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# Structural and crystal chemical properties of alkali rare-earth double phosphates \*



ALLOYS AND COMPOUNDS

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## ABSTRACT

When appropriately activated, alkali rare-earth double phosphates of the form:  $M_3RE(PO_4)_2$  (where M denotes an alkali metal and RE represents either a rare-earth element or Y or Sc) are of interest for use as inorganic scintillators for radiation detection at relatively long optical emission wavelengths. These compounds exhibit layered crystal structures whose symmetry properties depend on the relative sizes of the rare earth and alkali-metal cations. Single-crystal X-ray and powder neutron diffraction methods were used here to refine the structures of the series of rare-earth double phosphate compounds:  $K_3RE(PO_4)_2$  with RE = Lu, Yb, Er, Ho, Dy, Gd, Nd, Ce, plus Y and Sc - as well as the compounds:  $A_3Lu(PO_4)_2$ , with A = Rb, and Cs. The double phosphate  $K_3Lu(PO_4)_2$  was reported and structurally refined previously, and it exhibited two lower-temperature phases. The compound K<sub>3</sub>Yb(PO<sub>4</sub>)<sub>2</sub> reported here also exhibits a new second phase that occurs at  $T = 120 \degree C$  with a transformation to hexagonal *P*-3 space group symmetry and a Yb-ion coordination number reduction from seven to six. This latter result was confirmed using EXAFS. Comprehensive structural data and structural systematics are reported here for a number of alkali rare-earth double phosphates. Additionally, single-crystal growth methods for the preparation of large single crystals of these compounds are described, and the thermal expansion properties of the present series of alkali rare-earth double phosphates, as determined by both X-ray and neutron diffraction methods, are presented. These data represent a structural and thermal characteristics basis for continuing research on the use of alkali rare-earth double phosphates as scintillators for radiation detection – as well as for future studies of the fundamental phase properties of these compounds at elevated pressures.

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### 1. Introduction

Rare-earth phosphates in both the orthophosphate and alkali rare-earth double phosphate forms continue to be studied as

<sup>1</sup> Deceased.

single-crystal hosts for use as inorganic scintillators for radiation detection applications [1–12]. In particular, alkali double phosphates of rare-earth elements with the general formula  $M_3RE(PO_4)_2$  (where M denotes an alkali metal and RE represents either a rareearth element or Y or Sc) are candidate materials for use as gammaray scintillators. When activated with  $Ce^{3+}$ , these materials exhibit relatively high scintillation light yields, rapid decay times, relatively short attenuation lengths, and the potential for growth in large single-crystal forms. Additionally, since they scintillate in the wavelength region above ~450 nm, they are amenable for use in combination with silicon solid-state detectors instead of photomultiplier tubes. Also, when isotopically enriched <sup>6</sup>Li is substituted on the alkali metal ion site, the  $Ce^{3+}$ -activated compounds are of interest for applications as scintillators for neutron detection [11].

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Fig. 1. The "pinwheel"-type atomic configurations characteristic of, or related to, the glaserite structure are shown in the "ideal glaserite", "distorted glaserite", and monoclinic ("arcanite-type") forms that are under consideration here. Note that for the monoclinic distortion of the glaserite form that resembles the arcanite structure, the top phosphate group is bidentate. (After Ref. [26]).

The structures of these compounds are closely related to the glaserite structure. Glaserite (or aphthitalite) is an anhydrous sulfate (K,Na)<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>, found in volcanic fumaroles. The glaserite structure and its derivatives are common in the A<sub>2</sub>X<sub>2</sub>O<sub>4</sub> molybdates, tungstates, phosphates, and silicates [13–17]. The M<sub>3</sub>RE(XO<sub>4</sub>)<sub>2</sub> compounds with M = Rb, K, and RE = a rare earth, Sc, or Y, and X = P, As, or V were reported previously by Melnikov et al. [18,19] who prepared the double phosphate compounds by a reaction of the orthophosphate REPO<sub>4</sub> with M<sub>2</sub>CO<sub>3</sub> in the presence of H<sub>3</sub>PO<sub>4</sub> at 450–700 °C for 50–150 h. This process resulted in powder M<sub>3</sub>RE(PO<sub>4</sub>)<sub>2</sub> compounds based on the K<sub>3</sub>Na(PO<sub>4</sub>)<sub>2</sub> glaserite structure [20,21] – consisting of an (NaO<sub>6</sub>) trigonal antiprism (an octahedron) that shares its six corners with (PO<sub>4</sub>) tetrahedra. These



**Fig. 2.** The layered structure (monoclinic  $P2_1/m$ ) of most of the  $A_3RE(PO_4)_2$  compounds investigated in this work. Phosphate tetrahedra are light lavender, the REO<sub>7</sub> polyhedron is blue, and the A-site atoms are large purple balls. In this monoclinic distortion of the glaserite structure, the alkali ions are located within channels of the unit cell, and one of the six PO<sub>4</sub> tetrahedra in each "pinwheel" shares an edge with the rare-earth polyhedra.



Fig. 3. Colorless single crystals of  $K_3$ Yb(PO<sub>4</sub>)<sub>2</sub> grown as described in Section 3 illustrate the crystal growth habit, still entrained inside the solidified flux of the Pt crucible.



**Fig. 4.** Relatively large flat plates (~1.0 to 1.5 cm on a side) of clear single crystals of  $K_3Lu(PO_4)_2$  are shown that were cleaved from flux-grown crystals after their removal from the growth crucible. Single crystals of this compound typically grew larger than crystals of the other alkali rare earth double phosphates.

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