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$(M\text{Bi})_{46}\text{V}_8\text{O}_y$-Family type ($M$=Pb; Sr; Ca; Cd; $\text{Na}_{0.5}\text{Bi}_{0.5}$) : Syntheses, crystal structures and conductivity properties

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Suggested running head: $(M\text{Bi})_{46}\text{V}_8\text{O}_y$-Family type ($M$=Pb; Sr; Ca; Cd; $\text{Na}_{0.5}\text{Bi}_{0.5}$)

Suggested figure for Graphical abstract: Fig.0 with the legend

"$(\text{O}(\text{Bi},\text{Pb})_4\text{-VO}_4)$ typical structural organization"

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Abstract: Phases, with nominal formulas $(M\mathrm{Bi})_{46}\mathrm{V}_8\mathrm{O}_y$ (M=Pb, Sr, Ca, Cd, Na$_{0.5}$Bi$_{0.5}$), were prepared as powder samples, as well as single crystals of closely related compositions. Single crystal structure determinations were realized using X-ray diffraction on a Bruker 4KCCD Apex diffractometer. In this series, the cell is related to the fluorite δ-Bi$_2$O$_3$: it is orthorhombic, with $\vec{a}_0=3/2\,\vec{a}_F-3/2\,\vec{b}_F$, $\vec{b}_0=3/2\,\vec{a}_F+3/2\,\vec{b}_F$, $\vec{c}_0=3\,\vec{c}_F$ when nominal ratio are either M_{10}/Bi$_{36}$ (M=Sr-Na$_{0.5}$Bi$_{0.5}$) or Pb$_3$/Bi$_{43}$. Two types of monoclinic structures can be obtained from Pb$_6$/Bi$_{40}$ nominal ratio, either with $\vec{a}_m=3/2\,\vec{a}_F+3/2\,\vec{b}_F+3\,\vec{c}_F$, $\vec{b}_m=-3/2\,\vec{a}_F+3/2\,\vec{b}_F$, $\vec{c}_m=-3\,\vec{a}_F-3\,\vec{b}_F$ (1), or $\vec{a}_m=3/2\,\vec{a}_F+3/2\,\vec{b}_F-3\,\vec{c}_F$, $\vec{b}_m=-3/2\,\vec{a}_F+3/2\,\vec{b}_F$, $\vec{c}_m=5/2\,\vec{a}_F+5/2\,\vec{b}_F+4\,\vec{c}_F$ (2). For nominal Sr-Na$_{0.5}$Bi$_{0.5}$ compositions, the structure refinements led to $M_{10-\delta}\mathrm{Bi}_{36+\delta}\mathrm{V}_8\mathrm{O}_y$ non stoichiometric materials. In all structures, a cationic "slab" model was identified by the stacking of [(Bi,M, V) / Bi,M / (Bi,M, V)] layers. In these slabs, vanadium atoms are located in the external layers. The systematic stacking of 2 slabs (i.e. 6 cationic layers) allows the description of all the structures, except for Pb$_6$/Bi$_{40}$ nominal composition where a stacking of either 2 or 3 successive slabs is needed. In this description, the interslab distances are systematically larger than inter layer distances within the slabs. Along with the oxygen atoms, the cations determine a long range network of OBi$_4$ and O(Bi,M)$_4$ anti-tetrahedrons, distributed over the whole structure, and VO$_4$ located at the slab-interslab interfaces. The conductivity properties of materials with $M_{10}\mathrm{Bi}_{36}\mathrm{V}_8\mathrm{O}_{84}$ nominal compositions are presented. They likely result from the oxide ion mobility (of the OBi$_4$ and O(Bi,M)$_4$ entities) within the interslab spaces.

Key words   - strontium bismuth vanadium based mixed oxide.

                       - lead bismuth vanadium based mixed oxide.

                       - cadmium bismuth vanadium based mixed oxide.

                       - sodium bismuth vanadium based mixed oxide

                       - single crystal structure refinement.

