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# Structure, Infrared and Raman spectroscopic studies of newly synthetic $\mathbf{A}^{\mathrm{II}}\left(\mathbf{S b}^{\mathbf{V}}{ }_{0.50} \mathrm{Fe}^{\mathrm{III}}{ }_{0.50}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathbf{A}=\mathrm{Ba}, \mathrm{Sr}, \mathrm{Pb})$ phosphates with yavapaiite structure 

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#### Abstract

The synthesis and structural study of three new $\mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Ba}, \mathrm{Sr}$, Pb, ) phosphates belonging to the $\mathrm{A}-\mathrm{Sb}-\mathrm{Fe}-\mathrm{P}-\mathrm{O}$ system were reported here for the first time. Structures of [Ba], $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ compounds, obtained by solid state reaction in air atmosphere, were determined at room temperature from X-ray powder diffraction using the Rietveld method. $\mathrm{Ba}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}[\mathrm{Ba}]$ features the yavapaiite-type structure, with space group $C 2 / m, Z=2$ and $a=8.1568(4) \AA ; b=5.1996(3) \AA$ $\mathrm{c}=7.8290(4) \AA ; \beta=94.53(1)^{\circ} . \mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Sr}, \mathrm{Pb})$ compounds have a distorted yavapaiite structure with space group $C 2 / c, Z=4$ and $a=16.5215(2) \AA$; $\mathrm{b}=5.1891(1) \AA \quad \mathrm{c}=8.0489(1) \AA ; \quad \beta=115.70(1)^{\circ} \quad$ for $\quad[\mathrm{Sr}] ; \quad \mathrm{a}=16.6925(2) \AA$; $\mathrm{b}=5.1832(1) \AA \mathrm{c}=8.1215(1) \AA ; \beta=115.03(1)^{\circ}$ for $[\mathrm{Pb}]$. Raman and Infrared spectroscopic study was used to obtain further structural information about the nature of bonding in selected compositions.


Keywords: Antimony and Iron phosphate; yavapaiite structure; Raman and IR spectroscopy; Rietveld analysis.

Abbreviations: $\quad \mathrm{Ba}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}=[\mathrm{Ba}], \quad \mathrm{Sr}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}=[\mathrm{Sr}]$, $\mathrm{Pb}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}=[\mathrm{Pb}], T Y=$ True Yavapaiite, $D Y=$ Distorted Yavapaiite.

## Introduction

Crystal structures of $\mathrm{A}_{(1-\mathrm{x})} \mathrm{A}^{\prime}{ }_{\mathrm{x}} \mathrm{PO}_{4}$ phases have been revealed in previous studies. Such materials can include a mixing of $A^{\mathrm{II}} / A^{\text {,lV }}$ ions leading to $\left(A_{0.5}^{\mathrm{II}} A^{\mathrm{IV}}{ }_{0.5}\right) \mathrm{PO}_{4}$ phases [1-3] or a mixture of $\mathrm{A}^{\mathrm{II}}, \mathrm{A}^{\text {,III }}$ and $\mathrm{A}^{\text {, }}$ IV ions as in the case of $\mathrm{A}^{\mathrm{II}}{ }_{1 / 3} \mathrm{~A}^{, \mathrm{III}}{ }_{1 / 3} \mathrm{~A}^{,, \mathrm{IV}}{ }_{1 / 3} \mathrm{PO}_{4}\left(A^{\mathrm{II}}=\mathrm{Mg}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Sr} ; A^{, \mathrm{III}}=\mathrm{Sm}, \mathrm{Gd}, \mathrm{Nd} ; A^{,}{ }^{, \mathrm{IV}}=\mathrm{Zr}, \mathrm{Ce}, \mathrm{Th}\right)$ compounds [4]. As a result of various cationic substitution in A sites of $\mathrm{A}^{\mathrm{III}} \mathrm{PO}_{4}$ phases, new family of oxides crystallizing in several structural types as Monazite, Zircon (Xenotime), Scheelite, Cheralite, Nasicon and Yavapaiite type compounds have been synthesized and characterized [1-18]. For smaller $\mathrm{M}^{\mathrm{IV}}$ ions, as in the $\mathrm{Ba}^{\mathrm{II}}{ }_{0.5} \mathrm{M}^{\mathrm{IV}}{ }_{0.5} \mathrm{PO}_{4}\left(\mathrm{M}^{\mathrm{IV}}=\mathrm{Ti}, \mathrm{Zr}, \mathrm{Hf}, \mathrm{Ge}, \mathrm{Sn}, \mathrm{Mo}\right)$ series, a monoclinic structure isotypic of the $\mathrm{K}_{0.5} \mathrm{Fe}_{0.5} \mathrm{SO}_{4}$ yavapaïte ( $C 2 / m$ space group) is obtained [6-9]. Note that these phases have a structure which is made of layers of $\mathrm{Ba}^{\mathrm{II}}$ cations in tenfold coordination, alternating with dense slabs built up of corner-connected of $\mathrm{M}^{\mathrm{IV}} \mathrm{O}_{6}$ octahedra and $\mathrm{PO}_{4}$ tetrahedra. This structure changes into a trigonal one at high temperature ( $P-3 \mathrm{~m} 1$ ) through a simple mechanism involving the unfolding of the $\left[\mathrm{M}\left(\mathrm{PO}_{4}\right)_{2}\right]_{\mathrm{n}}{ }^{2-}$ layers [19]. Numerous compounds among the $\mathrm{A}^{\mathrm{I}} \mathrm{M}^{\mathrm{IV}}\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Ba}, \mathrm{Pb}, \mathrm{Sr}, \mathrm{Ca} ; \mathrm{M}=\mathrm{Ge}, \mathrm{Ti}, \mathrm{Mo}$, $\mathrm{Zr}, \mathrm{Sn}, \mathrm{Pu}, \mathrm{Np}, \mathrm{U}, \mathrm{Th})$ family have structures which are related to the yavapaiite type structure. In fact, their structure is strongly dependant to the nature and/or size of the $\mathrm{A}^{\mathrm{II}}$ and $\mathrm{M}^{\mathrm{IV}}$ cations. More recently the relationships between composition and crystal structure of some $\mathrm{A}^{\mathrm{II}} \mathrm{M}^{\mathrm{IV}}\left(\mathrm{PO}_{4}\right)_{2}$ compounds are established [20]. Thus, Morin et al. have shown that the structure of $\mathrm{PbSn}\left(\mathrm{PO}_{4}\right)_{2}$ (space group $P 2_{1} / n$ ) is related to the yavapaiite type but the lead atoms are located in zigzag tunnels instead of layers [10]. This last structure was explained by the presence of an active $\mathrm{Pb}^{\mathrm{II}}$ lone pair which has been localized from electrostatic interactions. The $\mathrm{AZr}\left(\mathrm{PO}_{4}\right)_{2}(A=\mathrm{Ca}, \mathrm{Sr}$ and Ba$)$ have a different crystal structure at room temperature. Whereas $\mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}$ has a monoclinic yavapaiite structure, the $\operatorname{SrZr}\left(\mathrm{PO}_{4}\right)_{2}$ is triclinic ( $P \overline{1}$ space group) at room temperature and during heating, the compound shows two other polymorphic forms. $\mathrm{SrZr}\left(\mathrm{PO}_{4}\right)_{2}$ undergoes a triclinic to monoclinic transition at 405 K , and then to trigonal at 1196K [11]. Structural study of the $\mathrm{SrZr}\left(\mathrm{PO}_{4}\right)_{2}-\mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}$ system reveals the occurrence of two phase transitions during heating and the space group has changed from $P 2 / c$ to $C 2 / m$ at 400 K followed by monoclinic-to-hexagonal (or trigonal) transition at 1060 K [21]. The $P 2 / c-C 2 / m$ phase transition can be explained by the fact that the $P 2 / c$ space group is a Maximal klassengleiche subgroups of $C 2 / m$ ( $\mathrm{n}^{\circ} 12$ ) as a result of the loss of centring translations [22]. In the case of $\mathrm{CaZr}\left(\mathrm{PO}_{4}\right)_{2}$, the structure was first shown to be orthorhombic ( $P 2_{1} 2_{1} 2_{1}$ space group) and totally different from the yavapaite one [12]. Recently, their crystal structure has been revised by ab initio Rietveld analysis of X-ray powder diffraction data [13]. The structure is shown to be orthorhombic with space group Pna2 ${ }_{1}$. A reversible second order transition was confirmed by high temperature XRD analysis and the space group is (Pnma, $\mathrm{Z}=4$ ). Results of single-crystal X -ray diffraction analysis show that both $\mathrm{SrM}^{\mathrm{IV}}\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{M}=\mathrm{Ti}, \mathrm{Sn})$ materials are isostructural and crystallise in a distorted yavapaiite-structure ( $D Y$ ) with monoclinic $C 2 / c$ space group [14]. X-ray Rietveld analysis shows also that high-temperature $\beta-\operatorname{SrGe}\left(\mathrm{PO}_{4}\right)_{2}(C 2 / m$ space group) are isotypic with the true yavapaiite (TY) whereas the low-temperature $\alpha-\operatorname{SrGe}\left(\mathrm{PO}_{4}\right)_{2}$ and the $\mathrm{CaGe}\left(\mathrm{PO}_{4}\right)_{2}$ (C2/c space group) are distorted derivatives [8]. In the same context note that the phase transition from $C 2 / c$ to $C 2 / m$, which was reported for $\operatorname{SrGe}\left(\mathrm{PO}_{4}\right)_{2}$, is in good agreement with the fact that $C 2 / c$ is a maximal klassengleiche subgroups of $C 2 / m$ resulting from an enlargement of the unit cell [22]. Actinide barium phosphate, $\mathrm{Ba} A n^{\mathrm{IV}}\left(\mathrm{PO}_{4}\right)_{2}\left(A n^{\mathrm{IV}}=\mathrm{Th}, \mathrm{Np}\right)$ can also be seen as modified yavapaiite derivatives
with increased coordination numbers for Ba (XIV) and $\mathrm{Th} / \mathrm{Np}$ (VIII) [23]. On the other hand, $\mathrm{SrNp}\left(\mathrm{PO}_{4}\right)_{2}$ structure is more related to cheralite than to yavapaiite [24]. Recently intensive research activities, realized by some of us, are particularly focused on characterization of phosphates belonging to the $\mathrm{A}-\mathrm{Sb}-\mathrm{Fe}-\mathrm{P}-\mathrm{O}(\mathrm{A}=\mathrm{Mn}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Sr}$, $\mathrm{Pb})$ systems. Results of investigations led particularly to synthesis and characterization of a series of $\mathrm{A}^{\mathrm{II}}{ }_{0.50} \mathrm{Sb}^{\mathrm{V}} \mathrm{Fe}^{\mathrm{II}}\left(\mathrm{PO}_{4}\right)_{3}(\mathrm{~A}=\mathrm{Mn}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Sr}, \mathrm{Pb})$ Nasicon phases ( $R \overline{3}$ space group). Structures of $\mathrm{A}^{\mathrm{II}}{ }_{0.50} \mathrm{Sb}^{\mathrm{V}} \mathrm{Fe}^{\mathrm{III}}\left(\mathrm{PO}_{4}\right)_{3}$ compounds show an ordered distribution of $\mathrm{A}^{\text {II }}$ ions in M1 sites and $\mathrm{Sb}^{\mathrm{V}} / \mathrm{Fe}^{\mathrm{III}}$ ions within the Nasicon framework [15-18]. In our more recently reported works the phosphate $\mathrm{Ca}^{\mathrm{II}}{ }_{1 / 3} \mathrm{Bi}^{\mathrm{III}}{ }_{1 / 2} \mathrm{Sb}^{\mathrm{V}}{ }_{1 / 6} \mathrm{PO}_{4}$ which include a mixture of $A^{\mathrm{II}}, A^{, \mathrm{III}}$ and $A^{,,{ }^{\mathrm{V}}}$ ions has been isolated [25]. It crystallizes with the high temperature $\mathrm{BiPO}_{4}$ monoclinic structure variety ( $P 2_{1} / m$ space group). So, in a continuation of our scientific search for new materials likely to exhibit interesting physical properties and belonging to the A-Sb-Fe-P-O systems, synthesis and structural characterisation of the three $\mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}_{0.5} \mathrm{~V}^{-5} \mathrm{Fe}^{\mathrm{II}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Ba}, \mathrm{Sr}, \mathrm{Pb})$ compounds are undertaken. In order to obtain further structural information about the nature of bonding in the crystalline solids, a Raman and Infrared spectroscopic study of selected phases is also presented.

