



Article

Novel Hydrothermal Synthesis of Pure and Doped Ammonium and Potassium Titanyl Phosphates using a Green Heterogeneous Reaction

Holdsworth, Alistair F., Gamza, Monika, Mao, Runjie, Eccles, Harry and Bond, Gary

Available at <https://clock.uclan.ac.uk/29334/>

Holdsworth, Alistair F., Gamza, Monika orcid iconORCID: 0000-0003-3360-4006, Mao, Runjie, Eccles, Harry orcid iconORCID: 0000-0002-1652-3370 and Bond, Gary orcid iconORCID: 0000-0001-5347-2341 (2019) Novel Hydrothermal Synthesis of Pure and Doped Ammonium and Potassium Titanyl Phosphates using a Green Heterogeneous Reaction. ChemRxiv . (Submitted)

It is advisable to refer to the publisher's version if you intend to cite from the work.

For more information about UCLan's research in this area go to <http://www.uclan.ac.uk/researchgroups/> and search for <name of research Group>.

For information about Research generally at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLoK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the [policies](#) page.

Novel Hydrothermal Synthesis of Pure and Doped Ammonium and Potassium Titanyl Phosphates using a Green Heterogeneous Reaction

Alistair F. Holdsworth,^a Monika B. Gamza,^b Runjie Mao,^b Harry Eccles^{b*} and Gary Bond^b

a) School of Chemistry, University of Manchester, Manchester, UK; b) School of Physical Sciences and Computing, University of Central Lancashire, Preston, UK; *Corresponding author: HEccles@uclan.ac.uk

Vital inorganic materials are often inefficiently prepared in terms of time, reagents, and manpower. Hydrothermal methods in particular often take many days or even weeks to prepare the desired materials. In this communication, we demonstrate a novel heterogeneous, green synthesis route and the crystal lattice parameters of several pure and intermediate ammonium and potassium titanyl phosphates, representing a significant improvement over existing syntheses in reaction time, and precursors used.

Compounds of the form $A^+M^{4+}OPO_4$, such as ammonium and potassium titanyl phosphates (NTP and KTP) are well known for their nonlinear optical properties,¹⁻⁵ although other uses such as energy storage⁶ and ion exchange⁷ have been explored. These materials form in the orthorhombic crystal system with the $m2m$ point group and $Pna2_1$ space group, containing the A^+ ions in 1-dimensional channels.^{5,7,8} Syntheses are commonly achieved by high temperature fusion^{1,5} or flux-growth^{3-5,9} methods. Hydrothermal or solvothermal methods can be used^{2,5-7} requiring hazardous reagents and long reaction times.^{2,7}

Improving on existing syntheses, we demonstrate the novel preparation of four derivatives of the $K_{1-x}(NH_4)_xTiOPO_4$ system ($x = 0, 0.33, 0.66, 1$) by the reaction of nanoscale titanium dioxide with an excess of AH_2PO_4 in a mild, heterogeneous hydrothermal process (200 °C for 3 days).

The refined lattice parameters, cell volumes, particle sizes and observed TGA mass losses are shown in **Table 1**. The crystallites are produced in a narrow size distribution, as an agglomeration of platelets as can be seen in the SEM image in **Figure 1**.

Table 1: Lattice parameters a, b, c (Å), cell volume (Å³), particle size (µm) and observed TGA mass losses of NTP, KTP and intermediates.

X	Lattice Parameters and Cell Volume				Size	TGA
	a	b	c	Vol		
0.00	12.8438(8)	6.1434(4)	10.5802(7)	834.8	34.8	1.0%
0.33	12.8696(7)	6.4473(3)	10.5851(5)	878.3	25.0	2.8%
0.66	12.8382(9)	6.4278(5)	10.5834(7)	873.4	22.3	5.6%
1.00	12.9179(6)	6.5026(3)	10.5757(5)	888.4	27.1	9.5%

The lattice parameters for KTP ($x = 0$) match those found in the literature.^{5,8} We also observe the general increases in a and b parameters, and decrease in the c parameter upon exchange of K^+ for NH_4^+ .⁵ Upon partial replacement of K^+ for NH_4^+ ($x = 0.33$ and 0.66), little change in the a or c parameters is observed while b parameters increase markedly for both compounds, mirroring a prior synthesis of the similar $K_{0.5}(NH_4)_{0.5}TiOPO_4$.⁹ This effect is seemingly independent of the value of x . The increase in unit cell volume upon exchange of K^+ for NH_4^+ is primarily a result of the larger b parameter increasing the size of the channels within the crystal structure of the material through increase of O-Ti-O bond angles.^{4,5,9} The observed

TGA mass losses at 600 °C correspond to the expected mass losses of NH_3 for level of NH_4^+ present in each compound, decomposing on heating according to **Equation 1**.

