KMg₆(P₂O₇)₂P₃O₁₀: a Novel Phosphate with Two Distinct Anions

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Abstract

A novel mixed-anion phosphate, KMg₆(P₂O₇)₂P₃O₁₀, has been synthesized by spontaneous crystallization technique with K₂O-P₂O₅-Li₂O as a flux. Single-crystal X-ray analysis reveals that KMg₆(P₂O₇)₂P₃O₁₀ features two kinds of isolated anions, [P₂O₇] dimers and [P₃O₁₀] trimers. Such coexisting of two distinct anions in one polyphosphate, which has somewhat conflict with Pauling's parsimony () rule, is very rare in alkali metal and alkali-earth metal phosphates. This finding enriches the structural chemistry of phosphates and provides new perspective on the design of multiple anions materials. The thermal stability and a.c. conductivity of KMg₆(P₂O₇)₂P₃O₁₀ are also discussed in this paper.

Keywords: Mixed-anion phosphate, Pauling's parsimony rule, Infrared spectrum

Metal phosphates have attracted considerable interest during the past decades owing to their important applications in the fields of material science such as ionic conductors [1-3], solid electrolytes for batteries [4, 5], and nonlinear optics. For example, our group recently discovered a series of phosphates, including Rb₂Ba₃(P₂O₇)₂ [6], RbBa₂(PO₃)₅ [6], and Ba₅P₆O₂₀ [7], which are new deep-UV nonlinear optical materials of good performance. Unlike the borate [8, 9], phosphorus is only bound to four oxygen atoms to form a PO₄ tetrahedron, thus it can be more feasible to regulate and control the PO₄ tetrahedron to form diverse connection and arrangement patterns. According to the number of interconnected tetrahedra, phosphate anions can be isolated or infinite chains [10-12]. And the isolated anions can be classified into isolated [PO₄] groups, isolated clusters (written as P_nO_{3n+1}), isolated cyclic framework (written as P_nO_{3n} for n ≥ 3) or infinite [PO₃]_∞ chains [13]. Normally, phosphates contain only one kind of isolated anion, for example, KMgPO₄, KMg₄(PO₄)₃, KCa₁₀(PO₄)₇ with isolated [PO₄] tetrahedral [14-16], Rb₂Ba₃(P₂O₇)₂ and Na₂CaP₂O₇ with isolated [P₂O₇] dimers [6, 17], Ba₅P₆O₂₀ with isolated [P₃O₁₀] trimers [7], KMg(P₃O₉) with isolated [P₃O₉] rings [18], Ca₂(P₄O₁₂)·4H₂O with isolated [P₄O₁₂] rings [19], and Cs₂Mg₂P₆O₁₈ with isolated [P₆O₁₈] rings [20], as well as RbBa₂(PO₃)₅ with infinite [PO₃]_∞ chains [6]. These single anionic groups described above are consistent with Pauling's parsimony () rule, which suggests that ions with the same types in the crystal should have the similar coordination environment [21]. There are rather rare exceptions in phosphates,

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such as $\text{Na}_7\text{V}_4(\text{PO}_4)(\text{P}_2\text{O}_7)_4$ [22], $\text{Na}_4\text{Mg}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ [23], and $\text{LiMg}_3(\text{PO}_4)\text{P}_2\text{O}_7$ [13], but they are exclusively composed of $[\text{PO}_4]$ tetrahedra and $[\text{P}_2\text{O}_7]$ dimers.

According to the information mentioned above, single phosphate anion only exists in single-metal phosphate (such as alkali metal phosphate or alkali-earth metal phosphate), while mixed-metal phosphate is more likely resulting in two different kinds of phosphate anions. As far as mixed-metals phosphate (written as $\text{A}_x\text{B}_y\text{P}_m\text{O}_n$, A = alkali metal, B = alkali-earth metal), when the molar ratio of m/y is slightly greater than or equal one and the ratio of m/x is greater than two, mixed-anions phosphate may easily be formed. It is believed that various mixed-anions phosphate may be obtained by changing the element ratios based on the strategy. Herein, we report a novel phosphate $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ whose structure is built from two kinds of anions, isolated $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers.