## II. Experimental

Syntheses of $\mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Ba}, \mathrm{Sr}, \mathrm{Pb})$ phases, abbreviated as [ Ba ], $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ respectively, were carried out using conventional solid-state reaction techniques. Powder crystalline samples were prepared from mixtures of $\mathrm{Fe}_{2} \mathrm{O}_{3}$ (Prolabo, $99 \%$ ), $\mathrm{Sb}_{2} \mathrm{O}_{3}$ (Riedel-de Haën, $99.9 \%$ ), $\mathrm{NH}_{4} \mathrm{H}_{2} \mathrm{PO}_{4}$ (Riedel-de Haën, $99 \%$ ) and carbonates $\mathrm{SrCO}_{3}, \mathrm{BaCO}_{3}$ (Riedel-de Haën, $99 \%$ ) or nitrates $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ (Prolabo, $99 \%$ ) in stoichiometric proportions. The mixtures were heated progressively with intermittent grinding at $200^{\circ} \mathrm{C}(12 \mathrm{~h}), 600{ }^{\circ} \mathrm{C}(24 \mathrm{~h}), 750{ }^{\circ} \mathrm{C}(24$ h) and $800^{\circ} \mathrm{C}(48 \mathrm{~h})$ in air. Additional treatments up to $850^{\circ} \mathrm{C}(48 \mathrm{~h})$ are necessary for obtaining a pure sample. The products of reaction were characterised by X-ray diffraction (XRD) at room temperature with a Panalytical X'Pert-PRO ( $\theta-2 \theta$ ) diffractometer; $(\mathrm{CuK} \alpha)$ radiation $(45 \mathrm{kV}, 40 \mathrm{~mA})$. The data were collected over 8 h from 10 to $140^{\circ}(2 \theta)$, in steps of $0.01313^{\circ}$ for $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ phases and from 5 to $100^{\circ}$ (20), in steps of $0.016711^{\circ}$ for [Ba]. The Rietveld refinement of the structure was performed using the Fullprof program [26].
The infrared spectra were recorded in the form of KBr pellets in the wave number range $1500-400 \mathrm{~cm}^{-1}$ using a Bruker's VERTEX 70 spectrometer and the Raman spectra are recorded on RENISHAW 1000B spectrometer in the wave number range $50-1500 \mathrm{~cm}^{-1}$. All the spectra have been recorded at room temperature.

## 3. Results and discussion

According to the literature data, peak positions and intensities of the XRPD patterns of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ were close to those of the room temperature variety of $\mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}(C 2 / m$ space group, $\mathrm{Z}=2)$ [6], therefore its XRPD patterns can be indexed, in a first approximation, on a similar monoclinic cell. In the case of the $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Sr}, \mathrm{Pb})$ monophosphates, the peak positions and relative intensities of the XRPD patterns were almost similar to those of the yavapaiite $\mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}$ type-phase; however several additional weak extra reflections were observed.

### 3.1. Rietveld refinement and structural description of $\mathrm{Ba}\left(\mathbf{S b}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ phase

The Rietveld analysis in Le Bail's (profile matching) mode confirmed that [Ba] phase is compatible with the $C 2 / m$ space group. So, initial starting parameters for the Rietveld refinement of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ were based on those already reported by Fukuda et al. for the true yavapaiite $(T Y) \mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}$ phase in the $C 2 / m$ space group [6]. Soft constraints were applied to the P-O distances. This refinement leads to acceptable reliability factors. A comparison of the experimental and calculated XRD profile of [Ba] material is given in Figure 1. Results of the Rietveld refinement and selected interatomic distances are given in Tables 1 and 2 respectively. X-ray powder diffraction data, obtained from the 'observed intensities' of the Rietveld refinement ( $\mathrm{CuK} \alpha 1: 1.54056 \AA$ ), of [Ba] phase is presented in Table 3.
Structure of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ consists of three types of polyhedra, $\mathrm{BaO}_{10}, \mathrm{PO}_{4}$ and $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ (Fig. 2). It can also be viewed as being composed of alternating edgesharing $\mathrm{BaO}_{10}$ bicapped square antiprism and $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ octahedra forming chains parallel to c-axis (Fig. 2b). There are five chains per unit cell (Fig. 2a). Each $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ octahedral is bound by its vertices to six $\mathrm{PO}_{4}$ tetrahedra and shares two of its edges (i.e., $\mathrm{O}(3)-\mathrm{O}(3)$ one) to two $\mathrm{BaO}_{10}$ polyhedra (Fig. 3a and 3b). The framework can be described as consisting of dense slabs of $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ octahedra and $\mathrm{PO}_{4}$ tetrahedra interconnected via corner-sharing, alternating along the c -axis with layers of Ba cations in ten-fold coordination (Fig. 2a and 2c). The ten oxygen atoms of each $\mathrm{BaO}_{10}$ polyhedron belong to six phosphate $\mathrm{PO}_{4}$ groups. Eight of the oxygen atoms come from four bidentate $\mathrm{PO}_{4}$ groups and the two other oxygens belong to the other two monodentate $\mathrm{PO}_{4}$ groups (Fig. 3a and Fig. 3b). Projection onto ab plane of the structure of [Ba] compound shows that every $\mathrm{BaO}_{10}$ polyhedron is connected, via its $\mathrm{O}(1)-\mathrm{O}(1)$ edges, to six neighbouring $\mathrm{BaO}_{10}$ polyhedra (Fig. 3c). The six neighbouring Ba -Ba distances values vary between $4.836(3) \AA$ and $5.200(3) \AA$. In fact, within each $\mathrm{BaO}_{10}$ polyhedron, the $\mathrm{Ba}-\mathrm{O}$ distances values can divide to two groups (Table 2). The first group contains six relatively shortest $\mathrm{Ba}-\mathrm{O}$ distances with values varying between 2.75 and $2.83 \AA$ whereas the second group is formed by four longest $\mathrm{Ba}-\mathrm{O}$ distances with a value of $3.11 \AA$. Therefore, the coordinence of Ba atoms in $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ can be considered as $6+4$. Obtained $\mathrm{Sb}(\mathrm{Fe})-\mathrm{O}$ interatomic distances are consistent with the crystal radii values in six coordination of $\mathrm{Sb}^{5+}$ and $\mathrm{Fe}^{3+}$ ions [27]. Note that the similarity of the crystal radii of $\mathrm{Fe}^{3+}(0.785 \AA$, $\mathrm{HS})$ and $\mathrm{Sb}^{5+}(0.74 \AA)$ ions is in favor of their distribution in the same site. P-O distances values match well with those typically observed in phosphates and the O-P-O angles vary between 105 and $118^{\circ}$. In order to have more structural information, the bond valence sum (BVS) based on bond strength analysis [28] for $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ were also computed. As shown in Table 2, the BVS values calculated for $\mathrm{Ba}, \mathrm{Fe}, \mathrm{Sb}$ and P sites are relatively consistent with the expected formal oxidation state of $\mathrm{Ba}^{2+}, \mathrm{Fe}^{3+}, \mathrm{Sb}^{5+}$ and $\mathrm{P}^{5+}$ ions.

