Structure, Infrared and Raman spectroscopic studies of new A\textsuperscript{II}(Sb\textsuperscript{V}0.50Cr\textsuperscript{III}0.50)(PO\textsubscript{4})\textsubscript{2} (A = Ba, Sr, Pb) yavapaiite phases

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Abstract: Three new A\textsuperscript{II}(Sb\textsubscript{0.5}Cr\textsubscript{0.5})(PO\textsubscript{4})\textsubscript{2} (A\textsuperscript{II} = Ba, Sr, Pb) yavapaiite phases, abbreviated as [ASbCr], have been successfully synthesized by a conventional solid-state reaction in air atmosphere. Their crystal structures have been investigated by Rietveld analysis from the X-ray powder diffraction method. Results show that Ba(Sb\textsubscript{0.5}Cr\textsubscript{0.5})(PO\textsubscript{4})\textsubscript{2} crystallizes in monoclinic \textit{C2/m} space group (Z = 2) with cell parameters a = 8.140(1) Å; b = 5.175(1) Å; c = 7.802(1) Å and \(\beta = 94.387(1)^\circ\). Structures of A\textsuperscript{II}(Sb\textsubscript{0.5}Cr\textsubscript{0.5})(PO\textsubscript{4})\textsubscript{2} (A\textsuperscript{II} = Sr, Pb) compounds are comparable, and both crystallize in a distorted yavapaiite structure with \textit{C2/c} space group (Z = 4). Obtained monoclinic cell parameters are: a = 16.5038(2) Å; b = 5.1632(1) Å; c = 8.0410(1) Å; \(\beta = 115.85(1)^\circ\) for [SrSbCr] and a = 16.6842(2) Å; b = 5.156(1) Å; c = 8.115(1) Å; \(\beta = 115.35(1)^\circ\) for [PbSbCr]. Infrared and Raman spectroscopic study was undertaken to provide information about vibrations bonds within the studied yavapaiite materials.

Keywords: Rietveld Refinements analysis; X-ray powder diffraction; Yavapaiite structure; Infrared and Raman spectroscopy.

1. Introduction

Phosphates with general A\textsuperscript{II}M\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} formula have attracted significant attention for several decades due to their optical \textsuperscript{1-5}, magnetic \textsuperscript{6}, and dielectric properties \textsuperscript{7}. Furthermore, they have also proved attractive as potential candidates for the immobilization of tetravalent actinides \textsuperscript{8-11}. Therefore, it becomes of prime importance to investigate their crystal structure. Note that the nature and/or size of A\textsuperscript{II} and M\textsuperscript{IV} cations have a significant effect on the crystal structure of A\textsuperscript{II}M\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} phases, and this has prompted many researchers to build a relationship between the composition and the crystal structure of certain compounds \textsuperscript{12,13}. The larger A\textsuperscript{II} cation can cause structural distortions, and more particularly, rotation of the PO\textsubscript{4} tetrahedra. This last phenomenon leads to the synthesis of new families of phases whose structures are linked to each other’s \textsuperscript{12-28}. Among these families, the attracted A\textsuperscript{II}M\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} yavapaiite-type phases have a structure consisting of layers of A\textsuperscript{II} ions in tenfold coordination alternating with dense slabs of M\textsuperscript{IV}O\textsubscript{6} and PO\textsubscript{4} polyhedra. Several derivatives have been observed, at room temperature, for the structure above type. It has been reported that in the case where the ionic radius of M\textsuperscript{IV} shifts slightly towards high values, like in Ba\textsuperscript{II}M\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} (M\textsuperscript{IV} = Np, U, Th) \textsuperscript{29,30}, a super-yavapaiite, with a structure similar to the archetype RbEu(SO\textsubscript{4})\textsubscript{2} \textsuperscript{31} (space group \textit{C2/c}, Z=4), is formed. Such a structure-type is made of layers of Ba\textsuperscript{II}O\textsubscript{14} polyhedral alternating with dense slabs of M\textsuperscript{IV}O\textsubscript{6} square-based antiprisms and PO\textsubscript{4} tetrahedra. The high coordination of Ba\textsuperscript{II} and M\textsuperscript{IV} (M\textsuperscript{IV} = Np, U, Th) ions was shown to be consistent with their large size. For small A\textsuperscript{II} and M\textsuperscript{IV} cations, as in the case of SrM\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} (M\textsuperscript{IV} = Ge, Ti, Sn) \textsuperscript{20,22} and PbM\textsuperscript{IV}(PO\textsubscript{4})\textsubscript{2} (M\textsuperscript{IV} = Ge and Ti) \textsuperscript{2}, a distorted yavapaiite structure-type with \textit{C2/c} space group (Z=4) was reported. This latter structure has a double lattice along the a-axis. Compared to the true-yavapaiite type, the M\textsuperscript{IV} cation remains in octahedral polyhedral, whereas the A\textsuperscript{II} cation coordination decreases to eight capped with two supplemental oxygen ions. The PbSn(PO\textsubscript{4})\textsubscript{2} structure crystallizes in the \textit{P2\textsubscript{1}/n} space group under noncompact yavapaiite form with a [Sn(PO\textsubscript{4})\textsubscript{2}]\textsuperscript{2-} skeleton built of corner-linked SnO\textsubscript{6} octahedra and PO\textsubscript{4} tetrahedra. In contrast, the Pb\textsuperscript{6+} cations are distributed in double tunnels in place of sheets \textsuperscript{22}. On the other hand, SrM(PO\textsubscript{4})\textsubscript{2} (M = Np, U) was described as a modified cheralite structure (\textit{Cmca} space group, Z=8) \textsuperscript{32}.

