperature range over which the water molecules are retained in the structure; such water molecules are usually lost in the range room temperature to 150 °C. Mixed proton and electronic conduction at high temperatures (200–1000 °C) is also found in some perovskite oxides such as $SrCeO_3$ in the presence of water vapour.[4–8] With the aim to search for proton conductors, we are investigating cerium phosphates in the M_2O–CeO_2–P_2O_5–H_2O (M = NH_4, Na, K) systems and have found a new family of compounds, $M_2Ce(PO_4)_2{\cdot}H_2O$ (M = NH_4, Na, K), among which $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ showed proton conduction in the temperature range 40–200 °C.

Hydrothermal crystallization of $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ was carried out in a stainless-steel autoclave with a Teflon liner under autogenous pressure. $NH_3{\cdot}H_2O$ (26% solution), 85% H_3PO_4 and freshly prepared $Ce(OH)_4{\cdot}xH_2O$ were mixed in the molar composition ratio $14NH_3:3.5P_2O_5:CeO_2:100H_2O$. The autoclave was sealed and heated in an oven at 140 °C for 5–7 days and the crystalline products which formed were filtered, washed with distilled water, and dried at ambient temperature.

The crystalline products were identified by X-ray powder diffraction (XRD) on a Rigaku D/MAX-IIIA diffractometer using Cu-Kα (λ = 1.5418 Å) radiation. The XRD data of $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$, indexed as an orthorhombic system, are listed in Table 1, and the lattice parameters were optimized by least-squares refinements, resulting in refined values of a = 12.72(1), b = 14.00(4), c = 16.10(1) Å, U = 2868 Å^3. The composition of the yellow powder product was analysed by chemical analyses for P and Ce and elemental analyses for N and H. The results showed that the products contain 38.2, 15.4, 6.2 and 2.3 mass% for Ce, P, N, and H, respectively, corresponding to a composition $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$; water content was determined by differential thermal analysis–thermogravimetric analysis (DTA–TGA). The IR spectrum, recorded on a Nicolet 5DX Model FT spectrometer, showed several medium–strong absorption bands in the region 400–700 cm^{-1} and strong absorption bands in the region 900–1200 cm^{-1}, attributed to PO_4 bending and stretching vibrations. In addition an absorption band at 1405 cm^{-1} was ascribed to an NH_4^+ bending vibration, and a band at 1630 cm^{-1}, to a H_2O bending mode; a strong absorption band at 2400–3500 cm^{-1}, is a combination of NH_4^+ and H_2O stretching vibrations.[9] This indicated that the products contained water, as confirmed by DTA–TGA. The Raman spectrum, recorded with a T64000 double spectrometer (France) with an argon-ion laser (488.0 nm line, 200 MW), showed several weak absorption bands in the region 100–300 cm^{-1} attributed to crystal-lattice vibrations. Absorption bands at 400–700 and 900–1200 cm^{-1} can be attributed to PO_4 bending and stretching vibrations, respectively,[9] indicating only the presence of phosphate anion (PO_4^{3-}) in the compound. DTA–TGA showed that $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ decomposed into P_2O_5, $CePO_4$ and O_2 at 800 °C. The reactions during thermal decomposition may be summarized by eqns. (1)–(5).

$$(NH_4)_2Ce(PO_4)_2{\cdot}H_2O \rightarrow (NH_4)_2Ce(PO_4)_2 + H_2O \ (120\,°C) \tag{1}$$

$$(NH_4)_2Ce(PO_4)_2 \rightarrow NH_4Ce(HPO_4)(PO_4) + NH_3 \ (210\text{–}300\,°C) \tag{2}$$

$$NH_4Ce(HPO_4)(PO_4) \rightarrow Ce(HPO_4)_2 + NH_3 \ (300\text{–}360\,°C) \tag{3}$$