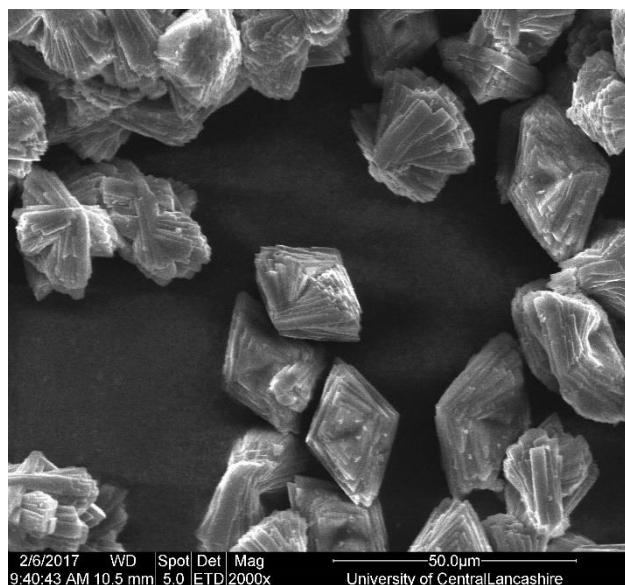
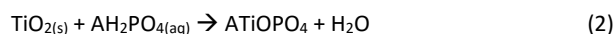


Figure 1: Exemplar SEM image of KTP microcrystals.

These observations demonstrate our manufacturing technique is consistent with the older, less efficient processes. We have demonstrated the production of phase-pure NTP, KTP and doped intermediates using mild hydrothermal conditions in quantitative yield with half the reaction time of typical hydrothermal syntheses.⁷ The use of corrosive or harmful reagents ($TiCl_4$ and H_3PO_4)⁷ is also avoided. These represent some initial studies, and it is likely the synthetic process can be further optimised for greater efficiency and scale, or transferred to a higher volume hydrothermal flow method for preparation in nanoscale form.¹⁰

Given the heterogeneous reaction mechanism (**Equation 2**), different sizes or phases of TiO_2 precursor could be used to tune the size and morphology of the product.



Similarly, the use of surfactants or other capping agents in the synthetic process could allow for the production of finer platelets with higher surface area.¹¹ Other materials of technological significance could be synthesised using greener reagents and under the milder conditions as we have demonstrated here with appropriate adaption of existing synthetic methodologies.

Experimental, Notes, References, and Acknowledgements

Ammonium and potassium dihydrogen phosphates and titanium dioxide ($D_{10} = 0.133 \mu\text{m}$, $D_{50} = 0.199 \mu\text{m}$, $D_{90} = 489 \mu\text{m}$) were acquired from Sigma or Fisher and used as procured. Syntheses were conducted in a hydrothermal autoclave (Parr 4748) for 3 days at 200 °C. Deionised water ($> 18 \text{ M}\Omega/\text{cm}$) was used for all reactions. 80 ml of 1 M AH_2PO_4 and 1.3 g of TiO_2 were used for all reactions. The TiO_2 was added to the phosphate solution and vigorously stirred before transferring to the autoclave and reacted under autogenous pressure. Products were washed several times with deionised water before analysis. X-Ray Powder Diffraction (PXRD) patterns were collected using a Bruker D2 Phaser diffractometer equipped with a $\text{Cu } \alpha$ radiation source. Lattice parameters of $\text{K}_{1-x}(\text{NH}_4)_x\text{TiOPO}_4$ ($x = 0, 0.33, 0.66, 1$) were derived from refinements of PXRD patterns using the Jana2006 software package.¹² XRD Patterns are shown in **SI Figure 1** Scanning electron microscopy was conducted using a, FEI Quanta 200 SEM equipped with an EDAX Sapphire microanalyser. Particle Size Distribution (PSD) was determined using dynamic light scattering (DLS) with a Malvern Mastersizer 2000. Samples were first sonicated in deionised water to disperse any agglomerates before analysis. Thermogravimetric analysis was conducted using a Mettler Toledo TGA 1 STAR, heating from ambient to 700 °C at 20 °C/min under a 30 ml/min flow of nitrogen. TGA responses are shown in **SI Figure 2**.