                       - electrical conductivity properties

                       - structure-conductivity properties correlation

1. Introduction

Because of its excellent ionic conduction properties, the cubic fluorite type ($_F$) δ-Bi_2O_3 (approximately 1 S.cm^{-1} at 750°C) [1], and its related phases were very largely studied. Many bismuth containing mixed oxides adopt structure types closely connected to this variety [2-14].

In 1997, Watanabe identified the $Bi_{23}V_{84}O_{44.5}$ phase ($\equiv Bi_{46}V_8O_{89}$) with a triclinic lattice [15]. According to Darriet [16], this phase is characterized by a monoclinic cell: $a=20.0100(4)$Å, $b=11.6445(4)$Å, $c=20.4136(4)$Å and $\beta=107.27(3)°$, space group P21/c. The structure can be described by the stacking along the $\vec{c}$ axis, of 6 atomic layers with twice the sequence: 2 layers $[Bi_{14}V_4O_{31}]$ + 1 layer $[Bi_{18}O_{27}]$. In 1983, another vanadate $Bi_{14}V_4O_{31}$ ($\equiv Bi_{42}V_{12}O_{93}$) [17] was observed with a monoclinic cell $a=19.720$Å, $b=11.459$Å, $c=80.160$Å and $\beta=90.50°$ and either C2, Cm or C2/m space group. The structure determination did not succeed, but the cell is also related to the fluorite structural type. In 2005, $Bi_{50}V_4O_{85}$ was deferred in the binary diagram Bi_2O_3-V_2O_5 [18]; it is also monoclinic (I2/m space group) with the lattice parameters $a=11.8123(3)$Å, $b=11.7425(2)$Å, $c=16.5396(2)$Å, $\beta=90.14(1)°$. To stabilize this phase, an air quenching from 920°C to room temperature is necessary. Under a low temperature annealing, it transforms into a mixture of sillenite type [19, 20] and fluorite type phases. The poor quality of $Bi_{50}V_4O_{85}$ crystals, due to the thermal instability of this compound, did not allow a reliable structural determination. Nevertheless, Darriet succeeded in locating the heavy atoms, making it possible to propose the sequence: 1 layer $[Bi_{14}V_4O_{31}]$ + 2 layers $[Bi_{18}O_{27}]$. In fact, these phases ($Bi_{14}V_4O_{31}$, $Bi_{46}V_8O_{89}$, $Bi_{50}V_4O_{85}$) constitute 3 members of a general family type $Bi_{18-4m}X_{4m}O_{27+4m}$ (X=V, P), where m is the ratio of the number of $[Bi_{14}X_4O_{31}]$ layers to the total number of layers yielding the definition of the phase. According to this model, the structure of $Bi_{14}P_4O_{31}$ (m=1) results from the repetition of 16x $Bi_{14}P_4O_{31}$ layers parallel to the (001) plane; $Bi_{46}X_8O_{89}$ (X=V, P and m=2/3) is formed from the stacking of $[Bi_{14}X_4O_{31}, Bi_{18}O_{27}, Bi_{14}X_4O_{31}]$ successive layers, while $Bi_{50}V_4O_{85}$ (m=1/3) results from $[Bi_{14}V_4O_{31}, Bi_{18}O_{27}, Bi_{18}O_{27}]$ layers.

On the other hand, $Pb_5Bi_{18}P_4O_{42}$ was identified and characterized [21] as a phase with a fluorite-type structure. Its structure was determined by synchrotron single-crystal X-ray diffraction in a monoclinic cell (I2/m S.G.; a $\cong 3/2*\sqrt{2}*a_F$, b$\cong 3/2*\sqrt{2}*a_F$, c$\cong 3*a_F$, $\beta\approx 90°$). The structure was described by the sequence of lead atoms and disordered phosphates