$$Ce(HPO_4)_2 \rightarrow Ce_2P_4O_{13} + H_2O + O_2 \ (434\,°C) \tag{4}$$

$$Ce_2P_4O_{13} \rightarrow CePO_4 + P_2O_5 \ (700\text{–}800\,°C) \tag{5}$$

Impedance spectra, measured by the ac impedance technique using a ZL5 frequency analyser in the frequency range of 0.012–100 kHz, were characteristic of proton conductors with an interfacial impedance at lower frequencies, followed at higher frequency by a depressed semicircle, characteristic of the bulk electrical response. Intersection of the circle with the real axis indicated the bulk resistance. The proton conductivities of the compound were 2.35×10^{-6} S cm^{-1} at 40 °C and 4.23×10^{-4} S cm^{-1} at 200 °C, respectively. Comparison with other proton conductors such as $(H_3O)Ze_2(PO_4)_3$ ($\sigma_{200\,°C} < 10^{-5}$ cm^{-1}),[5] $Ce(HPO_4)_2{\cdot}nH_2O$ which showed ionic conduction in humid air ($\sigma_{200\,°C} < 5 \times 10^{-5}$ S cm^{-1})[10] and H_3O^+-β″/β-Al_2O_3 ($\sigma_{200\,°C} < 5 \times 10^{-5}$ S cm^{-1}),[11] showed that $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ had a higher proton conductivity despite the absence of retained water in the structure at medium tem-

Table 1 Powder X-ray diffraction data of $(NH_4)Ce(PO_4)_2{\cdot}H_2O$

h	k	l	d_{obs}/Å	d_{calc}/Å	I/I_0
2	0	0	6.368	6.360	100
0	3	1	4.460	4.482	13
1	3	0	4.427	4.381	12
3	0	0	4.249	4.240	16
0	4	1	3.426	3.420	61
0	1	5	3.136	3.138	55
2	4	1	3.022	3.012	44
3	3	3	2.708	2.709	16
5	0	1	2.513	2.513	22
3	5	1	2.312	2.312	8
0	1	7	2.270	2.270	9
1	1	7	2.236	2.234	4
2	4	5	2.222	2.221	5
1	6	2	2.207	2.207	5
0	4	6	2.128	2.130	20
1	6	3	2.110	2.110	16
6	3	1	1.948	1.952	9
5	2	5	1.920	1.920	15
3	5	5	1.891	1.891	11
6	4	0	1.814	1.813	5
7	2	1	1.748	1.748	20
5	3	6	1.717	1.717	9
2	8	1	1.677	1.678	8
5	2	7	1.659	1.658	11
1	0	10	1.596	1.597	4

perature ranges; this implies that NH_4^+ ions carry the charge in the transportation process.

In summary, a new proton conducting compound, $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$ was synthesized from the hydrothermal system NH_3–CeO_2–P_2O_5–H_2O. This polycrystalline compound which undergoes phase transformations above 210 °C, shows proton conductivities of *ca.* 10^{-6} to *ca.* 10^{-4} S cm^{-1} in the temperature range 40–200 °C.

This work was supported by the NSFC through a National Outstanding Youth Science Foundation (S. F.) and Pang-Deng Plan in China.

References

1 J. B. Goodenough, *Solid State Microbatteries*, ed. J. R. Akridge and M. Balkanski, Plenum, New York, 1990, p. 195.
2 A. Potier and D. Rousselet, *J. Chim. Phys.*, 1973, **70**, 873.
3 M. G. Shilton and A. T. Howe, *Mater. Res. Bull.*, 1977, **12**, 701.
4 H. Uchida, N. Maeda and H. Iwahara, *J. Appl. Electrochem.*, 1982, **12**, 645.
5 A. Clearfield, B. D. Roberts and M. A. Subramanian, *Mater. Res. Bull.*, 1984, **19**, 219.
6 S. Feng and M. Greenblatt, *Chem. Mater.*, 1993, **5**, 1277.
7 S. Feng and M. Greenblatt, *Chem. Mater.*, 1992, **4**, 1257.
8 G. Alberti, M. Bracardi and M. Cascida, *Solid State Ionics*, 1982, **7**, 243.
9 Y. Xu, S. Feng and W. Pang, *J. Solid State Chem.*, 1995, **119**, 197.
10 P. Barboux, R. Morineau and J. Livage, *Solid State Ionics*, 1988, **27**, 221.
11 Chju Kun Kuo, Aichun Tan, Partho Sarkar and S. Nicholson, *Solid State Ionics*, 1990, **38**, 251.

Received, 31st January 1996; Com. 6/00751A