### 3.2. Rietveld refinement and structural description of $\mathbf{A}\left(\mathbf{S b}_{0.5} \mathbf{F e}_{0.5}\right)\left(\mathbf{P O}_{4}\right)_{2}$ ( $\mathrm{A}=$ $\mathbf{S r}, \mathbf{P b}$ ) phases

An attempt to refine the diffraction patterns of the $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Sr}$, Pb ) compounds with the known $(T Y) \mathrm{BaZr}\left(\mathrm{PO}_{4}\right)_{2}$ structural model ( $C 2 / m$ space group) yielded to anomalous high reliability factors and intensity residuals. Figure 4a gives, for example, a comparison between observed, calculated, and difference XRD patterns of $[\mathrm{Pb}]$ in the $10-35^{\circ}$ ( $2 \theta$ range). Note that several small peaks which are indicated by a vertical arrow at the vicinity of $2 \theta^{\circ}$ equal to $18,25,28$ and 29 remain unindexed. In fact, in the case of $\mathrm{PbSb}_{0.5} \mathrm{Fe}_{0.5}\left(\mathrm{PO}_{4}\right)_{2}[\mathrm{~Pb}]$, this last refinement gives values of the unit-cell parameters $\left(a_{T Y}=8.121 \AA, b_{T Y}=5.181 \AA, c_{T Y}=7.587 \AA\right.$,
$\beta_{T Y}=94.0^{\circ}$ and $V_{T Y}=319 \AA^{3}$ ) which are relatively comparable to those obtained for the $(T Y) \mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
In the following section, the indexing of the $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ XRPD patterns was performed by means of the computer program DICVOL [29]. The first 40 peak positions, with a maximal absolute error of $0.02^{\circ}(2 \theta)$, were used as input data. For each phase, four monoclinic cells were found but only one result corresponding to a satisfactory figure of merit [29] is retained for the next stages of refinements. Note, for example, that in the case of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ the obtained unit-cell parameters are $a=8.121 \AA ; \quad b=5.181 \AA, \quad c=15.152 \AA, \quad \beta=94.0^{\circ}$ and $V=636 \AA^{3}$. The corresponding figures of merit are (M20/F20 $=146.5 / 236.9(0.0013,65)$ and $(\mathrm{F}(31)=48.7(0.0015,434))$. A careful analysis of this last result shows that the unit cell volume $\left(\mathrm{V}=636 \AA^{3}\right)$ is doubled as result of the doubling of the lattice parameter c in the $D Y$ (Distorted Yavapaiite) (ie.: $a_{D Y}=a_{T Y}=8.121 \AA, b_{D Y}=b_{T Y}=5.181 \AA$, $c_{D Y}=2 \times c_{T Y}=15.152 \AA$, and $\beta_{D Y}=94.0^{\circ}$ ). Until this stage of refinement, we can admit the existence of a group subgroup relationship between the space group of $[\mathrm{Pb}]$ and that of the $C 2 / m$ space group of the $T Y$. This last group-subgroup relation is a consequence direct of the enlargement of the unit cell [22]. The Check-Group program, which is integrated within the Fullprof-suite program [30], has been used to obtain the ordered list of possible space groups (see details in [Pb]Cell choice 3.spg as supplementary information file). Among the thirteen possible space groups (ie. $I 12 / a 1\left(\mathrm{n}^{\circ} 15\right), I 1 a 1\left(\mathrm{n}^{\circ} 9\right), I 121\left(\mathrm{n}^{\circ} 5\right), \operatorname{Ilm} 1\left(\mathrm{n}^{\circ} 8\right), I 12 / m 1\left(\mathrm{n}^{\circ} 12\right), P 12_{1} / c 1\left(\mathrm{n}^{\circ} 14\right), P 1 c 1$ ( $\mathrm{n}^{\circ} 7$ ), $P 12 / c 1\left(\mathrm{n}^{\circ} 13\right), \quad P 12_{1} 1\left(\mathrm{n}^{\circ} 4\right), \quad P 12_{1} / m 1\left(\mathrm{n}^{\circ} 11\right), \quad P 12 / m 1 \quad\left(\mathrm{n}^{\circ} 10\right), \quad P 1 m 1\left(\mathrm{n}^{\circ} 6\right)$, $\left.P 121\left(\mathrm{n}^{\circ} 3\right)\right)$, the $I 2 / a\left(\mathrm{n}^{\circ} 15\right)$ was found with the satisfactory merit factors. Given that I12/a1 (cell choice 3) is not a standard space group, the cell edges of the doubled-cell $D Y$ in the standard $C 2 / c\left(n^{\circ} 15\right)$ space group (cell choice 1) can be deduced by the following vectorial relations ( $a_{1}=-a_{3}-c_{3}, b_{1}=b_{3}, c_{1}=a_{3}$ ) (Fig. 5) [31]. Calculated values of the derived unit-cell parameters, in the standard $C 2 / c$ space group, are $a_{1}=16.681 \AA ; b_{1}=5.183 \AA, c_{1}=8.121 \AA$ and $\beta_{1}=115.04^{\circ}$. By using the following vectorial relations ( $a_{2}=-a_{1}-c_{1}, b_{2}=b_{1}, c_{2}=a_{1}$ ), values of the cell parameters in the non-standard A2/n ( $\mathrm{n}^{\circ} 15$ ) space groups (cell choice 2 ) can also be easily deduced (Fig. 5) (ie. $a_{2}=15.152 \AA, b_{2}=5.181 \AA, c_{2}=16.681 \AA$ and $\beta_{2}=150.96^{\circ}$ ). In order to reverified the correctness of the choice of the standard space group (cell choice 1 ), the use of Check-Group program with the unit-cell parameters of $a_{1}, b_{1}, c_{1}$ and $\beta_{1}=115.04^{\circ}$ was performed (see details in [Pb]Cell choice 1.spg as supplementary information file). The results show that among the thirteen possible space groups only the $C c\left(n^{\circ} 9\right)$ and $C 2 / c\left(n^{\circ} 15\right)$ space groups were found with the satisfactory merit factors (Table 4). Results of the Le Bail fitting (profile matching) program [32], realized in both $C c$ and $C 2 / c$ space group for the [ Sr$]$ and $[\mathrm{Pb}]$ materials, show comparable and lower reliability factors. Comparison between observed and calculated XRD patterns obtained from the Le Bail fitting program of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$, in the $10-35^{\circ}$ ( $2 \theta$ range), is given in figure 4 b . As it will be shown later, the unindexed reflections in figure 4 a appear as the $h+l=2 n+1$ superstructure reflections of a $C 2 / c$ doubled cell similar to that obtained by Zhao et al. for $\operatorname{SrTi}\left(\mathrm{PO}_{4}\right)_{2}$ [14]. Note that among the two possible $C c$ and $C 2 / c$ space groups, the choice of structural refinement in the high-symmetry $C 2 / c$ space group seems to be the most probable.
In the succeeding step of Rietveld refinement, the initial starting structural parameters were based on those already reported for $\mathrm{SrTi}\left(\mathrm{PO}_{4}\right)_{2}$ phase ( $C 2 / c$ space group). The A and $\mathrm{Sb}(\mathrm{Fe})$ atoms in $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ phases are supposed to occupy respectively the two special $4 \mathrm{e}(0,-\mathrm{y}, 3 / 4)$ and $4 \mathrm{c}(1 / 4,1 / 4,0)$ Wyckoff positions whereas the P , and O atoms are located in the general 8 f Wyckoff positions. During the Rietveld
refinement, a soft constraint were applied to the P-O distances and anisotropic thermal factors for Pb atoms in $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ phase are also used. For both [ Sr$]$ and [ Pb$]$ phases, the last hypothesis of structural refinement led to lower reliability factors (Tables 5 and 6). Observed, calculated, and difference XRD patterns of both compounds are shown in Figures 6 and 7. Selected interatomic distances of [ Sr ] and [ Pb ] phases are gathered in Tables 7 and 8 respectively. X-ray powder diffraction data, obtained from the "observed intensities" of the Rietveld refinement $(\mathrm{CuK} \alpha 1: 1.54056 \AA$ ), of both phases are given in Tables 9 and 10.
Given that $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ compounds are isomorphous, only the structure of $\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ will be discussed in detail as a representative. $\mathrm{Sr}_{\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}}$ is a 3D diorthophosphate which crystallises in a distorted yavapaiite structure-type. In fact, although the $[\mathrm{Sr}]$ phase has a $C 2 / c$ space group and their $a$-parameter is the double in comparison to that of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$, both materials have a similar 3D network. The structure of $[\mathrm{Sr}]$ can be described as constructed by alternating $\left[\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\right]^{2-}$ anionic sheets and $\mathrm{Sr}^{2+}$ cationic sheets along the [101] direction (Fig. 8). The $\mathrm{Sr}^{2+}$ sheets reside among those of $\left[\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\right]^{2-}$ sheets alternatively and join them through Coulombic action of $\mathrm{Sr}^{2+}$ cations and $\mathrm{O}^{2-}$ anions to form the 3D framework of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$. The Sr atom is coordinated by ten oxygen atoms from six $\mathrm{PO}_{4}$ tetrahedra (two of them in a unidentate fashion and four of them in edge-sharing fashion) (Fig. 8b). Careful analysis of the A-O distances $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ within $\mathrm{AO}_{10}$ polyhedron of $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ compounds shows that A atom is surrounded by eight oxygen atoms with 'normal' bond distances $(2.585(2)-2.792(2) \AA$ for $[\mathrm{Sr}]$ and $2.651(3)-2.697(2) \AA$ for $[\mathrm{Pb}])$ and two oxygen atoms with 'abnormal' bond distances (3.448(2) $\AA$ for $[\mathrm{Sr}]$ and $3.546(3) \AA$ for $[\mathrm{Pb}])$ (Tables 7 and 8). Therefore, the coordinence of A atoms in both $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ phases can be considered as $8+2$. In all cases $\mathrm{A}-\mathrm{O}$ distances values $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ are comparable with those of the $\mathrm{Sr}-\mathrm{O}$ and $\mathrm{Pb}-\mathrm{O}$ ones which are already obtained for $\operatorname{SrTi}\left(\mathrm{PO}_{4}\right)_{2}$ and $\mathrm{PbTi}\left(\mathrm{PO}_{4}\right)_{2}$ materials [14,33]. Within the $\mathrm{Sr}^{2+}$ cationic sheets every $\mathrm{SrO}_{10}$ polyhedron is connected, via its $\mathrm{O}(4)-\mathrm{O}(4)$ edges, to six neighbouring $\mathrm{SrO}_{10}$ polyhedra (Fig. 8c). The six neighbouring $\mathrm{Sr}-\mathrm{Sr}$ distance values vary between $4.536(3) \AA$ and $5.189(3) \AA$. In $[\mathrm{Pb}]$ phase, the corresponding $\mathrm{Pb}-\mathrm{Pb}$ distances, within the $\mathrm{Pb}^{2+}$ cationic sheets, are ranging between $4.510(3) \AA$ and $5.518(3) \AA$. The dispersion of A-A distances $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ values is in close relation with the connection mode between the $\mathrm{AO}_{10}$ polyedra. Every $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ octahedron is interconnected via common corners $\left(\mathrm{O}(1), \mathrm{O}(2)\right.$ and $\mathrm{O}(3)$ atoms) to six $\mathrm{PO}_{4}$ tetrahedra and shares two of its edges (i.e., $\mathrm{O}(1)-\mathrm{O}(2)$ one) to two $\mathrm{SrO}_{10}$ polyhedra (Fig. 8b). Obtained $\mathrm{Sb}(\mathrm{Fe})-\mathrm{O}$ interatomic distances are consistent with the crystal radii values in six coordination of $\mathrm{Sb}^{5+}$ and $\mathrm{Fe}^{3+}$ ions (Tables 7 and 8) [27]. P-O distances values match well with those typically observed in orthophosphates. In order to have more structural information, the bond valence sum (BVS) [28] for $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ phases were also computed. As shown in Tables 7 and 8 , the BVS values calculated for $\mathrm{A}, \mathrm{Fe}, \mathrm{Sb}$ and P sites are relatively consistent with the expected formal oxidation state of $\mathrm{A}^{2+}, \mathrm{Fe}^{3+}, \mathrm{Sb}^{5+}$ and $\mathrm{P}^{5+}$ ions.
It is of interest to note that our attempts to synthesize $\mathrm{CaSb}_{0.5} \mathrm{Fe}_{0.5}\left(\mathrm{PO}_{4}\right)_{2}$ was not satisfactory, although identical synthesis conditions have been applied. Indeed analysis of the obtained XRD spectra shows principally the presence of a mixture of the already known $\mathrm{Ca}_{0.50} \mathrm{SbFe}\left(\mathrm{PO}_{4}\right)_{3}$ Nasicon phase and two $\mathrm{Ca}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ (PDF number 81-2257) and $\mathrm{SbOPO}_{4}$ (PDF number 84-830) phosphates which are identified as minority phases $[16,34,35]$. Our experimental result shows that $\left[\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\left(\mathrm{PO}_{4}\right)_{2}\right]^{2-}$ yavapaiite framework appears well adapted to bigger $\mathrm{Sr}^{2+}, \mathrm{Pb}^{2+}$ and $\mathrm{Ba}^{2+}$ cations.