1. R. H. Jarman, *Solid State Ionics*, 32/33, 1989, 45-49.
2. Y. Zhao, G. Zhu, X. Jiao, W. Liu and W. Pang, *J. Mater. Chem.*, 2000, **10**, 463-467.

3. X. Wang, X. Yuan, W. Li, J. Qi, S. Wang and D. Shen, *J. Cryst. Growth*, 2002, 237-239, 672-676.
4. P. Rejmanjova, J. Baruchel, P. Villeval and C. Saunal, *J. Cryst. Growth*, 1997, 180, 85-93.
5. M. M. Eddy, T. E. Gier, N. L. Keder, G. D. Stucky, D. E. Cox, J. D. Bierlein and G. Jones, *Inorg. Chem.*, 1988, 27, 11, 1856-1858.
6. L. Mu, L. Ben, Y.-S. Hu, H. Li, L. Chen and X. Huang, *J. Mater. Chem. A*, 2016, **4**, 7141-7147.
7. I. Bortun, L. N. Bortun and A. Clearfield, *Solv. Extr. Ion Exch.*, 1998, 16, 2, 669-681.
8. J. D. Bierlein and H. Vanherzeele, *J. Opt. Soc. Am. B.*, 1989, **6**, 4, 622-633
9. M. L. Phillips, T. E. Gier, M. M. Eddy, N. L. Keder, G. D. Stucky and J. D. Bierlein, *Sol. State Ionics*, 1989, 32/33, 147-153.
10. R. I. Gruar, C. J. Tighe and J. A. Darr, *Ind. Eng. Chem. Res.*, 2013, 52, 15, 5270-5281.
11. L. Kumari, W. Z. Li, S. Kuklarni, K. H. Wu, W. Chen, C. Wang, C. H. Vannoy and R. M. Leblanc, *Nanoscale Res. Lett.*, 2010, 5, 1, 149-157.
12. V. Petricek, M. Dusek and L. Palatinus, *Z. Kristallogr.*, 2004, 229, 5, 345-352.

We wish to thank Dr A. Isreb, Mrs T. Garcia-Sorribes, Mr J. C. Donnelly and Mr P. Bentley for technical assistance and Prof K. K. Singh and her group for provision of analytical equipment. This work was funded as part of the EPSRC project "Advanced Waste Treatment using Nanostructured Hybrid Composites" EP/M026485/1.