Single crystals of $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ were grown by spontaneous crystallization technique with $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{Li}_2\text{O}$ as a flux (experiment details are described in the Supporting information). The crystal structure was determined by single-crystal X-ray diffraction (XRD) using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K (for detailed crystallographic data, see Tables S1-S4 in the Supporting Information). The phase purity was confirmed by powder XRD, whose pattern matches well with the calculated one based on the single-crystal XRD analysis (Fig. S1 in the Supporting Information). The infrared spectrum was measured on a Bruker VERTEX70 spectrometer with KBr pellets as a standard in the range of $400\text{--}2000 \text{ cm}^{-1}$, and the thermal stability was investigated by the differential scanning calorimetric (DSC) analysis on a NETZSCH STA 449C thermal analyzer (the DSC was calibrated with Al_2O_3). Temperature dependence of the a.c. conductivity was obtained from the imaginary part of the dielectric constants, which was performed on TH2828A impedance analyzer at 100 kHz.

$\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ crystallizes in the monoclinic space group $P2_1/m$ with cell parameters of $a = 5.2611(3) \text{ \AA}$, $b = 26.3309(14) \text{ \AA}$, and $c = 6.3800 \text{ \AA}$. In the structure of $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$, isolated $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers are connected by Mg-O polyhedra through corner-sharing to form a three-dimensional (3D) framework with K^+ cations located in void space to maintain the charge balance (Fig. 1a). The structural environment of every atom will be depicted as following.

Four crystallographically distinct phosphorus atoms, which are all coordinated with four oxygen atoms, construct isolated $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers via corner-sharing (Fig. 1b, c). $[\text{P}_3\text{O}_{10}]$ trimers are surrounded by parallel $[\text{Mg}_6\text{O}_{26}]$ columns, and $[\text{P}_2\text{O}_7]$ dimers serve as the bridges between the adjacent $[\text{Mg}_6\text{O}_{26}]$ columns along the b -axis (Fig. 1a). As shown in Fig. 1b, the $\text{P}(1)\text{O}_4$ tetrahedron shares the apical oxygen atom O(2) with $\text{P}(2)\text{O}_4$ tetrahedron to form one isolated $[\text{P}_2\text{O}_7]$ dimer. One $\text{P}(3)\text{O}_4$ tetrahedron is linked with two $\text{P}(4)\text{O}_4$ tetrahedra through sharing the apical oxygen atom O(9) to form one $[\text{P}_3\text{O}_{10}]$ trimer (Fig. 1c). The rest oxygen atoms in $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers are all connected to $[\text{Mg}_6\text{O}_{26}]$ columns via corner-sharing. The P-O distances and O-P-O angles of the $\text{P}(1)\text{O}_4$ tetrahedron are in the ranges of $1.509(3)\text{--}1.590(2) \text{ \AA}$ and $100.50(125)\text{--}1113.074(119)^\circ$, respectively. The corresponding P-O distances and O-P-O angles in one $\text{P}(2)\text{O}_4$, $\text{P}(3)\text{O}_4$ and $\text{P}(4)\text{O}_4$ groups are $1.489(2)\text{--}1.590(2) \text{ \AA}$ and $103.400(123)\text{--}114.030(131)^\circ$, $1.497(3)\text{--}1.567(2) \text{ \AA}$ and $103.881(106)\text{--}118.560(191)^\circ$, $1.497(3)\text{--}1.635(2) \text{ \AA}$ and $100.211(116)\text{--}115.821(120)^\circ$, respectively. These data are normal, as compared with other phosphates, such as $\text{Rb}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$ and $\text{Ba}_5\text{P}_6\text{O}_{20}$ previously reported by our group [6, 7].

Fig. 1. (a) View of the $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ structure in the bc plane. Mg-O polyhedra, gray. (b) Isolated $[\text{P}_2\text{O}_7]$ dimer. (c) Isolated $[\text{P}_3\text{O}_{10}]$ trimer. (d) View of $[\text{Mg}_6\text{O}_{24}]$ column in the ab plane.