This last result agrees with the recent report by some of us about the relationships between composition and crystal structure [20]. Indeed we can conclude that for alkaline earth metal cations of smaller and/or equal size than the $\mathrm{Ca}^{2+}$ ions, the $\left[\mathrm{SbFe}\left(\mathrm{PO}_{4}\right)_{3}\right]^{-}$Nasicon framework seems to be the more stable.

### 3.3 Raman spectroscopy

Raman and Infrared spectroscopic study was undertaken in order to obtain further structural information about the nature of bonding in $\mathrm{A}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ $(\mathrm{A}=\mathrm{Sr}, \mathrm{Pb})$ phases. Given that the yavapaiite structure contains both isolated $\mathrm{PO}_{4}$ groups and isolated $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ groups, the vibrational pattern is obviously typical of an orthophosphate. Note that the vibrational modes of tetrahedral $\mathrm{PO}_{4}$ molecules are well known [36]. Generally the IR and Raman spectroscopic study of orthophosphate shows that phosphate group vibrations are strong compared to the lattice modes and metal-oxygen vibrations. The IR and Raman band positions of the four ( $v_{1}, v_{2}, v_{3}$ and $v_{4}$ ) modes observed in the spectra of the $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ phases (Figs. 9 and 10) are close to those expected for yavapaiite phosphate type materials [37]. Thus, the symmetric non degenerate PO stretching modes $\left(v_{1}\right)$ are observed in the range 920$1040 \mathrm{~cm}^{-1}$ while antisymmetric doubly degenerate PO stretching $\left(v_{2}\right)$ are located in the $430-480 \mathrm{~cm}^{-1}$ range. The symmetric, triply degenerate OPO bending $\left(v_{3}\right)$ is observed between 1070-1170 $\mathrm{cm}^{-1}$ and the triply degenerate, antisymmetric and harmonic OPO bending $\left(v_{4}\right)$ is observed in the range $540-650 \mathrm{~cm}^{-1}$.
The Sb-O...P bonds existing in both compounds have an average length of $2.00 \AA$. Their stretching vibrations are probably coupled with the O-P-O bending $v_{4}$ mode. As was already observed for $\mathrm{SbOPO}_{4}$ phase [38], the frequencies found between 575 and $650 \mathrm{~cm}^{-1}$ in Raman and Infrared spectra of $[\mathrm{Sr}]$ and $[\mathrm{Pb}]$ phases can be assigned empirically to $\mathrm{Sb}-\mathrm{O}$ stretching modes involving $\mathrm{Sb}-\mathrm{O}-\mathrm{P}$ linkage. In the lattice modes region, the translational modes of $\mathrm{Sr}^{2+}$ or $\mathrm{Pb}^{2+}, \mathrm{Fe}^{3+}, \mathrm{Sb}^{5+}$ and $\mathrm{PO}_{4}{ }^{3-}$ ions as well as librational modes of $\mathrm{PO}_{4}{ }^{3-}$ ions and $\mathrm{FeO}_{6}, \mathrm{SbO}_{6}$ groups should be expected. At wavenumbers below $450 \mathrm{~cm}^{-1}$ strong coupling between the different bending vibrations O-P-O, O-Sb-O, Sb-O-P is expected [39]. The Raman bands observed at 364 and $370 \mathrm{~cm}^{-1}$ could be assigned to $\mathrm{Fe}^{3+}-\mathrm{O}$ stretching modes of vibrations similar to those observed in $\mathrm{Li}_{3} \mathrm{Fe}_{2}\left(\mathrm{PO}_{4}\right)_{3}$ [40]. The low frequency modes observed below 270 $\mathrm{cm}^{-1}$ can be easily attributed to translational modes of the $\mathrm{Sr}^{2+} \mathrm{or}_{\mathrm{Pb}^{2+}}, \mathrm{Fe}^{3+}, \mathrm{Sb}^{5+}$ and $\left(\mathrm{PO}_{4}\right)^{3-}$ ions.