The main aim of our present work is to investigate the possibility of synthesizing numerous compounds in which the transition metal exhibits a reduced

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oxidation state. As a result of our investigation, \(\text{A}^{II}(\text{Sb}^{6+}, \text{Fe}^{3+})_{2}(\text{PO}_4)_{2}\) (\(\text{A}^{II} = \text{Sr}, \text{Pb}, \text{Ba}\)) and \(\text{Ba}^{4+}(\text{Nb}^{5+}, \text{M}^{3+})_{2}(\text{PO}_4)_{2}\) (\(\text{M}^{3+} = \text{Al}, \text{Cr}, \text{Fe}, \text{In}\)) compounds have been synthesized and characterized by some of us. The crystal structure of \(\text{Ba}^{4+}(\text{Sb}^{6+}, \text{Fe}^{3+})_{2}(\text{PO}_4)_{2}\) and \(\text{Ba}^{4+}(\text{Nb}^{5+}, \text{M}^{3+})_{2}(\text{PO}_4)_{2}\) belongs to the true-yavapaiite structure (\(\text{C}2/m\) space group, \(Z = 2\)). In contrast, \(\text{A}^{II}(\text{Sb}^{6+}, \text{Fe}^{3+})_{2}(\text{PO}_4)_{2}\) (\(\text{A}^{II} = \text{Sr}, \text{Pb}, \text{Ba}\)) phases exhibit a distorted yavapaiite structure type with \(\text{C}2/c\) space group (\(Z = 4\)). So, in a continuation of our scientific search, we synthesized new \(\text{A}^{II}(\text{Sb}^{6+}, \text{Cr}^{3+})_{2}(\text{PO}_4)_{2}\) (\(\text{A}^{II} = \text{Sr}, \text{Pb}, \text{Ba}\)) yavapaiite phases. The obtained materials have been structurally characterized by using X-ray powder diffraction. In order to get further structural information about the nature of bonding in the crystalline solids, Infrared and Raman spectroscopic study of selected phases is also presented.

### 2. Experimental

\(\text{A}^{II}(\text{Sb}_{0.5}\text{Cr}_{0.5})(\text{PO}_4)_{2}\) (\(\text{A}^{II} = \text{Ba, Sr, Pb}\)) materials were prepared by conventional solid-state reaction from stoichiometric amounts of carbonates \(\text{SrCO}_3\) (Riedel-de Haën, 99%), \(\text{BaCO}_3\) (Riedel-de Haën, 99%) or nitrates \(\text{Pb(NO}_3)_2\) (Prolabo, 99%), \(\text{Cr}_2\text{O}_3\) (Prolabo, 99%), \(\text{Sb}_2\text{O}_3\) (Riedel-de Haën, 99.9%), \(\text{NH}_4\text{H}_2\text{PO}_4\) (Riedel-de Haën, 99%). Powders were mixed and ground and then heated in an air atmosphere between 200 and 750°C. To obtain a pure sample, a final treatment at 800°C for 48 hours, with periodic intermediate regrinding, is necessary.

X-ray powder diffraction data (XRPD) for \(\text{A}^{II}(\text{Sb}_{0.5}\text{Cr}_{0.5})(\text{PO}_4)_{2}\) (\(\text{A}^{II} = \text{Ba, Sr, Pb}\)) were collected, at room temperature, on X-Ray diffractometer (PANalytical X'Pert Pro) using monochromatized CuK\(\alpha\) radiation (50 kV, 40 mA). The patterns were scanned in the 10–90° 2\(\theta\) range with a counting time of 30 s per step. The full pattern refinements were performed by the Rietveld refinement method with the aid of FullProf program 35 embedded in WinPlotr software. A pseudo-Voigt function described the peak shape, and the background level was modeled by linear interpolation. The refined parameters were: scale factor, zero shift, lattice constants, peak profile, asymmetry parameters, atomic positions, and independent isotropic atomic displacement parameters. Infrared spectroscopic analyses were performed using a Bruker’s VERTEX 70 spectrometer. All measurements were performed at room temperature. Raman scattering spectra were recorded on powder with a HORIBA, LabRAM HR Evolution spectrometer, equipped with an ionized argon laser. The finely ground substance is spread on a glass slide. The electrodes were illuminated with a 532 nm beam in ambient air.

