

**[o.m9.p1] Investigation of the Alkaline Earth Phosphates: Crystal Structure of a New Strontium Hydrogen Phosphate Form.** L.B. Taher and L. Smiri<sup>(a)</sup>; Y. Laligant and V. Maisonneuve<sup>(b)</sup>, <sup>(a)</sup>Laboratoire de Chimie Inorganique et Structurale, Faculté des Sciences de Bizerte, 7021 Jarzouna, Tunisie; <sup>(b)</sup>Laboratoire des Fluorures, UPRES-A CNRS 6010, Faculté des Sciences, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 9, France.

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The X-ray single-crystal structure is reported for a new form of strontium hydrogen phosphate ( $\gamma$ -SrHPO<sub>4</sub>) ( $\gamma$ -Sr). The cell is orthorhombic (Pbca) with  $a_0=8.131(3)\text{\AA}$ ,  $b_0=9.258(5)\text{\AA}$ ,  $c_0=18.084(7)\text{\AA}$ ,  $V=1361.31(2)\text{\AA}^3$ ,  $Z=16$ , and  $R=0.039$ . The atomic arrangement consists of a succession along [001] of two kinds of HPO<sub>4</sub><sup>2-</sup> alternating planes denoted as P(1) and P(2). These sheets are held together by Sr<sup>2+</sup> cations. Here we find the same arrangement as observed in the monoclinic CaBa(HPO<sub>4</sub>)<sub>2</sub><sup>1</sup> (CaBa). Further interaction linkages are provided by strong hydrogen bonds established within the phosphate sheets. The features of the hydrogen bonding system (dimers in P(1) and infinite chains in P(2)) are defined by the H/PO<sub>4</sub><sup>3-</sup> ratio as has been found in CaBa and some sulfate structures e.g. KHSO<sub>4</sub><sup>2</sup>, where H/SO<sub>4</sub><sup>2-</sup> ratio is also 1. The unit cell deformation of CaBa ( $b_m \sim a_0$ ,  $a_m \sim b_0$ ,  $c_m \sim 1/2c_0$ ) can be directly related to the nature of the cations coordination; one kind of ninefold ions (2Sr<sup>2+</sup>) with average distances 2.703 Å for Sr(1)O<sub>9</sub> and 2.660 Å for Sr(2)O<sub>9</sub>, is replaced by (Ba<sup>2+</sup>, Ca<sup>2+</sup>) ions with  $\langle \text{Ba-O} \rangle = 2.846\text{\AA}$  and  $\langle \text{Ca-O} \rangle = 2.462\text{\AA}$  in BaO<sub>9</sub> and CaO<sub>7</sub> polyhedra, respectively. The lattice distortion is coupled with small rotation of the HPO<sub>4</sub> tetrahedra along the  $a_m$  axis. Moreover, the slight increase of  $a_0$  (8.131 Å) compared to  $b_m$  (7.930 Å) is caused by: (i) a radius change of the ions, where two Sr<sup>2+</sup> cations ( $r_{IX}(\text{Sr}^{2+})=1.31\text{\AA}$ ) are replaced by a relatively small Ca<sup>2+</sup> ( $r_{VII}(\text{Ca}^{2+})=1.07\text{\AA}$ ) and large Ba<sup>2+</sup> ( $r_{IX}(\text{Ba}^{2+})=1.47\text{\AA}$ ) cations, (ii) a reduction in the distance between P(2) atoms along the infinite phosphate chains in CaBa (4.280 Å as compared to 4.369 Å for  $\gamma$ -Sr). This decrease in the P-P distance is accompanied by a decrease in the P(2)-P(2)-P(2) angle (137.06° to 135.77°). The approximately doubling of  $c_0$  ( $c_m=9.865\text{\AA}$ ) is due to the orientation of the tetrahedra in two successive layers either of P(1) type or of P(2) type.

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**[o.m9.p2] Lead(II) Heptanoate: structure and thermal properties.** M. François<sup>a</sup>, J.P. Rivera<sup>c</sup>, F. Lacouture<sup>a</sup>, C. Didierjean<sup>b</sup>, E. Rocca<sup>a</sup>, J. Steinmetz<sup>a</sup>, <sup>a</sup>LCSM, UMR 7555 and <sup>b</sup>LCM3B, UPRESA N°7036, BP 239, F54506 Vandoeuvre-les-Nancy Cedex. <sup>c</sup>DCMAA, Université de Genève, 30 quai E. Ansermet, CH-1211 Genève 4 (Suisse)  
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Electrochemical studies have shown that sodium linear monocarboxylate inhibits the corrosion of lead in aqueous solution. Particularly, the efficiency of these compounds with a general formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>n-2</sub>COONa (n=7 to 11) is depending on the chain length of the aliphatic group. The Lead passivation was attributed to the growth of passive layers containing metallic soap Pb(C<sub>n</sub>H<sub>2n-1</sub>O<sub>2</sub>)<sub>2</sub>. The general aim of these studies concerns new protective treatments less polluting than usual process as phosphatation or chromatation used in metal protection. To optimize the treatments, for example by varying the chain length of the aliphatic carboxylate group, it is necessary to better understand the interactions between the surface of the metal, oxidized or not, and the metallic soap, which needs the knowledge of the crystallographic structure formed by the hydrophobic and protecting metallic soap. Thus, crystallographic structure but also thermal behaviour of this compound have been investigated.

Pb(C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>)<sub>2</sub> soap metal protecting lead surface have a triclinic structure (space group P $\bar{1}$  with  $a=4.8590(1)\text{\AA}$ ,  $b=7.3090(10)\text{\AA}$ ,  $c=23.1920(10)\text{\AA}$ ,  $\alpha=91.54(1)^\circ$ ,  $\beta=95.66(1)^\circ$ ,  $\gamma=90.90(1)^\circ$ ,  $V=819.2(2)\text{\AA}^3$ ,  $d_x=1.887\text{g/cm}^3$ ,  $Z=2$ ) from 2069 unique reflections ( $R1=0.0606$ ,  $wR2=0.1262$ ). It is characterized, at 20°C, by layers perpendicular to the c axis, in which one bidentate carboxylate group among the two bridges the lead atoms along [010] while the other bidentate carboxylate group does not participate in bridging. Nevertheless, the cohesion of the sheets along [100] is assumed by Van der Waals interactions where takes place the lone pair 6s<sup>2</sup> of the lead. The lead atoms are six O-coordinated in a very distorted polyhedron. The thermal properties are analyzed by thermogravimetry, differential calorimetry and polarized light microscopy. Absence of structural water in that compound is confirmed by TGA measurements and micro Raman spectrometry. The compound presents the following sequence of phase transitions (LC = liquid crystal) on heating : crystal - 88 °C → LC<sub>1</sub> - 90 °C → LC<sub>2</sub> - 107 °C → isotropic and on cooling : crystal - 74 °C ← LC<sub>1</sub> - 79 °C ← LC<sub>2</sub> - 101 °C ← isotropic. The two liquid crystal phases are at the present time not yet identified. With the polarizing microscope, they neither present the characteristics of a nematic nor of a smectic (A or C) liquid crystal phase.

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