## Conclusion

A new family of double phosphate with general formula $\mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ $(\mathrm{A}=\mathrm{Ba}, \mathrm{Sr}, \mathrm{Pb})$ were prepared by solid state reaction method and caracterised from X-ray powder diffraction using the Rietveld method. Note that phases with a mixing of $\mathrm{Sb}^{\vee}$ and $\mathrm{Fe}^{\mathrm{III}}$ ions in the octahedral M sites of the $\mathrm{A}^{\mathrm{II}} \mathrm{M}^{\mathrm{IV}}\left(\mathrm{PO}_{4}\right)_{2}$ yavapaiite structure-types were studied here for the first time. $\mathrm{Ba}\left(\mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ features
 $\mathrm{Pb}\left(\mathrm{Sb}_{0.5}^{\mathrm{V}} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ crystallize in monoclinic system with space group $C 2 / c$ (distorted yavapaiite type structure). The $\left[\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\right]^{2-}$ yavapaiite framework appears well adapted to bigger $\mathrm{Sr}^{2+}, \mathrm{Pb}^{2+}$ and $\mathrm{Ba}^{2+}$ cations. Contrary to these last results, for smaller alkaline earth metal cations as $\mathrm{Ca}^{2+}$, the $\left[\mathrm{SbFe}\left(\mathrm{PO}_{4}\right)_{3}\right]^{-}$Nasicon framework seems to be the more stable. Further investigations on the relationships between composition and crystal structure, as well as research on potential application of phases of general formula $\mathrm{A}^{\mathrm{II}}\left(\mathrm{M}^{\mathrm{V}}{ }_{0.5} \mathrm{~B}^{\mathrm{II}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ were in progress.

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## Figures captions

Figure 1. Experimental ( $\bullet \bullet \bullet$ ) calculated (-), and difference profile of the XRD pattern of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Figure 2. View of the structure of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{a})$; rows of $\mathrm{BaO}_{10}, \mathrm{PO}_{4}$ and $\mathrm{Sb}(\mathrm{Fe}) \mathrm{O}_{6}$ polyhedra along c -axis (b) and projection in the ac plane (c).
Figure 3. Array of $\mathrm{BaO}_{8}$ polyhedra in (a) and (b); view of $\mathrm{BaO}_{8}\left(\mathrm{BaO}_{8}\right)_{6}$ polyhedra in (c) within the structure of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.

Figure 4. Experimental ( $\bullet \bullet \bullet$ ) calculated (-), and difference profile of the XRD pattern, in the $10-35^{\circ}$ ( $2 \theta$ range), of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ with refinement in $\mathrm{C} 2 / m$ in (a) and $C 2 / c$ in (b). Unindexed peaks are indicated by a vertical arrow.

Figure 5. View along the b-axis of the three Monoclinic space groups $\mathrm{C} 2 / \mathrm{c}$ (cell choice 1), A2/n (cell choice 2) and I2/a (cell choice 3). The unique b -axis points upwards from the page and the subscripts of the labels of the axes indicate the cell choice.
Figure 6. Experimental ( $\bullet \bullet \bullet$ ) calculated (-), and difference profile of the XRD pattern of $\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Figure 7. Experimental $(\bullet \bullet \bullet)$ calculated (-), and difference profile of the XRD pattern of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Figure 8. Projection of the structure of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ in the ac plane (a); rows of polyhedra along a-axis (b) and $\mathrm{SrO}_{8}\left(\mathrm{SrO}_{8}\right)_{6}$ polyhedra (c)
Figure 9. Raman spectra of $\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ (a) and $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ (b).
Figure 10. I R. Spectra of of $\mathrm{Sr}_{\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2} \text { (a) and } \mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2} \text { (b). } \text {. } \text {. }{ }^{\text {(b) }} \text {. }}$

## Tables captions

Table 1. Results of the Rietveld refinement of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 2. Selected interatomic distances and calculated Bond valence sum (BVS) for $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 3. Powder diffraction data of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{CuK} \alpha_{1} ; \lambda=1.5406 \AA\right)$

Table 4. Ordered list of possible space groups obtained from the Check-Group program for $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$
Table 5. Results of the Rietveld refinement of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 6. Results of the Rietveld refinement of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 7. Selected interatomic distances and calculated Bond valence sum (BVS) for $\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 8. Selected interatomic distances and calculated Bond valence sum (BVS) for $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
Table 9. Powder diffraction data of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{CuK} \alpha_{1} ; \lambda=1.5406 \AA\right)$.
Table 10. Powder diffraction data of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{CuK} \alpha_{1} ; \lambda=1.5406 \AA\right)$.

Table 1. Results of the Rietveld refinement of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.

| $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { Space group, } C 2 / m\left(\mathrm{~N}^{\circ} 12\right) ;\left[\mathrm{Z}=2 ; \mathrm{a}=8.1568(4) \AA ; \mathrm{b}=5.1996(3) \AA \mathrm{c}=7.8290(4) \AA ; \beta=94.53(1)^{\circ}\right. \text {; } \\ & \left.\mathrm{V}=331(1) \AA^{3}\right] \end{aligned}$ |  |  |  |  |  |  |
| Profile parameters |  |  |  |  |  |  |
| Pseudo-Voigt function, $\mathrm{PV}=\eta \mathrm{L}+(1-\eta) \mathrm{G} ; \eta=0.27(1)$ |  |  |  |  |  |  |
| Half-width parameters, $\mathrm{U}=0.126(4), \mathrm{V}=0.012$ (3), and $\mathrm{W}=0.010$ (1) |  |  |  |  |  |  |
| Conventional Rietveld R-factors, $\mathrm{R}_{\mathrm{WP}}=9.6 \% ; \mathrm{R}_{\mathrm{P}}=6.9 \% ; \mathrm{R}_{\mathrm{B}}=3.9 \% ; \mathrm{R}_{\mathrm{F}}=2.6 \%$ |  |  |  |  |  |  |
| Atom | Site |  | mic coordin |  | $\mathrm{B}_{\text {iso }}\left(\AA^{2}\right)$ | Occupancy |
| Ba | 2c | 0 | 0 | 0.5 | 1.3(1) |  |
| (Sb,Fe) | 2a | 0 | 0 | 0 | 0.5(1) | 0.5/0.5 |
| P | 4 i | 0.3645(2) | 0 | 0.2024(3) | 0.8(1) | 1 |
| $\mathrm{O}(1)$ | 4 i | 0.3111(6) | 0 | 0.3871(4) | 0.7(1) | 1 |
| $\mathrm{O}(2)$ | 4 i | 0.2309(6) | 0 | 0.0516(6) | 0.7(1) |  |
| $\mathrm{O}(3)$ | 8 j | 0.4766(5) | 0.2351(5) | 0.1833(5) | 0.7(1) | 1 |

Table 2. Selected interatomic distances and calculated Bond valence sum (BVS) for $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.

| $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ |  |  |
| :---: | :---: | :---: |
| $\mathrm{Sb}(\mathrm{Fe})$-O distances ( $\AA$ ) | P-O distances ( A ) | $\mathrm{Ba}-\mathrm{O}$ distances ( A ) |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(2)=1.895(5)$ | $\mathrm{P}-\mathrm{O}(1)=1.543(4)$ | $2 \times \mathrm{Ba}-\mathrm{O}(1)=2.752(6)$ |
| $4 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(3)=2.009$ (3) | $\mathrm{P}-\mathrm{O}(2)=1.542(5)$ | $4 \times \mathrm{Ba}-\mathrm{O}(3)=2.829(4)$ |
| Aver. $\langle\mathrm{Sb}$ (Fe)-O> $=1.95(1)$ | $2 \times \mathrm{P}-\mathrm{O}(3)=1.541(4)$ | $4 \times \mathrm{Ba}-\mathrm{O}(1)=3.114(3)$ |
|  | Aver. $\langle\mathrm{P}-\mathrm{O}\rangle=1.54$ (1) | Aver. $\langle\mathrm{Ba}-\mathrm{O}\rangle=2.92(1)$ |
| Bond Valence Sums (BVS) |  |  |
| $\begin{gathered} \mathrm{BVS}(\mathrm{Sb}(\mathrm{Fe}))=4.7 \\ (\text { should be } 4) \end{gathered}$ | BVS $(\mathrm{P})=4.9$ | $\operatorname{BVS}(\mathrm{Ba})=1.8$ |