### 3. Results and Discussion

#### 3.1. Rietveld refinement and structural description of \(\text{Ba}(\text{Sb}_{0.5}\text{Cr}_{0.5})(\text{PO}_4)_{2}\)

According to the literature data, most barium orthophosphate compounds have been mentioned as entirely isotopic with true-yavapaiite (T.Y). Analysis of the powder XRD pattern using the Rietveld refinement in Le Bail’s of \([\text{BaSbCr}]\) phase revealed the presence of a crystallized phase exhibiting peak positions lines that match with \(\text{Ba}(\text{Sb}_{0.5}\text{Cr}_{0.5})(\text{PO}_4)_{2}\); monoclinic phase 33. Thus, starting structural parameters for the Rietveld refinement were taken from the true-yavapaiite phase mentioned above 33. This refinement yielded to acceptable reliability factors (i.e., \(R_{wp} = 8.9\%\); \(R_{p} = 6.4\%\); \(R_{B} = 3.7\%\); \(R_{F} = 2.5\%\)). The main refined parameters are given in Table 1. Observed, calculated, and difference XRD patterns of \([\text{BaSbCr}]\) phase are presented in Figure 1.

| Atom     | Site | Wyckoff positions | \(B_{	ext{int}}(\text{Å}^2)\) | Occupancy |
|----------|------|-------------------|-------------------------------|-----------|
| \(\text{Ba}\) | 2c   | 0                 | 2.1(1)                        | 1         |
| \(\text{Sb(Cr)}\) | 2a   | 0                 | 2.0(5)                        | 0.5/0.5   |
| \(\text{P}\) | 4i   | 0.3672(2)         | 2.014(3)                      | 2.1(5)    |
| \(\text{O(1)}\) | 4i   | 0.2384(6)         | 0.0503(4)                     | 1.2(1)    |
| \(\text{O(2)}\) | 4i   | 0.3050(6)         | 0.3867(6)                     | 1.2(1)    |
| \(\text{O(3)}\) | 8j   | 0.4761(5)         | 0.2483(5)                     | 0.1862(5) |

Table 1. Crystallographic data of \(\text{Ba}(\text{Sb}_{0.5}\text{Cr}_{0.5})(\text{PO}_4)_{2}\) (\(\text{C}2/m\) space group, \(Z = 2\)).
The crystal structure of Ba(Sb\textsubscript{0.5}Cr\textsubscript{0.5})(PO\textsubscript{4})\textsubscript{2} can be described as made of layers of Ba\textsuperscript{II} cations in tenfold coordination, alternating with dense slabs built up of corner-connected of M\textsuperscript{IV}O\textsubscript{6} octahedra and PO\textsubscript{4} tetrahedra (Figure 2). Note that each PO\textsubscript{4} tetrahedron presents one free oxygen pointing out of the layer. Sb\textsuperscript{V} and Cr\textsuperscript{III} cations are octahedrally surrounded by nine oxygen atoms belonging to six PO\textsubscript{4} groups to form Sb(Cr)O\textsubscript{6} octahedral geometry. Reciprocally, each PO\textsubscript{4} tetrahedron is connected to three Sb(Cr)O\textsubscript{6} octahedra via vertex-sharing oxygen atoms. Oxygen atoms tenfold coordinate the Ba\textsuperscript{II} cation from eight bidentate PO\textsubscript{4} groups, and the other two oxygen atoms belong to the two other unidentate PO\textsubscript{4} groups. The BaO\textsubscript{10} is linked to six other BaO\textsubscript{10} adjacent polyhedra via edges and corners.

The main distances values of [BaSbCr] are reported in Table 2. The analysis of Ba-O distances values, within BaO\textsubscript{10} polyhedra, shows that they can be considered as formed by six slightly shortest values ranging from 2.695(6) to 2.767(4) Å and four longer one with an average value of 3.123(3) Å. Thus, the coordination of barium cations can be regarded as 6+4 type. Obtained Sb(Cr)-O bond distances values are comparable to those found for other antimony and chromium phosphate. Mean P-O bond lengths value (i.e.,1.55(1) Å) is fairly regular, and in good agreement with those usually found in the
yavapaiite-type phases. For more structural information, the bond valence sums (BVS) were calculated from Brown's method. Calculated values for Ba, Cr, Sb, and P are relatively compatible with their oxidation state in Ba(Sb0.5Cr0.5)(PO4)2 (Table 2). X-ray data, collected from the ‘observed intensities’ of the Rietveld refinement (CuKα1: 1.5406 Å), of [BaSbCr] compound, are listed in Table 3.