constituting a two-dimensional assembly parallel to the (a,c) plane. Between these layers, Bi-O layers are located to form a three-dimensional array. However, this structure can also be considered as a stacking of 2 $Bi_{12}Pb_2P_4O_{30}$ layers sandwiching a single $Bi_{12}Pb_6O_{24}$ layer. For the vanadate, refinements of the powder pattern yielded the cell parameters a=12.009(4)Å, b=11.711(5)Å, c=16.143(7)Å and β=90.11(2)°. Isomorphous $Pb_5Bi_{18}X_4O_{42}$ homologues (X=V or As) were characterized [22] by powder X ray diffraction. Very similar overall compositions $Pb_5Bi_{17}X_5O_{43}$ (X=P, V, As) were also identified [23]. $Pb_5Bi_{17}P_5O_{43}$ crystallizes with a superstructure of δ-Bi_2O_3 form. Its structure was solved using synchrotron radiation in the cell: a=11.341(2)Å, b=16.604(3)Å, c=11.432(2)Å, β=93.73(3)° and Im space group. A combination with powder neutron diffraction allowed the localization of heavy atoms (Bi and Pb) implied in the formula, as well as the oxygen atoms. The structure can be described as a succession of layers ($Bi_{10}Pb_6P_2O_{26}$, $Bi_{14}P_4O_{31}$, $Bi_{10}Pb_4P_4O_{29}$).

In a quasi-general manner, in such a series of homologous materials, the conductivity increases from the phosphate to arsenate and the vanadate derivative. For the vanadium based materials, the reported conductivity Arrhenius plots show a decrease of the σ performances from $Bi_{46}V_8O_{89}$ to $Pb_5Bi_{18}V_4O_{42}$ and then $Pb_5Bi_{17}V_5O_{43}$. Due to the analogy of each structure to the δ-Bi_2O_3 fluorite type, they are assumed to be oxide ion conductors.

Thus, it appeared interesting to investigate the pseudo-binary system $Pb_5Bi_{18}V_4O_{42}$-$Bi_{46}V_8O_{89}$ in order to prepare new original phases, with a possible attracting conductivity property resulting from an optimal Pb^{2+} for Bi^{3+} substitution rate. This substitution could enhance the conductivity due to the increase of the mobile oxide ion number, and increase the structural stability in relation to the decrease of the vacancy ratio. The presence of a non-bonding $6s^2$ lone pair induces a high polarisability for both cations which facilitates the mobility of the oxide ions. In such a material, the coexistence of Pb^{2+} and Bi^{3+} isoelectronic ions, cannot be identified from X-ray diffraction crystal structure. For this reason, the structural investigations which have been realized, could not be used to consider any accurate structure-conductivity property correlations. In order to dodge this handicap to identify the location of Pb^{2+}, we have also examined the possibility of substituting this cation in $Pb_5Bi_{18}V_4O_{42}$, by other divalent M^{2+} (Sr^{2+}, Ca^{2+}, Cd^{2+}) or mixed equivalent ones ($Bi^{3+}_{0.5}Na^+_{0.5}$), which can be easily differentiated from bismuth, assuming they will be located in crystallographic sites equivalent to the lead ones; the obtained structural results, which were used to evaluate the formula(s) of the lead containing sample(s), will be (firstly) described in this paper.

2. Experimental.

2.1. Syntheses.

$M_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ powder samples for different compositions (M=Sr, Ca, Cd, Na$_{0.5}$Bi$_{0.5}$ with x=0; M=Pb with x varying from 0 to 1, by x step of 0.1) were prepared by solid state reaction. Bi$_2$O$_3$ (Aldrich, 99.9%) and V$_2$O$_5$ (Aldrich, 99.6%) were used as the main starting materials; "divalent cations" were introduced into the achieved different phases from SrCO$_3$ (Aldrich, 98.0%), CaCO$_3$ (Aldrich, 99.0%), CdO (Carlo Erba, 99.0%), a mixture Na$_2$CO$_3$ (Aldrich, 99.5%)-Bi$_2$O$_3$ in Na/Bi equimol proportions, or PbO (Riedel de Haën, 99%) with their correct stoichiometric amounts. For each composition, the reagents were weighed, placed in an agate mortar, and thoroughly grinded and homogenized. These mixtures were deposited in gold boats and heated in static air atmosphere for five 15 hrs treatments. Each one, ended by an air quenching, was followed by a regrinding. The treatment temperatures ranged between 600 and 800°C with a step temperature 50°C. Completion of the reaction was indicated by the reproducibility of the X-ray patterns after the two last treatments.

