

Hydrothermal synthesis and characterization of $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

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

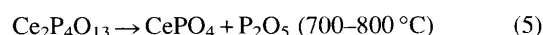
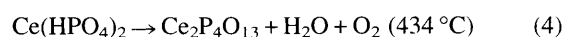
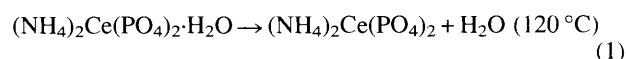
A new monohydrated ammonium cerium phosphate $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is hydrothermally synthesized from the system $\text{NH}_3\text{-CeO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and characterized by powder X-ray diffraction, differential thermal analysis-thermogravimetric analysis, elemental chemical analysis, IR, Raman and impedance spectroscopy.

Most solids that show proton conduction at room temperature are hydrates¹⁻³ 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 $\text{M}_2\text{O-CeO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ ($\text{M} = \text{NH}_4, \text{Na}, \text{K}$) systems and have found a new family of compounds, $\text{M}_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{NH}_4, \text{Na}, \text{K}$), among which $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ showed proton conduction in the temperature range 40–200 °C.

Hydrothermal crystallization of $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was carried out in a stainless-steel autoclave with a Teflon liner under autogenous pressure. $\text{NH}_3\text{-H}_2\text{O}$ (26% solution), 85% H_3PO_4 and freshly prepared $\text{Ce}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ were mixed in the molar composition ratio $14\text{NH}_3:3.5\text{P}_2\text{O}_5:\text{CeO}_2:100\text{H}_2\text{O}$. 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-III A diffractometer using $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The XRD data of $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 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 $a = 12.72(1)$, $b = 14.00(4)$, $c = 16.10(1) \text{ \AA}$, $U = 2868 \text{ \AA}^3$. 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 $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$; 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 $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ 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).



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 $2.35 \times 10^{-6} \text{ S cm}^{-1}$ at 40 °C and $4.23 \times 10^{-4} \text{ S cm}^{-1}$ at 200 °C, respectively. Comparison with other proton conductors such as $(\text{H}_3\text{O})\text{Zr}_2(\text{PO}_4)_3$ ($\sigma_{200 \text{ }^\circ\text{C}} < 10^{-5} \text{ cm}^{-1}$),⁵ $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ which showed ionic conduction in humid air ($\sigma_{200 \text{ }^\circ\text{C}} < 5 \times 10^{-5} \text{ S cm}^{-1}$)¹⁰ and $\text{H}_3\text{O}^+ \cdot \beta\text{-Al}_2\text{O}_3$ ($\sigma_{200 \text{ }^\circ\text{C}} < 5 \times 10^{-5} \text{ S cm}^{-1}$),¹¹ showed that $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ 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 $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	<i>I</i> / <i>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, $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was synthesized from the hydrothermal system $\text{NH}_3\text{-CeO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. 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 $40\text{-}200^\circ\text{C}$.

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