Magnesium atoms in the structure are coordinated by five or six oxygen atoms to form MgO_5 polyhedra (namely $\text{Mg}(2)\text{O}_5$) and MgO_6 octahedra (namely $\text{Mg}(1)\text{O}_6$ and $\text{Mg}(3)\text{O}_6$), respectively (Fig. 1d). They are interconnected by edge-sharing to each other to form isolated C-shape columns stretching along the a -axis (Fig. 1a), which can be regarded as a row of $[\text{Mg}_6\text{O}_{26}]$ polymers overlapping together hand in hand (Fig. 1d).

According to Pauling's parsimony (V) rule, the number of chemically different coordination environments for a given ion in a crystal tends to be small, which is conducive to maintain the periodicity and stability of material structure [21]. Thus, two distinct anionic clusters ($[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers) coexisting in $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ reduce the tendency of structural stability. It seems that the edging-sharing Mg-O polyhedra stretching along the a -axis result in two distinct mixed anion clusters. Meanwhile, these clusters have similar topological structure, i.e. all appearing in the form of short chain, which decreases the conflict with Pauling's fifth rule. Further in-depth studies are still in progress. To the best of our knowledge, there are only several phosphates with mixed P-O anions, such as $\text{Na}_7\text{V}_4(\text{PO}_4)(\text{P}_2\text{O}_7)_4$ [22], $\text{Na}_4\text{Mg}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ [23], and $\text{LiMg}_3(\text{PO}_4)\text{P}_2\text{O}_7$ [13], but they are exclusively composed of $[\text{PO}_4]$ tetrahedra and $[\text{P}_2\text{O}_7]$ dimers; there are no examples that such two kinds of clusters coexist in one phosphate containing only alkali metal and alkali earth metal cations.

As shown in Fig. S2 in the Supporting Information, the DSC data show one sharp endothermic peak around 890°C in the heating curve, and have no peak in the cooling curve. In addition, the residues after the DSC analysis gave a powder XRD pattern different from the original powders (Fig. S1). These results demonstrate that $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ is an incongruently melting compound.

The vibration spectrum for isolated $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers can be regarded as combination vibrations of P-O, P-O-P and P-O, P-O-P, O-P-O, respectively [23]. As shown in Fig. 2, there are five characteristic absorption bands with frequencies $443\text{--}493\text{ cm}^{-1}$, $546\text{--}585\text{ cm}^{-1}$, $706\text{--}738\text{ cm}^{-1}$, 996 cm^{-1} , and $1048\text{--}1384\text{ cm}^{-1}$. These bands can be assigned to δ_s (O-P-O), δ_{as} (O-P-O), ν_s (P-O) and ν_{as} (P-O-P), ν_{as} (P-O), respectively. These results are consistent with that of the structural analysis.

Fig. 2. Infrared spectrum of $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$.

As shown in Fig. 3, the a.c. conductivity of $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ with values of 2.07×10^{-12} to $4.93 \times 10^{-12} \text{ S} \cdot \text{m}^{-1}$ were obtained according to the relation $\sigma = 2\pi f \epsilon'' \epsilon_0$, where f is the frequency, ϵ'' is the imaginary part of the dielectric permittivity and ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$). It displays a positive slope with increasing temperature in the range of 27-68 °C, indicating that the title compound is of the characteristic of a semiconductor [24].

Fig. 3. The a.c. conductivity of $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$.

In summary, a novel phosphate $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$, which is composed of two kinds of isolated anions, $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers, was synthesized through spontaneous crystallization technique. Its structure is composed of isolated C-shape $[\text{Mg}_6\text{O}_{26}]$ columns stretching along the a -axis, which are further bridged by isolated $[\text{P}_2\text{O}_7]$ dimers and $[\text{P}_3\text{O}_{10}]$ trimers through corner-sharing to form a 3D framework. Infrared spectrum confirms that the P-O groups exist in the form of polymers. This coexisting of two distinct anions in one polyphosphate, which has somewhat conflict with Pauling's parsimony () rule, adds a new example to the mixed-anion phosphate family. The DSC measurement shows that $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ is stable up to 890 °C. Temperature dependence of the a.c. conductivity reveals that $\text{KMg}_6(\text{P}_2\text{O}_7)_2\text{P}_3\text{O}_{10}$ is of the characteristic of a semiconductor. Discovery of this compound enriches the structural chemistry of phosphates and may provide new perspective on the design of multiple anions materials.