Single crystals were obtained from the powder sample melting at 1000°C, followed by slow cooling at 1°C/h until 840°C and then furnace disconnection; the cooling process was so uncontrolled. The selection of good quality crystals was based upon the sharpness of the diffraction spots.

2.2. The characterizations of the produced phases

A Bruker X8 CCD 4K diffractometer was used for the crystallographic characterization of the single crystals, which were made for all M compositions at ambient temperature. The crystal structures were solved using SIR97 software[24], and refined with the JANA2000 program [25]. In the structural refinements, VO$_4$ tetrahedra were regarded as rigid molecular groups. The rigidity of the vanadate group was determined by a number of common parameters for all the constituting atoms. Each position of the rigid group was defined by 3 swing angles (Φ, χ, ψ) and a translation vector (xtrans, ytrans, ztrans). The conditions of data collection are gathered in Tables I and II. Atomic positions and thermal parameters are available as supplementary materials.

Sintered pellets (diameter and thickness about 5 mm) were elaborated from materials sintering at 850°C for 48h, for investigating their electrical conductivity properties. The relative density of the sintered samples was nearly 85%. Gold electrodes were then sputtered

on both flat faces of the pellets and measurements were done by impedance spectrometry in the range 1-10^6 Hz using a Schlumberger 1170 frequency response analyzer. Conductivity measurements were realized in static air atmosphere between 300 and 840°C (temperature step: 10°C). Each set of values was recorded after 1 h stabilization stage.

Guinier Lenné X-ray diffraction camera (gold grid sample holder; heating rate ≈20°C.h^{-1}) as well as differential thermal analysis (DTA Linseis L62; platinum crucibles; heating cooling rate 300°C.h^{-1}) were used to investigate the thermal behaviour of all samples in air, corroborating the conductivity properties investigation.

3. Results and discussion

3.1. Crystal structures in the $(M,Bi)_{46}V_8O_y$ family (M=Sr, Ca, Cd, $Bi_{0.5}Na_{0.5}$).

As an example for this family, the crystal structure determination process of the Sr based sample is presented in order to show the complexity of each stage. The investigation was initially undertaken in the most symmetrical proposed orthorhombic lattice, i.e. in the Immm space group, after merging the equivalent reflections (R(F^2)$_{int}$=0.063 after absorption correction [21]). At this stage, the structural resolution did not succeed either by direct method, nor by Patterson interpretation. A reinvestigation was undertaken in a cell of lower symmetry, (monoclinic I) and yielded a R(F^2)$_{int}$ factor of about 0.057 with absorption correction. The structural refinement was thus conducted in the monoclinic I cell (a=11.9411(5)Å, b=11.7063(5)Å, c=16.3652(7)Å, β=90.059(3)°). The tested space groups were respectively I2/m, I2 and Im. In the two first cases, the refinements were not conclusive. The best structural refinement was found in the Im non-centrosymetric space group. Fourteen heavy atom positions (including 6 mixed sites Sr/Bi) were identifed and refined. Ten oxygen atoms were located by successive Fourier difference syntheses. At this point, the vanadium atomic environments were incomplete. Refinement of the anisotropic thermal coefficients of of bismuth, strontium and vanadium atoms, lead to the reliability factor 0.0609.In place of monoclinic Im S.G, the Platon software [Spek 1990] suggested to use the orthorhombic symmetry, with a non-centrosymetric Imm2 space group. Using these characteristics, a structural refinement was realized without introducing oxygen around vanadium atoms. The reliability factor converged towards 0.0642 with 93 refined parameters instead of 154 previously. The Platon software, used a second time, proposed the centro-symetric Immm space group. Six bismuth atoms positions, with one mixed site Sr1/Bi1b and one site fully