Table 3. Powder diffraction data of $\mathrm{Ba}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{Cu} K \alpha_{1} ; \lambda=1.5406 \AA\right)$

| hkl | $\mathrm{d}_{\text {obs }}(\AA)$ | $\begin{gathered} \hline 100 \mathrm{I} / I_{0} \\ \text { (obs) } \end{gathered}$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ (\mathrm{cal}) \end{gathered}$ | hkl | $\mathrm{d}_{\text {obs }}(\mathrm{A})$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ \text { (obs) } \end{gathered}$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ (\mathrm{cal}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 001 | 7.8045 | 4 | 4 | 132 | 1.5455 | 6 | 5 |
| 110 | 4.3805 | 100 | 90 | -422 | 1.5150 | 6 | 5 |
| 200 | 4.0656 | 60 | 69 | -224 | 1.4887 | 5 | 4 |
| 002 | 3.9023 | 33 | 31 | -512 | 1.4811 | 3 | 3 |
| -111 | 3.8913 | 30 | 30 | 314 | 1.4654 | 4 | 5 |
| 111 | 3.7524 | 33 | 33 | -404 | 1.4667 | 4 | 4 |
| -201 | 3.7284 | 21 | 21 | 330 | 1.4602 | 7 | 6 |
| 201 | 3.4944 | 3 | 4 | 422 | 1.4502 | 5 | 6 |
| -112 | 2.9774 | 85 | 78 | 224 | 1.4271 | 2 | 1 |
| -202 | 2.9334 | 10 | 10 | 512 | 1.4063 | 2 | 3 |
| 112 | 2.8541 | 50 | 50 | -332 | 1.3871 | 1 | 1 |
| 202 | 2.7104 | 9 | 10 | 600 | 1.3552 | 2 | 2 |
| 020 | 2.5998 | 30 | 28 | 332 | 1.3489 | 1 | 1 |
| 310 | 2.4035 | 34 | 36 | 040 | 1.3000 | 3 | 3 |
| -311 | 2.3437 | 1 | 1 | -134 | 1.2902 | 2 | 2 |
| -203 | 2.2744 | 3 | 2 | 134 | 1.2693 | 2 | 2 |
| 311 | 2.2531 | 2 | 2 | -116 | 1.2617 | 5 | 4 |
| 220 | 2.1903 | 5 | 4 | 240 | 1.2382 | 1 | 1 |
| 022 | 2.1636 | 18 | 17 | 042 | 1.2333 | 1 | 1 |
| -221 | 2.1326 | 7 | 6 | 206 | 1.2114 | 2 | 1 |
| -312 | 2.1136 | 14 | 12 | 424 | 1.2017 | 3 | 3 |
| 400 | 2.0328 | 5 | 6 | 530 | 1.1859 | 1 | 1 |
| 312 | 1.9853 | 6 | 6 | -316 | 1.1791 | 1 | 1 |
| 004 | 1.9511 | 16 | 14 | 514 | 1.1724 | 3 | 2 |
| 222 | 1.8762 | 9 | 9 | 043 | 1.1628 | 1 | 1 |
| -402 | 1.8642 | 4 | 4 | -425 | 1.1542 | 2 | 1 |
| -313 | 1.8304 | 3 | 3 | 334 | 1.1459 | 2 | 2 |
| -204 | 1.8159 | 9 | 9 | 532 | 1.1169 | 1 | 1 |
| -114 | 1.8112 | 11 | 10 | 316 | 1.1118 | 2 | 2 |
| 114 | 1.7548 | 7 | 7 | 440 | 1.0951 | 2 | 2 |
| 402 | 1.7472 | 6 | 9 | 044 | 1.0818 | 1 | 1 |
| 130 | 1.6951 | 4 | 3 | 712 | 1.0668 | 2 | 1 |
| 131 | 1.6509 | 1 | 1 | -244 | 1.0569 | 2 | 1 |
| 420 | 1.6014 | 2 | 2 | -534 | 1.0403 | 3 | 2 |
| -132 | 1.5642 | 8 | 8 | 800 | 1.0164 | 1 | 1 |
| 510 | 1.5521 | 5 | 5 |  |  |  |  |

${ }^{\mathrm{a}}$ Diffraction lines with $I_{\mathrm{obs}}<1$ are omitted.

Table 4. Ordered list of possible space groups obtained from the Check-Group program for $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$

| Space-groups <br> number | Hermann-Mauguin Symbol of <br> space groups | Merit <br> factors |
| :---: | :---: | :---: |
| 9 | $C 1 c 1$ | 2.70 |
| 15 | $C 12 / c 1$ | 2.70 |
| 5 | $C 121$ | 1.97 |
| 8 | $C 1 m 1$ | 1.97 |
| 12 | $C 12 / m 1$ | 1.97 |
| 14 | $P 12_{1} / c 1$ | 1.38 |
| 7 | $P 1 c 1$ | 1.35 |
| 13 | $P 12 / c 1$ | 1.35 |
| 4 | $P 12_{1} 1$ | 1.01 |
| 11 | $P 12_{1} / m 1$ | 1.01 |
| 10 | $P 12 / m 1$ | 1.00 |
| 6 | $P 1 m 1$ | 1.00 |
| 3 | $P 121$ | 1.00 |

Table 5. Results of the Rietveld refinement of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
$\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$
Space group, $\quad C 2 / c \quad\left(\mathrm{~N}^{\circ} 15\right) ; \quad[\mathrm{Z}=4 ; \quad \mathrm{a}=16.5215(2) \AA ; \quad \mathrm{b}=5.1891(1) \AA \quad \mathrm{c}=8.0489(1) \AA$;
$\beta=115.70(1)^{\circ} ; \mathrm{V}=622(1) \AA^{3}$
Profile parameters
Pseudo-Voigt function, $P V=\eta L+(1-\eta) G ; \eta=0.384(3)$
Half-width parameters, $\mathrm{U}=0.0122(2), \mathrm{V}=-0.0054(2)$, and $\mathrm{W}=0.0045(1)$
Conventional Rietveld R-factors, $\mathrm{R}_{\mathrm{WP}}=4.1 \% ; \mathrm{R}_{\mathrm{P}}=2.8 \% ; \mathrm{R}_{\mathrm{B}}=4.3 \% ; \mathrm{R}_{\mathrm{F}}=2.6 \%$

| Atom | Site | Atomic coordinates |  |  |  | $\mathrm{B}_{\text {iso }}\left(\AA^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sr | 4 e | 0 | $0.2985(1)$ | 0.75 | $1.0(1)$ | Occupancy |
| $(\mathrm{Sb}, \mathrm{Fe})$ | 4 c | 0.25 | 0.25 | 0 | $0.14(1)$ | $0.5 / 0.5$ |
| P | 8 f | $0.1431(1)$ | $0.7579(3)$ | $0.7588(1)$ | $0.45(2)$ | 1 |
| $\mathrm{O}(1)$ | 8 f | $0.1449(2)$ | $1.0196(5)$ | $0.8615(5)$ | $0.22(3)$ | 1 |
| $\mathrm{O}(2)$ | 8 f | $0.1591(2)$ | $0.5270(5)$ | $0.8954(4)$ | $0.22(3)$ | 1 |
| $\mathrm{O}(3)$ | 8 f | $0.2219(2)$ | $0.7647(6)$ | $0.7067(4)$ | $0.22(3)$ | 1 |
| $\mathrm{O}(4)$ | 8 f | $0.0498(2)$ | $0.7225(6)$ | $0.6017(4)$ | $0.22(3)$ | 1 |

Table 6. Results of the Rietveld refinement of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.
$\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$
Space group, $\quad C 2 / c \quad\left(\mathrm{~N}^{\circ} 15\right) ; \quad[\mathrm{Z}=4 ; \quad \mathrm{a}=16.6925(2) \AA ; \quad \mathrm{b}=5.1832(1) \AA \quad \mathrm{c}=8.1215(1) \AA$; $\beta=115.03(1)^{\circ} ; \mathrm{V}=637(1) \AA^{3}$ ]
Profile parameters
Pseudo-Voigt function, $P V=\eta L+(1-\eta) G ; \eta=0.438$ (4)
Half-width parameters, $\mathrm{U}=0.048(1), \mathrm{V}=-0.008(1)$, and $\mathrm{W}=0.005(1)$
Conventional Rietveld R-factors, $\mathrm{R}_{\mathrm{WP}}=4.1 \% ; \mathrm{R}_{\mathrm{P}}=6.1 \% ; \mathrm{R}_{\mathrm{B}}=4.5 \% ; \mathrm{R}_{\mathrm{F}}=3.1 \%$

| Atom | Site | Atomic coordinates |  |  |  | $\mathrm{B}_{\text {iso }}\left(\AA^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pb | 4 e | 0 | $0.3106(7)$ | 0.75 | ---- | Occupancy |
| $(\mathrm{Sb}, \mathrm{Fe})$ | 4 c | 0.25 | 0.25 | 0 | $0.06(1)$ | $0.5 / 0.5$ |
| P | 8 f | $0.1455(3)$ | $0.7587(6)$ | $0.7626(2)$ | $0.57(5)$ | 1 |
| $\mathrm{O}(1)$ | 8 f | $0.1444(2)$ | $1.0213(6)$ | $0.8636(3)$ | $0.07(1)$ | 1 |
| $\mathrm{O}(2)$ | 8 f | $0.1612(3)$ | $0.5326(6)$ | $0.9013(3)$ | $0.07(1)$ | 1 |
| $\mathrm{O}(3)$ | 8 f | $0.2212(7)$ | $0.7634(4)$ | $0.7049(6)$ | $0.07(2)$ | 1 |
| $\mathrm{O}(4)$ | 8 f | $0.0520(2)$ | $0.7107(5)$ | $0.6090(5)$ | $0.07(2)$ | 1 |


| Anisotropic <br> Betas $\times 10^{4}$ | $\mathrm{~B}_{11}$ | $\mathrm{~B}_{22}$ | $\mathrm{~B}_{33}$ | $\mathrm{~B}_{12}$ | $\mathrm{~B}_{13}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Pb | $18.8(0.5)$ | $76.4(3.1)$ | $202.8(2.6)$ | 0 | $35.7(0.9)$ |

Table 7. Selected interatomic distances and calculated Bond valence sum (BVS) for $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.