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References

- [1] L. Sebastian, J. Gopalakrishnan, Lithium ion mobility in metal oxides: a materials chemistry perspective, *J. Mater. Chem.* 13 (2003) 433-441.
- [2] N. Anantharamulu, K.K. Rao, M. Vithal, G. Prasad, Preparation, characterization, impedance and thermal expansion studies of $\text{Mn}_{0.5}\text{MSb}(\text{PO}_4)_3$ ($\text{M} = \text{Al, Fe and Cr}$), *J. Alloy. Compd.* 479 (2009) 684-691.
- [3] K. Nagamine, K. Hirose, T. Honma, T. Komatsu, Lithium ion conductive glass-ceramics with $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and YAG laser-induced local crystallization in lithium iron phosphate glasses, *Solid State Ionics* 179 (2008) 508-515.
- [4] C. Delmas, A. Nadiri, J.L. Soubeyroux, The nasicon-type titanium phosphates $\text{ATi}_2(\text{PO}_4)_3$ ($\text{A}=\text{Li, Na}$) as electrode materials, *Solid State Ionics* 28 (1988) 419-423.
- [5] M.S. Whittingham, Lithium batteries and cathode materials, *Chem. Rev.* 104 (2004) 4271-4301.
- [6] S.G. Zhao, P.F. Gong, S.Y. Luo, L. Bai, Z.S. Lin, C.M. Ji, T.L. Chen, M.C. Hong, J.H. Luo, Deep-ultraviolet transparent phosphates $\text{RbBa}_2(\text{PO}_3)_5$ and $\text{Rb}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$ show nonlinear optical activity from condensation of $[\text{PO}_4]^{3-}$ units, *J. Am. Chem. Soc.* 136 (2014) 8560-8563.
- [7] S.G. Zhao, P.F. Gong, S.Y. Luo, L. Bai, Z.S. Lin, Y.Y. Tang, Y.L. Zhou, M.C. Hong, J.H. Luo, Tailored synthesis of a nonlinear optical phosphate with a short absorption edge, *Angew. Chem. Int. Ed.* 54 (2015) 4217-4221.
- [8] M. Touboul, N. Penin, G. Nowogrocki, Borates: a survey of main trends concerning crystal-chemistry, polymorphism and dehydration process of alkaline and pseudo-alkaline borates, *Solid State Sci.* 5 (2003) 1327-1342.
- [9] Z. Wang, M. Zhang, X. Su, S.L. Pan, Z.H. Yang, H. Zhang, L. Liu, $\text{Q}_{18}\text{Mg}_6(\text{B}_5\text{O}_{10})_3(\text{B}_7\text{O}_{14})_2\text{F}$ ($\text{Q} = \text{Rb and Cs}$): new borates containing two large isolated polyborate anions with similar topological structures, *Chem. Eur. J.* 21 (2015) 1414-1419.
- [10] A. Durif, M.T. Averbuch-Pouchot, J.C. Guitel, Crystal structure of a beryllium-potassium polyphosphate: $\text{BeK}(\text{PO}_3)_3$, *Z. Kristallogr.* 177 (1986) 165-170.
- [11] C. Martin, I. Tordjman, A. Durif, Crystal structure of barium potassium polyphosphate $\text{Ba}_2\text{K}(\text{PO}_3)_5$, *Z. Kristallogr.* 141 (1975) 403-411.
- [12] M.T. Averbuch-Pouchot, A. Durif, Structure of monobarium tetracaesium polyphosphate, *Acta Crystallogr. C* 42 (1986) 928-930.
- [13] S.C. Kim, M.S. Lee, J.Y. Kang, Y.I. Kim, S.J. Kim, Crystal structure and ion conductivity of a new mixed-anion phosphate $\text{LiMg}_3(\text{PO}_4)\text{P}_2\text{O}_7$, *J. Solid State Chem.* 225 (2015) 335-339.
- [14] G. Wallez, C.C. Justin, T.L. Mercier, M. Quarton, F. Robert, Crystal chemistry and