occupied by strontium (Sr2) were thus refined. Oxygen atoms were introduced from examination of Fourier difference maps around the two vanadium atoms (V1 and V2). The oxygen site occupancies were constrained in order to form two VO_4 tetrahedral entities. Residual peaks are still observed around vanadium atoms while the suggested model is thus an idealized model. The distances between V1 and O7, O8 and O9, and those between V2 and O10, O11 and O12 were also soft-constrained to the "ideal" value 1.65(2) Å. A last refinement cycle yielded a reliability value of 0.0596. In summary, it was impossible to solve the structure using the Immm space group, even if *in fine*, this space group is the actual one and thus used in the refinement process. The crystallographic characteristics, conditions of data collection and various refinement parameters are gathered in Table I-first column. The atomic coordinates and isotropic/equivalent* parameters and the atomic displacement parameters are given as supplementary materials.

Samples containing calcium or cadmium crystallise in analogous cells. Each structure determination has been undertaken using the non-centrosymmetric Pn2n space group. With a careful examination of the atomic positions, the Pnmn space group was finally selected. For calcium containing crystal, this element was distributed over a unique position and two Ca/Bi mixed sites. On the other hand, in the case of the cadmium based sample, Cd atoms occupy 3 mixed sites Cd/Bi with different occupancy rates. With $M=Bi_{0.5}Na_{0.5}$, the structure was finally refined in I2/m space group and Na was distributed over two Na/Bi mixed sites. The crystallographic characteristics of the three structures (M=Ca, Cd, $Bi_{0.5}Na_{0.5}$), the conditions of data collection and various refinement parameters are gathered in Table I-columns 2-4.

Each structure consists in a stacking of 6 cationic layers closely related to the cubic fluorite-type lattice (Fig.1-a). The M atoms are distributed in the layers in Bi/M mixed sites for all the compositions but, except for the Sr based sample, where one Sr atom lies in a distinct site. The vanadium atoms are located in two out of three layers. Their oxygen environment determines tetrahedral VO_4 entities (Fig.1-b) which are disordered over two positions. (Fig.2). The cationic environment of the remaining oxygen atoms determines a long range sub-lattice of closely linked OM_4 anti-tetrahedrons (Fig. 1c).

Table I : Principal characteristics of $M_{10}Bi_{36}V_8O_{84}$ (M=Sr, Cd, Ca, Na$_{0.5}$Bi$_{0.5}$) structure determinations on the X-ray single crystal diffractometer.