### Table 2. Selected interatomic distances (Å) and calculated Bond Valence Sum (BVS) for Ba(Sb0.5Cr0.5)(PO4)2

| BVS(Sb(Cr)) | P-O distances (Å) | Ba-O distances (Å) |
|-------------|-------------------|--------------------|
| BaSb0.5Cr0.5(PO4)2 |                     |                    |
| 2xSb(Cr)-O(2) | 1.950(4)          | 2xBa-O(1) = 2.695(5) |
| 4xSb(Cr)-O(3) | 1.971(5)          | 4xBa-O(3) = 2.767(4) |
| Aver. <Sb(Cr)-O> | 1.96(1)          | Aver. <Ba-O> = 2.90(1) |

### Table 3. Powder diffraction data of Ba(Sb0.5Cr0.5)(PO4)2 compound. Diffraction lines with Iobs< 1 are omitted (CuKα1: λ = 1.5406 Å).

| Ba(Sb0.50Cr0.50)(PO4)2 | 100 I/I0 (cal.) |
|------------------------|-----------------|
| hkl | dobs (Å) | 100 I/I0 (obs.) | HkI | dobs (Å) | 100 I/I0 (obs.) | 100 I/I0 (cal.) |
|------|--------|-----------------|-----|--------|-----------------|-----------------|
| 001  | 7.7794 | 5               | 312 | 1.9819 | 4              | 5              |
| 110  | 4.3634 | 100             | 004 | 1.9448 | 7              | 8              |
| 200  | 4.0582 | 61              | -222 | 1.9371 | 16             | 12             |
| 002  | 3.8897 | 33              | 222  | 1.8703 | 11             | 9              |
| -111 | 3.8742 | 19              | -402 | 1.8583 | 4              | 4              |
| 111  | 3.7405 | 36              | -313 | 1.8231 | 3              | 2              |
| -201 | 3.7165 | 22              | -204 | 1.8086 | 12             | 11             |
| 201  | 3.4902 | 5               | -114 | 1.8042 | 13             | 12             |
| -112 | 2.9647 | 77              | 114  | 1.7498 | 10             | 10             |
| -202 | 2.9220 | 9               | 402  | 1.7451 | 9              | 11             |
| 112  | 2.8459 | 53              | 130  | 1.6872 | 4              | 3              |
| 202  | 2.7066 | 11              | 131  | 1.6435 | 1              | 1              |
| 003  | 2.5931 | 22              | 420  | 1.5967 | 2              | 1              |
| 020  | 2.5874 | 26              | -314 | 1.5631 | 4              | 3              |
| 310  | 2.3976 | 36              | -132 | 1.5568 | 11             | 10             |
| -311 | 2.3362 | 3               | 024  | 1.5546 | 11             | 10             |
| -203 | 2.2651 | 2               | 510  | 1.5489 | 7              | 7              |
| 311  | 2.2487 | 2               | 132  | 1.5390 | 6              | 4              |
| 220  | 2.1817 | 3               | -422 | 1.5093 | 8              | 5              |
| 022  | 2.1543 | 18              | -224 | 1.4823 | 7              | 5              |
| -221 | 2.1235 | 5               | -512 | 1.4765 | 3              | 2              |
| 203  | 2.1130 | 9               | 314  | 1.4627 | 3              | 3              |
| -312 | 2.1057 | 12              | -404 | 1.4610 | 5              | 4              |

### 3.2. Rietveld refinement and structural description of A(Sb0.5Cr0.5)(PO4)2 (A = Sr, Pb) phases

The Rietveld refinement in Profil Matching of lead and strontium phases with the previous structural model (i.e., C2/m space group and Z = 2) leads to high-reliability factors. Furthermore, several small XRD diffraction lines (e.g., at 2θ ~ 18.17° and 28.33° for [PbSbCr]) remain unindexed, which appeared as the h+1l=2n+1 superstructure reflections of the C2/c doubled cell comparable to the Pb(Fe0.5Sb0.5)(PO4)2 material reported by Aatiq et al. It is of interest to note that the rotation of the oxygen atoms around their coordination polyhedra is the force driving for the crystal lattice distortion of [ASbCr] (A = Sr, Pb) concerning that of [BaSbCr]. Indeed, these alternating rotations of oxygen atoms cause a doubling of the crystal lattice and consequently lead to the appearance of superstructure lines in the [ASbCr] (A = Sr, Pb) X-ray powder diffraction spectra. Note that about the International Tables for Crystallography data, the C2/c (Z=4) is a subgroup of the C2/m (Z=2) so, the apparent relationship of the lattices and structures between the true (T, Y) (i.e., [BaSbCr]) and the distorted (D,Y) (i.e., [ASbCr] (A = Pb, Sr)) the
following vectorial equations link yavapaiite forms:

\[ a_{(x,y)} = 2a_{(x,y)} + b_{(x,y)} + c_{(x,y)} = a_{(x,y)} \]

Thus, the structural model suggested for [PbFeSb] was chosen as starting model for the Rietveld refinement, with the following distribution for the atomic positions: A \(^{II}\) (A = Pb, Sr) in 4e (0, -y, 3/4), Sb(Cr) in 4c (1/4, 1/4, 0) and P, O(1), O(2), O(3) and O(4) in 8f (x, y, z) positions. Structural refinement using the aforementioned model gives rise to satisfactory results. Good agreements between the experimental and calculated patterns are seen in Figure 3. The structural data are reported in Tables 4 and 5 for [SrSbCr] and [PbSbCr], respectively.