| $\mathrm{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$ |  |  |
| :---: | :---: | :---: |
| $\mathrm{Sb}(\mathrm{Fe})-\mathrm{O}$ distances ( A ) | P-O distances ( A ) | Sr-O distances ( A ) |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(1)=2.002(3)$ | $\mathrm{P}-\mathrm{O}(1)=1.583(3)$ | $2 \times \mathrm{Sr}-\mathrm{O}(1)=2.601(3)$ |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(2)=1.982(3)$ | $\mathrm{P}-\mathrm{O}(2)=1.569(3)$ | $2 \times \mathrm{Sr}-\mathrm{O}(2)=2.650(3)$ |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(3)=1.913(4)$ | $\mathrm{P}-\mathrm{O}(3)=1.532(4)$ | $2 \times \mathrm{Sr}-\mathrm{O}(4)=2.585(3)$ |
| Aver. $\langle\mathrm{Sb}(\mathrm{Fe})-\mathrm{O}\rangle=1.97(1)$ | $\mathrm{P}-\mathrm{O}(4)=1.522(3)$ | $2 \times \mathrm{Sr}-\mathrm{O}(4)=2.792(3)$ |
|  | Aver. $\langle\mathrm{P}-\mathrm{O}\rangle=1.55$ (1) | $2 \times \mathrm{Sr}-\mathrm{O}(4)=3.448(3)$ |
| Bond Valence Sums (BVS) |  | Aver. $\langle\mathrm{Sr}-\mathrm{O}\rangle=2.65(1)$ |
| $\begin{gathered} \mathrm{BVS}(\mathrm{Sb}(\mathrm{Fe}))=4.4 \\ (\text { should be } 4) \end{gathered}$ | BVS $(\mathrm{P})=4.8$ | BVS $(\mathrm{Sr})=1.9$ |

Table 8. Selected interatomic distances and calculated Bond valence sum (BVS) for $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}$.

| $\overline{\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}}$ |  |  |
| :---: | :---: | :---: |
| $\mathrm{Sb}(\mathrm{Fe})$-O distances ( A ) | P-O distances ( A ) | $\mathrm{Pb}-\mathrm{O}$ distances ( A ) |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(1)=2.022(5)$ | $\mathrm{P}-\mathrm{O}(1)=1.593$ (6) | $2 \times \mathrm{Pb}-\mathrm{O}(1)=2.651(6)$ |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(2)=1.995(5)$ | $\mathrm{P}-\mathrm{O}(2)=1.569(6)$ | $2 \times \mathrm{Pb}-\mathrm{O}(2)=2.697(6)$ |
| $2 \times \mathrm{Sb}(\mathrm{Fe})-\mathrm{O}(3)=1.920(8)$ | $\mathrm{P}-\mathrm{O}(3)=1.522(9)$ | $2 \times \mathrm{Pb}-\mathrm{O}(4)=2.684(6)$ |
| Aver. $\langle\mathrm{Sb}(\mathrm{Fe})-\mathrm{O}\rangle=1.98(1)$ | $\mathrm{P}-\mathrm{O}(4)=1.552(5)$ | $2 \times \mathrm{Pb}-\mathrm{O}(4)=2.669(5)$ |
|  | Aver. $\langle\mathrm{P}-\mathrm{O}\rangle=1.55(1)$ | $2 \times \mathrm{Pb}-\mathrm{O}(4)=3.546(6)$ |
| Bond Valence Sums (BVS) |  | Aver. $\langle\mathrm{Pb}-\mathrm{O}\rangle=2.67$ (1) |
| $\begin{gathered} \mathrm{BVS}(\mathrm{Sb}(\mathrm{Fe}))=4.3 \\ \quad(\text { should be } 4) \end{gathered}$ | $\operatorname{BVS}(\mathrm{P})=4.8$ | $\operatorname{BVS}(\mathrm{Pb})=1.8$ |

Table 9. Powder diffraction data of $\operatorname{Sr}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{CuK} \alpha_{1} ; \lambda=1.5406 \AA\right)$

| $h k l$ | $\mathrm{d}_{\text {obs }}(\AA)$ | $\begin{gathered} 100 I / I_{0} \\ \text { (obs) } \end{gathered}$ | $\begin{gathered} 100 \mathrm{I} / \mathrm{I}_{0} \\ (\mathrm{cal}) \end{gathered}$ | $h k l$ | $\mathrm{d}_{\text {obs }}(\AA)$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ \text { (obs) } \end{gathered}$ | $\begin{gathered} 100 I / I_{0} \\ (\mathrm{cal}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 7.4435 | 10 | 9 | -912 | 1.7301 | 4 | 4 |
| 110 | 4.9000 | 4 | 4 | 602 | 1.7280 | 19 | 16 |
| -111 | 4.3591 | 58 | 56 | -804 | 1.7254 | 14 | 15 |
| -202 | 4.0174 | 54 | 53 | -623 | 1.7214 | 1 | 1 |
| 111 | 3.8154 | 28 | 26 | 130 | 1.7182 | 2 | 1 |
| 400 | 3.7217 | 19 | 18 | -911 | 1.6919 | 15 | 14 |
| -311 | 3.7099 | 19 | 17 | -131 | 1.6910 | 5 | 5 |
| 002 | 3.6263 | 11 | 10 | -913 | 1.6741 | 1 | 1 |
| 310 | 3.5864 | 3 | 3 | 422 | 1.6642 | 3 | 2 |
| -402 | 3.4509 | 16 | 17 | 131 | 1.6534 | 6 | 5 |
| -312 | 3.0774 | 2 | 2 | -1002 | 1.6516 | 3 | 3 |
| 311 | 2.8765 | 100 | 100 | 330 | 1.6333 | 2 | 2 |
| 202 | 2.8146 | 6 | 7 | 114 | 1.6266 | 1 | 1 |
| -511 | 2.7865 | 74 | 75 | 223 | 1.6098 | 1 | 2 |
| -602 | 2.6529 | 10 | 11 | -821 | 1.5970 | 1 | 1 |
| 020 | 2.5946 | 39 | 40 | -424 | 1.5883 | 3 | 2 |
| 510 | 2.5825 | 3 | 3 | -132 | 1.5837 | 1 | 1 |
| 600 | 2.4812 | 4 | 3 | -332 | 1.5759 | 1 | 1 |
| 021 | 2.4430 | 3 | 3 | -224 | 1.5684 | 2 | 1 |
| -313 | 2.3799 | 67 | 69 | 331 | 1.5468 | 11 | 10 |
| 221 | 2.2268 | 4 | 4 | -515 | 1.5350 | 8 | 9 |
| 312 | 2.2250 | 3 | 3 | -531 | 1.5323 | 7 | 7 |
| -421 | 2.1946 | 5 | 5 | 132 | 1.5235 | 1 | 1 |
| 511 | 2.1868 | 3 | 3 | 820 | 1.5122 | 8 | 7 |
| -222 | 2.1795 | 1 | 1 | 513 | 1.5049 | 5 | 4 |
| 420 | 2.1284 | 32 | 30 | -532 | 1.5029 | 1 | 1 |
| -711 | 2.1271 | 6 | 6 | 530 | 1.4956 | 1 | 1 |
| -712 | 2.1233 | 2 | 2 | 1000 | 1.4887 | 3 | 3 |
| 002 | 2.1101 | 4 | 3 | -715 | 1.4868 | 3 | 3 |
| -422 | 2.0738 | 2 | 2 | 024 | 1.4862 | 18 | 16 |
| -802 | 2.0572 | 3 | 3 | -333 | 1.4530 | 10 | 9 |
| 113 | 2.0548 | 17 | 16 | -115 | 1.4483 | 4 | 4 |
| -404 | 2.0087 | 14 | 15 | 622 | 1.4382 | 11 | 11 |
| -713 | 1.9588 | 9 | 9 | -824 | 1.4367 | 15 | 15 |
| 421 | 1.9178 | 1 | 1 | -1113 | 1.4299 | 10 | 10 |
| 222 | 1.9077 | 22 | 19 | 332 | 1.4155 | 1 | 1 |
| -621 | 1.8838 | 2 | 2 | 404 | 1.4073 | 2 | 2 |
| 800 | 1.8609 | 13 | 12 | 531 | 1.4055 | 1 | 1 |
| -223 | 1.8586 | 2 | 2 | -1111 | 1.3952 | 2 | 1 |
| -622 | 1.8549 | 18 | 16 | -1022 | 1.3933 | 3 | 2 |
| -514 | 1.8460 | 1 | 1 | -915 | 1.3916 | 4 | 4 |
| -423 | 1.8398 | 1 | 1 | -731 | 1.3893 | 1 | 1 |
| 004 | 1.8131 | 8 | 7 | 133 | 1.3685 | 2 | 2 |
| 620 | 1.7932 | 2 | 1 | 224 | 1.3671 | 2 | 2 |
| 023 | 1.7687 | 3 | 3 | -1021 | 1.3628 | 1 | 1 |
| 313 | 1.7646 | 3 | 3 | 730 | 1.3419 | 1 | 1 |
| 711 | 1.7317 | 9 | 8 | 115 | 1.3398 | 1 | 1 |
| -606 | 1.3391 | 4 | 4 | -1224 | 1.1811 | 3 | 3 |
| -1204 | 1.3265 | 1 | 2 | -535 | 1.1773 | 3 | 3 |
| -1024 | 1.3101 | 3 | 3 | -641 | 1.1725 | 1 | 1 |
| -534 | 1.3013 | 1 | 1 | -243 | 1.1663 | 1 | 1 |
| 040 | 1.2973 | 4 | 4 | -1402 | 1.1660 | 5 | 5 |
| 713 | 1.2931 | 1 | 1 | -642 | 1.1654 | 1 | 1 |
| 532 | 1.2873 | 1 | 1 | 533 | 1.1634 | 1 | 1 |
| -206 | 1.2845 | 1 | 1 | -735 | 1.1551 | 1 | 1 |
| 240 | 1.2780 | 1 | 1 | -13 15 | 1.1525 | 2 | 2 |
| 041 | 1.2770 | 1 | 1 | -226 | 1.1512 | 5 | 5 |