- polymorphism of potassium-magnesium monophosphate, *J. Solid State Chem.* 136 (1998) 175-180.
- [15] P.E. Tomaszewski, M. Maczka, A. Majchrowski, A. Waskowska, J. Hanuza, Crystal structure and vibrational properties of $\text{KMg}_4(\text{PO}_4)_3$, *Solid State Sci.* 7 (2005) 1201-1208.
- [16] M.H. Sandstrom, D. Bostrom, $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ from single-crystal data, *Acta Crystallogr. E* 62 (2006) i253-i255.
- [17] J. Bennazha, A. Boukhari, E.M. Holt, Synthesis and crystal structure of $\text{Na}_2\text{CaP}_2\text{O}_7$, *Solid State Sci.* 1 (1999) 373-380.
- [18] R. Masse, J.C. Grenier, M.T. Averbuch-Pouchot, D. Tranqui, A. Durif, Etude cristallographique de trimetaphosphates hexagonaux du type $\text{MNH}_4(\text{PO}_3)_3$ ($\text{M} = \text{Zn Co Ca Cd Mg Mn}$). Etude dun cycle p309 dans un sel de potassium isomorphe $\text{MgK}(\text{PO}_3)_3$, *Bull. Soc. Fr. Minéral. Cristallogr.* 90 (1967) 158-161.
- [19] M. Schneider, K.H. Jost, H. Fichtner, Crystal structure of the cyclotetraphosphate $\text{Ca}_2(\text{P}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$, *Z. Anorg. Allg. Chem.* 500 (1983) 117-122.
- [20] N.N. Chudinova, E.V. Murashova, A.B. Ilyukhin, Double cyclohexaphosphates of cesium and divalent metals, *Inorg. Mater.* 39 (2003) 1298-1302.
- [21] L. Pauling, The nature of the chemical bond and the structure of molecules and crystals; an introduction to modern structural chemistry, 3rd ed, Cornell University Press: Ithaca, NY, 1960.
- [22] S.Y. Lim, H. Kim, J. Chung, J.H. Lee, B.G. Kim, J.J. Choi, K.Y. Chung, W. Cho, S.J. Kim, W.A. Goddard, Y.S. Jung, J.W. Choi, Role of intermediate phase for stable cycling of $\text{Na}_7\text{V}_4(\text{P}_2\text{O}_7)_4\text{PO}_4$ in sodium ion battery, *Proc. Natl. Acad. Sci. U.S.A.* 111 (2014) 599-604.
- [23] R. Essehli, B.E. Bali, S. Benmokhtar, H. Fuess, I. Svoboda, S. Obbade, Synthesis, crystal structure and infrared spectroscopy of a new non-centrosymmetric mixed-anion phosphate $\text{Na}_4\text{Mg}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, *J. Alloy. Compd.* 493 (2010) 654-660.
- [24] W.Q. Liao, Y. Zhang, C.L. Hu, J.G. Mao, H.Y. Ye, P.F. Li, S.P. Huang, R.G. Xiong, A lead-halide perovskite molecular ferroelectric semiconductor, *Nat. Commun.* 6 (2015) 7338.

Phosphate Containing Two Isolated Polyphosphate Anions

*Graphical Abstract - Synopsis

Two kinds of isolated polyphosphate anions, $[P_2O_7]$ clusters and $[P_3O_{10}]$ clusters, coexist in the phosphate $KMg_6(P_2O_7)_2P_3O_{10}$, which crystallizes in the monoclinic space group $P2_1/m$. Such coexisting of two distinct anions in one polyphosphate, which has somewhat conflict with Pauling's parsimony (**V**) rule, is very rare in alkali metal and alkali-earth metal phosphates. Discovery of this compound enriches the structural chemistry of phosphates and may provide new perspective on the design of multiple anions materials