Given that the structures of A \(^{II}\)(Sb\(_{0.5}Cr_{0.5}\))(PO\(_{4}\))\(_{2}\) (A \(^{II}\) = Sr, Pb) phases are comparable, we have select to describe only the structure of [PbSbCr].

**Table 4.** Crystallographic data of Sr(Sb\(_{0.5}Cr_{0.5}\))(PO\(_{4}\))\(_{2}\) (C2/c space group, Z=4).

| Atom   | Site | Wyckoff positions | B\(_{iso}\)(\(\AA^2\)) | Occupancy |
|--------|------|------------------|-----------------|-----------|
| Sr     | 4e   | 0                | 0.2916(6)       | 0.75      | 2.1(9) | 1 |
| Sb(Cr) | 4c   | 0.25             | 0.25            | 0         | 1.0(7) | 0.5/0.5 |
| P      | 8f   | 0.1410(2)        | 0.7561(6)       | 0.7561(3) | 0.9(9) | 1 |
| O(1)   | 8f   | 0.1419(7)        | 1.0124(5)       | 0.8464(1) | 0.8(1) | 1 |
| O(2)   | 8f   | 0.1551(6)        | 0.5412(5)       | 0.8940(4) | 1.8(1) | 1 |
| O(3)   | 8f   | 0.2217(3)        | 0.7779(2)       | 0.7161(8) | 1.8(1) | 1 |
| O(4)   | 8f   | 0.0482(3)        | 0.7265(2)       | 0.5982(7) | 1.8(1) | 1 |

**Table 5.** Crystallographic data of Pb(Sb\(_{0.5}Cr_{0.5}\))(PO\(_{4}\))\(_{2}\) (C2/c space group, Z=4).

| Atom   | Site | Wyckoff positions | B\(_{iso}\)(\(\AA^2\)) | Occupancy |
|--------|------|------------------|-----------------|-----------|
| Pb     | 4e   | 0                | 0.3140(4)       | 0.75      | 4.5 | 1 |
| Sb(Cr) | 4c   | 0.25             | 0.25            | 0         | 2.6(1) | 0.5/0.5 |
| P      | 8f   | 0.1461(3)        | 0.7569(6)       | 0.7597(8) | 2.5(1) | 1 |
| O(1)   | 8f   | 0.1473(6)        | 1.0154(2)       | 0.8690(2) | 3.0(1) | 1 |
| O(2)   | 8f   | 0.1640(6)        | 0.5464(2)       | 0.9036(8) | 2.0(1) | 1 |
| O(3)   | 8f   | 0.2245(7)        | 0.7708(3)       | 0.7065(7) | 2.0(1) | 1 |
| O(4)   | 8f   | 0.0485(4)        | 0.7287(2)       | 0.6155(6) | 2.0(1) | 1 |

Indeed, the crystal structure can be considered as composed of an alternation of anionic [(Sb\(_{0.5}Cr_{0.5}\))(PO\(_{4}\))\(_{2}\)]\(^{7-}\) sheets running parallel to (bc) plane built up of corner-linked Sb(Cr)O\(_6\) octahedra and PO\(_4\) tetrahedra. While the Pb\(^{II}\) cationic sheets are located amongst [(Sb\(_{0.5}Cr_{0.5}\))(PO\(_{4}\))\(_{2}\)]\(^{7-}\) and join them through columnic interactions between the Pb\(^{II}\) and O\(^{II}\) ions to create the 3D framework of [PbSbCr] (Figures 4a and 4b). The lead atom is surrounded by ten oxygen atoms belonging to six PO\(_4\) groups. Six vertices of different PO\(_4\) groups octahedrally coordinate each Sb(Cr)O\(_6\). In such a
way, each PO₄ tetrahedra is vertex-connected to three Sb(Cr)O₆ octahedra; the remaining unshared oxygen atoms of each tetrahedron has one vertex points into the interlayer where the Pb²⁺ cation takes place. Even though [ASbCr] (A = Sr, Pb) compounds crystallize in the C2/c space group, and its a-axis parameter is double compared to that of [BaSbCr] (C2/m space group, Z=2), the crystal structure of the three compounds has a similar 3D network.

Figure 3. Experimental (••••) calculated (— — —), and difference (— — —) profile of the XRD patterns of Aᴵᴵ(Sb₀.₅Cr₀.₅)(PO₄)₂ (Aᴵᴵ = Sr, Pb).