| -241 | 1.2750 | 1 | 1 | -1133 | 1.1278 | 3 | 3 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 731 | 1.2593 | 1 | 1 | 913 | 1.1246 | 2 | 2 |
| -931 | 1.2438 | 2 | 2 | 206 | 1.1188 | 1 | 1 |
| 1200 | 1.2406 | 1 | 1 | -935 | 1.1087 | 1 | 1 |
| -242 | 1.2345 | 1 | 1 | 1022 | 1.0934 | 1 | 1 |
| -1313 | 1.2333 | 1 | 1 | -841 | 1.0926 | 1 | 1 |
| 315 | 1.2185 | 8 | 7 | -317 | 1.0907 | 1 | 1 |
| -442 | 1.2143 | 2 | 2 | -444 | 1.0898 | 1 | 1 |
| 1002 | 1.2057 | 1 | 1 | 804 | 1.0846 | 1 | 1 |
| 1111 | 1.2034 | 6 | 6 | -1513 | 1.0771 | 1 | 1 |
| -626 | 1.1900 | 2 | 2 | 840 | 1.0642 | 2 | 1 |
| -1311 | 1.1832 | 1 | 1 | -1422 | 1.0636 | 3 | 3 |

${ }^{a}$ Diffraction lines with $I_{\text {obs }}<1$ are omitted.

Table 10. Powder diffraction data of $\mathrm{Pb}\left(\mathrm{Sb}_{0.5} \mathrm{Fe}_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{CuK} \alpha_{1} ; \lambda=1.5406 \AA\right)$

| hkl | $\mathrm{d}_{\text {obs }}(\mathrm{A})$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ \text { (obs) } \\ \hline \end{gathered}$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ (\mathrm{cal}) \\ \hline \end{gathered}$ | hkl | $\mathrm{d}_{\text {obs }}(\AA)$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ \text { (obs) } \\ \hline \end{gathered}$ | $\begin{gathered} 100 \mathrm{I} / I_{0} \\ (\mathrm{cal}) \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 7.5625 | 5 | 5 | -804 | 1.7357 | 7 | 9 |
| 110 | 4.9033 | 13 | 13 | -623 | 1.7262 | 3 | 2 |
| -111 | 4.3661 | 99 | 92 | 130 | 1.7166 | 5 | 5 |
| -202 | 4.0508 | 61 | 69 | -911 | 1.7116 | 12 | 11 |
| 400 | 3.7812 | 37 | 34 | -131 | 1.6897 | 3 | 2 |
| -311 | 3.7210 | 49 | 44 | -1002 | 1.6691 | 3 | 3 |
| 002 | 3.6795 | 29 | 22 | 131 | 1.6542 | 1 | 1 |
| 310 | 3.6140 | 11 | 9 | 114 | 1.6497 | 1 | 1 |
| -112 | 3.1583 | 3 | 3 | -331 | 1.6440 | 2 | 2 |
| -312 | 3.0888 | 4 | 5 | 330 | 1.6344 | 4 | 4 |
| 311 | 2.9131 | 100 | 100 | 223 | 1.6261 | 1 | 1 |
| 202 | 2.8658 | 14 | 14 | -821 | 1.6089 | 2 | 2 |
| -511 | 2.8065 | 77 | 78 | -424 | 1.5959 | 2 | 2 |
| 112 | 2.7665 | 2 | 2 | -132 | 1.5850 | 3 | 3 |
| -602 | 2.6726 | 14 | 18 | -332 | 1.5760 | 3 | 2 |
| -512 | 2.6321 | 2 | 3 | -823 | 1.5572 | 2 | 2 |
| 510 | 2.6126 | 5 | 5 | 331 | 1.5511 | 6 | 5 |
| 020 | 2.5916 | 26 | 30 | -515 | 1.5465 | 6 | 6 |
| 600 | 2.5208 | 10 | 9 | -521 | 1.5344 | 4 | 3 |
| 021 | 2.4444 | 8 | 8 | -1004 | 1.5277 | 9 | 7 |
| -221 | 2.4279 | 7 | 7 | -532 | 1.5039 | 3 | 2 |
| -313 | 2.3950 | 51 | 56 | 530 | 1.5003 | 11 | 9 |
| -113 | 2.3251 | 3 | 2 | -115 | 1.4661 | 3 | 3 |
| 312 | 2.2585 | 5 | 4 | 622 | 1.4566 | 9 | 8 |
| -513 | 2.2436 | 5 | 5 | -11 13 | 1.4412 | 11 | 12 |
| 221 | 2.2358 | 8 | 7 | 404 | 1.4329 | 1 | 1 |
| 402 | 2.2107 | 3 | 2 | 332 | 1.4230 | 2 | 2 |
| -421 | 2.1985 | 11 | 10 | -1111 | 1.4128 | 2 | 2 |
| -222 | 2.1831 | 5 | 4 | 821 | 1.4031 | 4 | 3 |
| -711 | 2.1483 | 2 | 2 | -915 | 1.3991 | 2 | 3 |
| 420 | 2.1377 | 28 | 25 | -732 | 1.3913 | 2 | 1 |
| 022 | 2.1188 | 6 | 5 | 133 | 1.5757 | 2 | 2 |
| 113 | 2.0825 | 16 | 15 | 730 | 1.3494 | 3 | 3 |
| -802 | 2.0762 | 7 | 10 | -1204 | 1.3363 | 1 | 1 |
| -404 | 2.0254 | 10 | 11 | -334 | 1.3147 | 1 | 1 |
| 710 | 1.9944 | 1 | 1 | -534 | 1.3044 | 1 | 1 |
| -713 | 1.9689 | 10 | 10 | -206 | 1.3007 | 1 | 1 |
| 421 | 1.9327 | 4 | 3 | 040 | 1.2958 | 2 | 2 |
| 222 | 1.9222 | 17 | 13 | -134 | 1.2863 | 1 | 1 |
| 800 | 1.8906 | 12 | 12 | -1115 | 1.2807 | 1 | 1 |
| -223 | 1.8668 | 3 | 3 | 041 | 1.2762 | 2 | 2 |
| -622 | 1.8605 | 16 | 13 | -241 | 1.2738 | 2 | 2 |
| -423 | 1.8449 | 4 | 3 | -932 | 1.2638 | 1 | 1 |
| 004 | 1.8397 | 6 | 5 | 1200 | 1.2604 | 1 | 1 |
| 313 | 1.7927 | 4 | 4 | -734 | 1.2581 | 1 | 1 |
| 023 | 1.7815 | 5 | 4 | -931 | 1.2509 | 1 | 1 |
| 602 | 1.7610 | 17 | 16 | -735 | 1.1587 | 1 | 1 |
| 241 | 1.2435 | 1 | 1 | -1132 | 1.1392 | 1 | 1 |
| -441 | 1.2370 | 4 | 4 | 1220 | 1.1335 | 2 | 1 |
| 1111 | 1.2233 | 4 | 3 | -643 | 1.1306 | 1 | 1 |
| -442 | 1.2140 | 1 | 1 | 641 | 1.1063 | 1 | 1 |
| 930 | 1.2047 | 1 | 1 | -1134 | 1.1010 | 1 | 1 |
| -626 | 1.1975 | 1 | 1 | -841 | 1.0957 | 1 | 1 |
| -934 | 1.1861 | 2 | 2 | -15 13 | 1.0879 | 1 | 1 |
| -535 | 1.1819 | 2 | 2 | -843 | 1.0789 | 1 | 1 |
| -1402 | 1.1803 | 2 | 2 | -1422 | 1.0742 | 2 | 1 |
| -641 | 1.1738 | 1 | 1 | 733 | 1.0690 | 1 | 1 |


| 732 | 1.1708 | 1 | 1 | 1221 | 1.0612 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| -243 | 1.1675 | 1 | 1 |  |  |  |  |
| -443 | 1.1621 | 2 | 2 |  |  |  |  |

${ }^{a}$ Diffraction lines with $I_{\text {obs }}<1$ are omitted.



(b)















## Highlights

-a new $\mathrm{A}^{\mathrm{II}}\left(\mathrm{Sb}^{\mathrm{V}} 0.5 \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\right)\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Sr}, \mathrm{Pb}, \mathrm{Ba})$ family of yavapaiite was described -a strategy of structural determination was applied

- IR and Raman of $\mathrm{A}^{\mathrm{II}} \mathrm{Sb}^{\mathrm{V}}{ }_{0.5} \mathrm{Fe}^{\mathrm{III}}{ }_{0.5}\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~A}=\mathrm{Sr}, \mathrm{Pb})$ was studied

