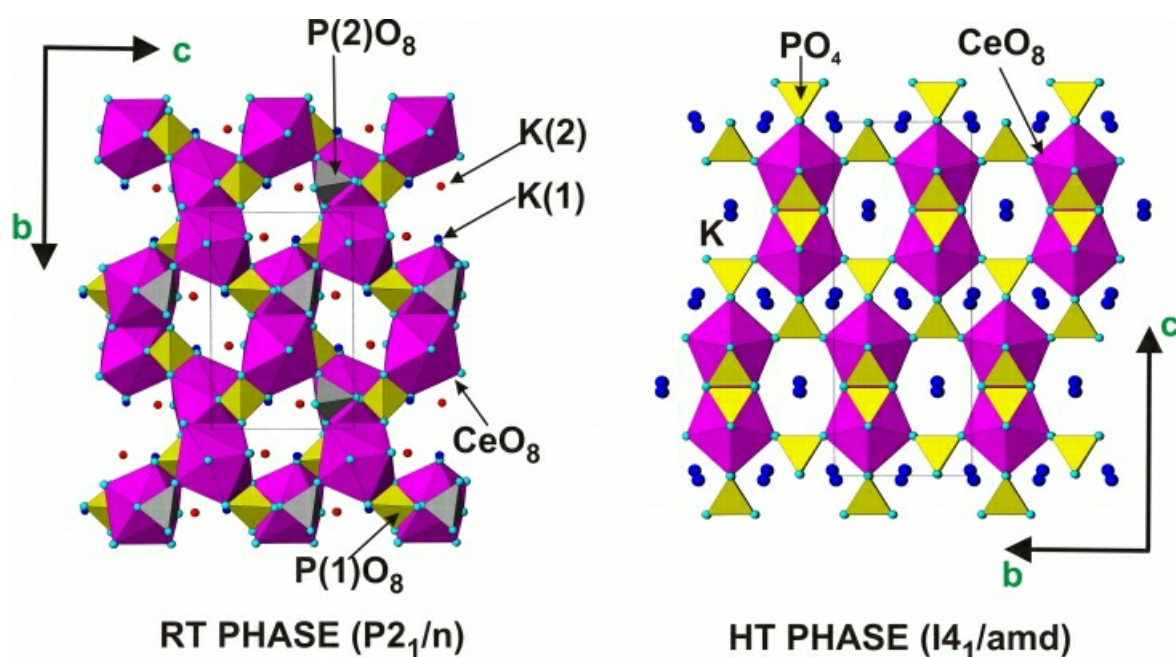


*K<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub>: A new complex phosphate of Ce(IV)*Samatha Bevara<sup>1</sup>, Srungarapu Nagabhusan Achary<sup>2</sup>, Avesh Kumar Tyagi<sup>2</sup><sup>1</sup>Homi Bhabha National Institute, Mumbai, India, <sup>2</sup>Chemistry Division, BARC, Mumbai, India  
E-mail: samathahcu@gmail.com

Complex phosphates of cerium have been subjects of research because of their rich structural chemistry and possible formation of open-framework topology and relevant physicochemical properties. However, the preparation of such complex phosphates is challenging owing to the unstable nature of Ce<sup>4+</sup>. Here in we present synthesis, crystal structure, phase transition and ion exchange properties of a new framework phosphate of Ce(IV). The yellow colored polycrystalline sample of K<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub> was prepared by solid state reaction of suitable reactants as reported earlier by us [1]. The analyses of the product by powder X-ray diffraction using synchrotron radiation revealed a monoclinic (P2<sub>1</sub>/n) lattice formed by CeO<sub>8</sub> and PO<sub>4</sub> polyhedra and isolated K<sup>+</sup> ions. The CeO<sub>8</sub> and PO<sub>4</sub> units are connected by sharing their edges and corners forming anionic [Ce(PO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> clusters and they are further connected to form an open tunnel containing framework structure. These tunnels are occupied by potassium ions to neutralize the net charge in the lattice. The structural stability and phase transition behaviors have been investigated in a wider temperature range by using thermal analyses and variable temperature X-ray and neutron diffraction. K<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub> undergoes a reconstructive structural transition at higher temperature (above 773K) while no transition down to 6K. The structure of the high temperature phase was obtained from the in situ high temperature XRD data and a tetragonal (I4<sub>1</sub>/amd) lattice is assigned to it. Structure of the high temperature phase is closely similar to that of the ambient temperature phase except small differences in the connections of CeO<sub>8</sub> and PO<sub>4</sub> in the anionic cluster. The refined unit cell parameters of the monoclinic phase at 300 K are: a = 9.1020(1) Å, b = 10.8132(1) Å, c = 7.6231(1) Å and angle = 111.14(1)°, V = 699.78(2) Å<sup>3</sup>, Z = 4, while those of high temperature tetragonal phase are: a = 6.8366(1) Å, c = 17.5091(1) Å, V = 818.35(1) Å<sup>3</sup>, Z = 4 (at 885K). The monoclinic to tetragonal phase transition is accompanied with a volume increase of about 14 %. Highly open and loosely packed structure of the tetragonal phase shows anisotropic thermal expansion with larger negative thermal expansion along c-axis (-15.3 × 10<sup>-6</sup> K<sup>-1</sup>) and an appreciable low volume thermal expansion (3.83 × 10<sup>-6</sup> K<sup>-1</sup>) as compared to that observed in ambient temperature monoclinic phase (41.30 × 10<sup>-6</sup> K<sup>-1</sup>). The open and loosely packed structure of K<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub> and labile nature of K<sup>+</sup> ions as well as close similarity in ionic radii of K<sup>+</sup> and Sr<sup>2+</sup> suggests it to be a promising material for selective exchange of Sr<sup>2+</sup> ions from nuclear waste [2]. The ion exchange properties have been evaluated by equilibrating the material with solutions containing radioactive <sup>90</sup>Sr<sup>2+</sup> ions. The observed distribution constant for <sup>90</sup>Sr is 8000mL/gm which is reasonably higher compared to existing sorption materials for <sup>90</sup>Sr removal from nuclear waste. This suggests that K<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub> can be a potential materials for separation of radioactive strontium from nuclear waste.

[1] Samatha, B. et al. (2016). Dalton Trans. 45. 980-991.

[2] Amphlett, C.B. Inorganic Ion Exchangers, Elsevier, Amsterdam, 1964.

**Keywords:** [Crystal Structure](#), [Phase Transition](#), [Ion Exchanger](#)