Figure 4. (a) View of the structure of Pb(Sb₀.₅Cr₀.₅)(PO₄)₂ showing Pb atoms, Sb(Cr)O₆ octahedra and PO₄ tetrahedra; (b) Projection in (ac) plane.

Table 6. Selected interatomic distances (Å) and calculated Bond Valence Sum (BVS) for Sr(Sb₀.₅Cr₀.₅)(PO₄)₂.

| SrSb₀.₅Cr₀.₅(PO₄)₂ | P-O distances (Å) | Sr-O distances (Å) |
|-------------------|-------------------|-------------------|
| Sb(Cr)-O distances (Å) | P-O(1) = 1.510(5) | 2xSr-O(1) = 2.583(3) |
| 2xSb(Cr)-O(1) = 2.071(4) | P-O(2) = 1.513(4) | 2xSr-O(2) = 2.658(3) |
| 2xSb(Cr)-O(2) = 2.067(5) | P-O(3) = 1.504(5) | 2xSr-O(4) = 2.569(3) |
| 2xSb(Cr)-O(3) = 1.992(5) | P-O(4) = 1.512(5) | 2xSr-O(4) = 2.849(3) |
| Aver. <Sb(Fe)-O> = 2.04(1) | Aver. <P-O> = 1.51(1) | Aver. <Sr-O> = 2.81(2) |

|  | Sr-O distances (Å) |
|-------------------|-------------------|
| BVS(Sb(Cr)) = 3.6 | BVS (P) = 5.3 |
| (should be 4) | BVS (Sr) = 1.9 |
Table 7. Selected interatomic distances (Å) and calculated Bond Valence Sum (BVS) for Pb(Sb0.5Cr0.5)(PO4)2.

| PbSb0.5Cr0.5(PO4)2 | P-O distances (Å) | Pb-O distances (Å) |
|---------------------|--------------------|--------------------|
| Sb-0 distances (Å)  | P-O(1) = 1.594(6)  | 2×Pb-O(1) = 2.700(6) |
| 2xSb(Cr)-O(1) = 1.993(5) | P-O(2) = 1.528(5)  | 2×Pb-O(2) = 2.733(6) |
| 2xSb(Cr)-O(2) = 2.010(5) | P-O(3) = 1.544(5)  | 2×Pb-O(4) = 2.692(6) |
| Aver.<Sb(Cr)-O> = 1.97(1) | P-O(4) = 1.553(5)  | 2×Pb-O(4) = 3.443(5) |
| Bond Valence Sums (BVS) | BVS (P) = 4.8 | Aver. <Pb-O> = 2.86(1) |
| BVS(Sb(Cr)) = 4.3 (should be 4) | | |

Table 8. Powder diffraction data of Sr(Sb0.5Cr0.5)(PO4)2 compound. Diffraction lines with Iobs < 1 are omitted (CuKα; λ = 1.5406 Å).