Supplementary Information

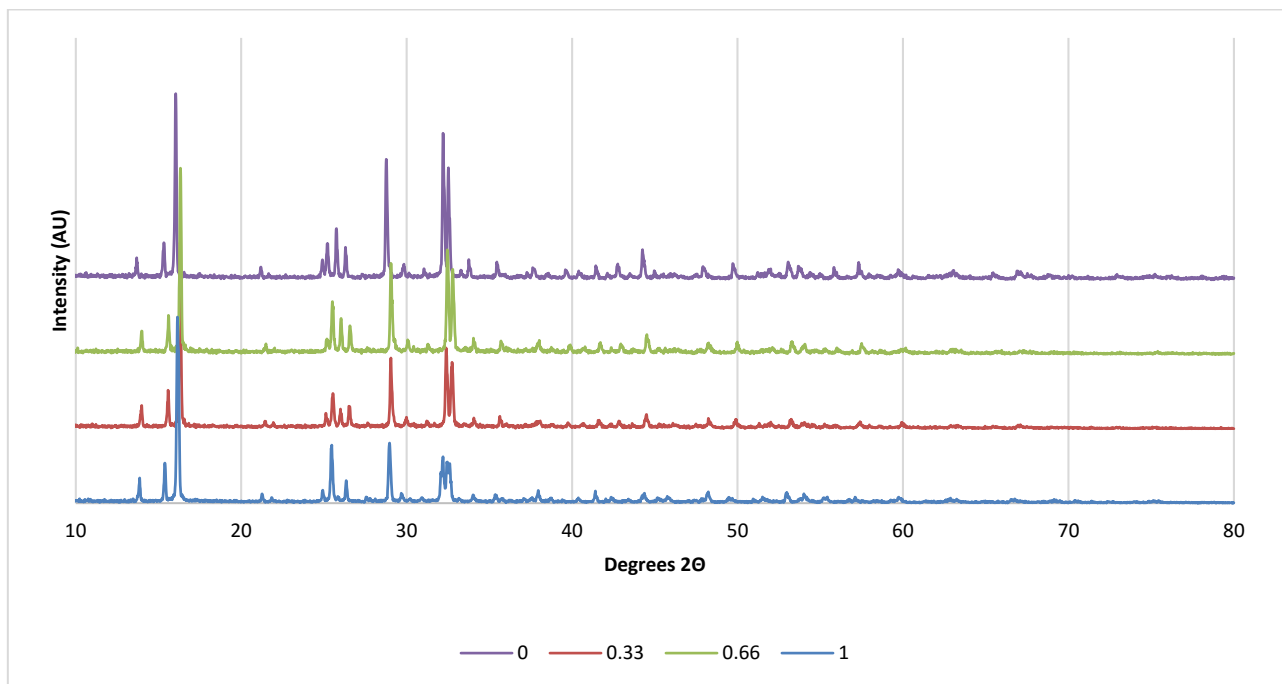


Figure S1: XRD patterns of prepared samples

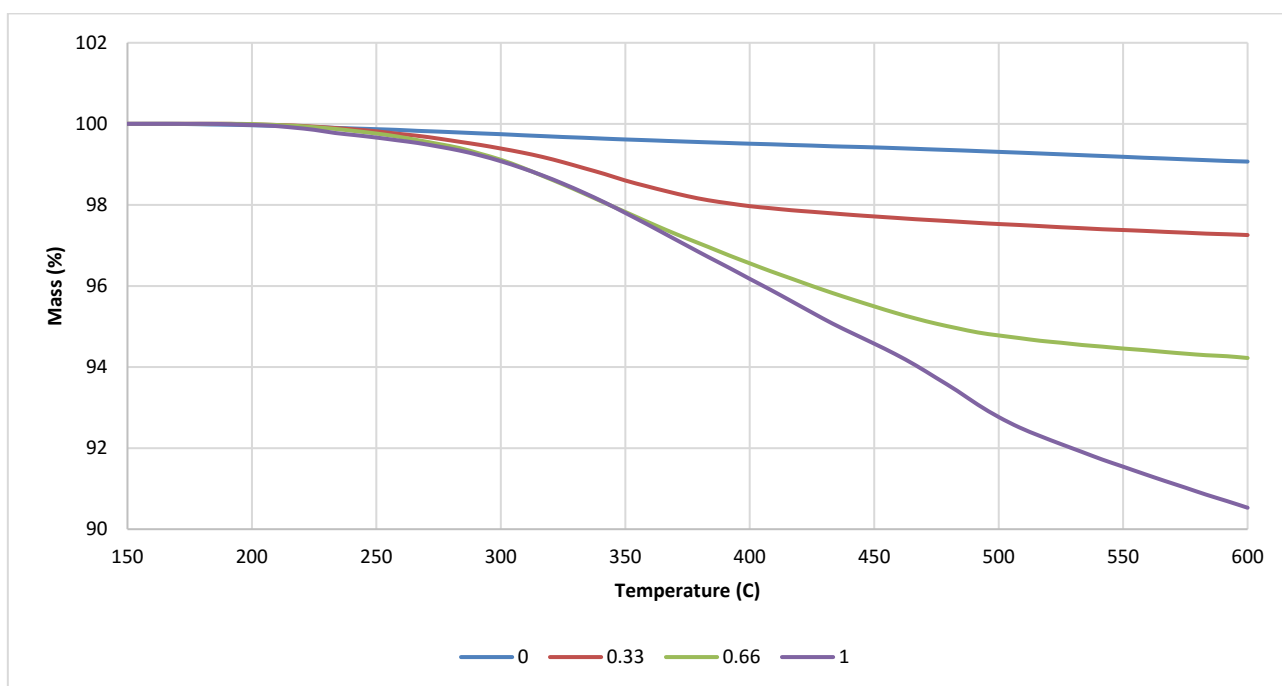


Figure S2: TGA responses of produced samples.