| Sr(Sb0.5Cr0.5)(PO4)2 | hkl | dobs (Å) | 100 I/Io (obs.) | 100 I/Io (cal.) | hkl | dobs (Å) | 100 I/Io (obs.) | 100 I/Io (cal.) |
|---------------------|-----|----------|----------------|----------------|-----|----------|----------------|----------------|
|                     | 2 0 0 | 7.4256 | 15 | 16 | 0 0 4 | 1.8090 | 5 | 5 |
|                     | 1 1 0 | 4.8769 | 5 | 3 | 6 2 0 | 1.7867 | 1 | 1 |
|                     | -1 1 1 | 4.3426 | 74 | 72 | 0 2 3 | 1.7624 | 3 | 3 |
|                     | -2 0 2 | 4.0141 | 58 | 64 | 3 1 3 | 1.7588 | 4 | 4 |
|                     | 1 1 1 | 3.7997 | 36 | 29 | 7 1 1 | 1.7262 | 15 | 16 |
|                     | 4 0 0 | 3.7128 | 20 | 20 | -8 0 4 | 1.7252 | 19 | 20 |
|                     | -3 1 1 | 3.6996 | 33 | 33 | 6 0 2 | 1.7225 | 14 | 12 |
|                     | 0 0 2 | 3.6179 | 14 | 14 | -6 2 3 | 1.7174 | 11 | 8 |
|                     | 3 1 0 | 3.5733 | 5 | 3 | 1 3 0 | 1.7096 | 2 | 2 |
|                     | -4 0 2 | 3.4503 | 19 | 19 | -9 1 1 | 1.6884 | 6 | 7 |
|                     | -3 1 2 | 3.0713 | 3 | 3 | -1 3 1 | 1.6828 | 6 | 6 |
|                     | 3 1 1 | 2.8657 | 100 | 100 | 4 2 2 | 1.6577 | 2 | 2 |
|                     | 2 0 2 | 2.8060 | 9 | 5 | -10 0 2 | 1.6497 | 3 | 2 |
|                     | -5 1 1 | 2.7802 | 76 | 73 | 1 3 1 | 1.6454 | 4 | 4 |
|                     | -6 0 2 | 2.6518 | 8 | 9 | 1 1 4 | 1.6220 | 2 | 1 |
|                     | 0 2 0 | 2.5816 | 36 | 36 | 2 0 4 | 1.6040 | 2 | 2 |
|                     | 5 1 0 | 2.5746 | 24 | 23 | 2 2 3 | 1.6038 | 1 | 1 |
|                     | 6 0 0 | 2.4752 | 4 | 2 | -8 2 1 | 1.5924 | 2 | 1 |
|                     | 0 2 1 | 2.4315 | 3 | 1 | -4 2 4 | 1.5845 | 2 | 2 |
|                     | -3 1 3 | 2.3759 | 60 | 57 | -1 3 2 | 1.5766 | 2 | 2 |
|                     | 2 2 1 | 2.2167 | 6 | 4 | -3 3 2 | 1.5692 | 1 | 1 |
|                     | -4 2 1 | 2.1863 | 6 | 4 | -2 2 4 | 1.5640 | 3 | 2 |
|                     | 5 1 1 | 2.1793 | 5 | 4 | 3 3 1 | 1.5396 | 9 | 5 |
|                     | -2 2 2 | 2.1713 | 2 | 2 | -5 1 5 | 1.5332 | 7 | 6 |
|                     | 4 2 0 | 2.1196 | 28 | 22 | -5 3 1 | 1.5259 | 5 | 5 |
|                     | 0 2 2 | 2.1015 | 5 | 2 | 8 2 0 | 1.5072 | 5 | 4 |
|                     | -4 2 2 | 2.0671 | 2 | 2 | 5 1 3 | 1.4999 | 5 | 3 |
|                     | -8 0 2 | 2.0555 | 4 | 4 | -7 1 5 | 1.4857 | 12 | 10 |
|                     | 1 1 3 | 2.0485 | 16 | 12 | 10 0 0 | 1.4851 | 5 | 5 |
|                     | -4 0 4 | 2.0070 | 8 | 9 | 0 2 4 | 1.4815 | 11 | 10 |
|                     | -7 1 3 | 1.9570 | 5 | 6 | -3 3 3 | 1.4475 | 7 | 7 |
|                     | 4 2 1 | 1.9099 | 2 | 2 | -1 1 5 | 1.4450 | 7 | 7 |
|                     | 2 2 2 | 1.8999 | 17 | 13 | -8 2 4 | 1.4344 | 15 | 13 |
|                     | 8 0 0 | 1.8564 | 11 | 11 | 6 2 2 | 1.4329 | 10 | 10 |
|                     | -6 2 2 | 1.8489 | 20 | 17 | -11 1 3 | 1.4284 | 9 | 10 |
|                     | -5 1 4 | 1.8440 | 9 | 7 | 3 3 2 | 1.4093 | 1 | 1 |
|                     | -4 2 3 | 1.8347 | 2 | 2 | |

The main interatomic distances are listed in Tables 6 and 7 for [SrSbCr] and [PbSbCr], respectively. The AIII-O (AIII = Sr, Pb) distances in the AO10 polyhedra of both phases indicate that eight oxygen anions surround the AII cation with typical distances values ranging from 2.569(3) to 2.849(3) Å for [SrSbCr]. In the 2.692(6)-2.733(6) Å values range for [PbSbCr]. The two other AIII-O distance values
are relatively high (i.e., 3.412(3) Å for Sr-O distances and 3.443(5) Å for Pb-O ones) (Tables 6 and 7). Therefore, the coordination of lead and strontium atoms in both phases can be considered as 8+2 type. In both phases, the $A^{III}-O$ ($A =$ Sr, Pb) distances values are comparable to those already reported for PbTi(OPO$_4$)$_2$ and SrTi(OPO$_4$)$_2$ phases. Sb(Cr)-O bond lengths within SbCr(O)O$_8$ octahedra range between 1.900(8) and 2.071(9) Å for both compounds. Obtained values are compatible with those calculated from the ionic radii of Sb$^{III}$ and Cr$^{III}$ cations in six coordination (Tables 6 and 7). In the case of PO$_4$ tetrahedra, obtained P-O bond distances for both [A$\text{SbCr}$] ($A^{III} =$ Sr, Pb) are comparable to those generally observed in orthophosphates. Bonds valence sums (BVS) calculated from Brown's method $^{37}$, indicated that lead, strontium, antimony, chromium, and phosphorus atoms are compatible with their expected oxidation state (i.e., Pb$^{II}$, Sr$^{II}$, Cr$^{III}$, Sb$^{IV}$) and P$^{VII}$. X-ray data, collected from the ‘observed intensities’ of the Rietveld refinement (CuKα1: 1.5406 Å), for [SrSbCr] compound, as a selected example, are listed in Table 8.

### 3.3. Infrared and Raman vibrational study

Infrared and Raman spectra of [BaSbCr] and [PbSbCr] are shown in Figures 5(a) and 5(b) respectively. According to literature data of phosphates with yavapaiite phases $^{33,34,39}$, bands related to PO$_4$ unit, in A(Sb$\text{SbCr}$)O$_5$(PO$_4$)$_2$ ($A^{III} =$ Ba, Pb), are relatively strong compared to that of Sb(Cr)-O one within SbCr(O)O$_8$ octahedra. Thus, assignment of the four ($\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$) PO$_4$ modes will take these last remarks into account. Note that in [ASbCr] ($A =$ Ba, Pb) materials, P–O distances vary between 1.52 and 1.59 Å with a mean P–O distance of 1.55 Å. Popovic et al. have formulated the following empirical relation $[\nu_{PO}(\text{cm}^{-1})] = 224500 \exp(-R/28.35)$, which connects P–O bond lengths and stretching frequencies where $R$ is the P–O bond lengths in Picometer (pm) $^{40}$. By replacing obtained P-O distance values in the above expression, the calculated frequencies values corresponding to both phosphates are ranging between 850 and 1060 cm$^{-1}$. These last values are relatively in agreement with those observed experimentally, between 865 and 1073 cm$^{-1}$ in the IR and Raman spectra (Figure 5). Thus the symmetric non-degenerate PO stretching modes ($\nu_{1(PO)}$) can be assigned to bands ranging between 860-990 cm$^{-1}$ while antisymmetric and doubly degenerate PO stretching ($\nu_{2(PO)}$) are located in the 1006-1073 cm$^{-1}$ range. However, the possibility of coupling between $\nu_{1(PO)}$ and $\nu_{2(PO)}$ stretching bands, around 1000 cm$^{-1}$, cannot be excluded. Bands existing between 400 and 497 cm$^{-1}$ are attributed to the symmetric, triply degenerate OPO bending ($\nu_{1(OPO)}$) modes. In contrast, those ranging between 530-615 cm$^{-1}$ are attributed to the triply degenerate, antisymmetric, and harmonic OPO bending ($\nu_{2(OPO)}$). The bands detected between 646 and 668 cm$^{-1}$ in IR and Raman spectra of both compounds can be associated with the stretching Sb–O vibrations. Similar Sb-O vibrations are already found around 650 cm$^{-1}$ for AF$\text{SbCr}$, Sb$\text{SbCr}$ (A = Sr, Pb) $^{31}$, at 630 cm$^{-1}$ for SrSb$\text{SbFe}$ (PO$_4$)$_2$ and Sb$\text{SbFe}$ (PO$_4$)$_2$ phases $^{27}$ and around 640 cm$^{-1}$ for MnSb$\text{SbFe}$ (PO$_4$)$_2$ ($M =$ Al, Fe, Cr) $^{41}$ and Mn$_2$SbFe (PO$_4$)$_2$ ($M =$ Mg, Ni) $^{42}$. The Raman bands observed at 366 cm$^{-1}$ could be assigned to Cr$^{III}$-O stretching modes of vibrations similar to those observed around 350 cm$^{-1}$ for Cr$^{II}$-O stretching modes in Na$_3$Cr$\text{SbFe}$ (PO$_4$)$_4$ $^{43}$. In low-frequency modes and more precisely for values below 270 cm$^{-1}$, the translational modes of A$^{II}$ (A = Sr, Pb), Cr$^{III}$, and Sb$^{V+}$ ions, as well as vibrational modes of PO$_4$, CrO$_6$, and SbO$_6$ groups, should be expected.

![Figure 5. Infrared (a) and Raman (b) spectra of A$^{III}$(Sb$\text{SbCr}$) (PO$_4$)$_2$ (A$^{III} =$ Ba, Pb) phases](image-url)

### 4. Conclusion

In the present work, the crystal structure of the three new A$^{III}$(Sb$\text{SbCr}$) (PO$_4$)$_2$ ($A^{III} =$ Ba, Sr, Pb) compounds have been determined. The results of the Rietveld refinement show that Ba(Sb$\text{SbCr}$) (PO$_4$)$_2$ crystallizes in monoclinic system with C2/m space
group \((Z=2)\) while \(A^2\left(Sb_{20}C_{60}\right)(PO_4)_{32}\) \((A^2=\text{Sr, Pb})\) phases have a monoclinic system with \(C2/c\) space group \((Z=4)\). The three studied compounds crystallize in the yavapaiite-type structure. Even though \([\text{ASbCr}]\) \((A=\text{Sr, Pb})\) compounds form in the \(C2/c\) space group and its \(a\)-axis parameter is double compared to that found for \([\text{BaSbCr}]\), the crystal structure of the three compounds has a similar 3D network. Observed Infrared and Raman bands are assigned according to the vibrations of \(\text{Sb(Cr)}O_6\) and \(\text{PO}_4\) polyhedra.

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