	Crystallographic data			
Nominal formula	$Sr_{10}Bi_{36}V_8O_{84}$	$Ca_{10}Bi_{36}V_8O_{84}$	$Cd_{10}Bi_{36}V_8O_{84}$	$Na_5Bi_{41}V_8O_{84}$
Refined formula	$Sr_{3.59(5)}Bi_{19.41(5)}V_4O_{42}$	$Ca_{4.207(4)}Bi_{18.793(4)}V_4O_{42}$	$Cd_{3.573(7)}Bi_{19.427(7)}V_4O_{42}$	$Na_{1.533(6)}Bi_{21.467(6)}V_4O_{42}$
Symmetry	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	I mmm (N°71)	P nmn (N°58)	P nmn (N°58)	I 2/m (N°12)
Cell parameters (Å)	a=11.9411(5) b=11.7063(5) c=16.3652(7)	a=11.9584(2) b=11.5275(2) c=16.0738(3)	a=11.9529(7) b=11.4873(3) c=15.965(1)	a=12.0352(3) b=11.5748(4) c=16.0686(5) β=90.115(2)°
Cell volume (Å³)	2287.6(2)	2215.77(8)	2192.2(2)	2238.4(1)
Relationship with δ-Bi₂O₃ cell	$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 3/2 & -3/2 & 0 \\ 3/2 & 3/2 & 0 \\ 0 & 0 & 3 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_\delta$			
Z	2	2	2	2
Density calculated (g.cm⁻³)	7.62	7.45	8.08	8.00
F000	4349	4144	4222	4450
	Intensity collection			
2θ range (°)	4.22 – 76.84	4.24 – 73.36	4.26 – 73.46	4.22 – 80.62
Data collected	$-20 \le h \le 20$ $-20 \le k \le 20$ $-28 \le l \le 28$	$-20 \le h \le 19$ $-26 \le k \le 26$ $-18 \le l \le 19$	$-16 \le h \le 20$ $-17 \le k \le 19$ $-26 \le l \le 20$	$-29 \le h \le 31$ $-20 \le k \le 20$ $-21 \le l \le 20$
No. of reflections collected	35353	69425	42451	37295
No. of reflections measured	3526	5712	5669	6664
No. of independent (I>3σ(I))	1757	3735	3023	3874
Redundancy	10.026	12.154	7.488	5.597
Completeness (%) / 2θ(°)	100 / 76.84°	99.9 / 73.36°	99.89 / 73.46°	95 / 71.94°
μ₁ (Mo, Kα) mm⁻¹	84.449	80.794	85.564	90.688
Tmin/Tmax ratio	0.255	0.288	0.188	0.233
R(F²)int before absorption correction	0.1542	0.1531	0.1903	0.2480
R(F²)int after absorption correction	0.0385	0.0576	0.0475	0.0860
	Refinement			
No. of parameters	82	130	112	109
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
R(F) obs/all	5.91 / 14.05	5.32 / 9.11	5.27 / 11.51	7.24 / 12.89
wR(F) obs/all	6.36 / 6.86	5.12 / 5.26	4.74 / 4.95	8.42 / 9.22
ρmax, ρmin (e-/Å³)	3.19 / -4.28	4.47 / -5.10	4.08 / -4.01	7.30 / -5.34
Second extinction correction	0.0024(8)	0.067(2)	0.0234(9)	0.018(1)

Figure 1: (010) projections of $Sr_{10}Bi_{36}V_8O_{84}$ related structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c).

Figure 2: Evidence of VO_4 disordering in $Sr_{10}Bi_{36}V_8O_{84}$ related structure.

3.2. $Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ series (x=0.4 and 0.7) crystal structures.

In the Bi_2O_3-PbO-V_2O_5 ternary system, X-ray powder investigation of the pseudo binary system $Pb_{10}Bi_{36}V_8O_{84}$-$Bi_{46}V_8O_{89}$ has been realized in order to identify possible original single phase materials. $Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ ($0 \leq x \leq 1$; x step 0.1) compositions were synthesized and characterized by X-ray powder diffraction (Fig.3). At both ends of this pseudo binary system, two different single phase (solid solution) domains are identified, respectively of $Pb_{10}Bi_{36}V_8O_{84}$-type [22] ($0 \leq x \leq 0.2$) and $Bi_{46}V_8O_{89}$-type [16] ($0.8 \leq x \leq 1$). In the intermediate compositional range, three different domains characteristic of binary mixtures are separated by two single phase compositions. The first one, at x=0.4, displays an original and simple pattern, while the second composition (x=0.7) has a pattern closely related to the x=0 end member: $Pb_{10}Bi_{36}V_8O_{84}$.

Fig. 3: Evolution of $Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ X-ray diffractograms versus x.

Applying the crystallization procedure described in the experimental section, single crystals suitable for X-ray structure determination were obtained for both nominal compositions $x = 0.4$-$Pb_6Bi_{40}V_8O_{86}$ and $x = 0.7$-$Pb_3Bi_{43}V_8O_{87.5}$.

Only one type of crystal was obtained for x=0.7, whereas two kinds of crystals were distinguished for x=0.4 composition (i.e. with two different unit cells). The three structures were investigated and solved. Their crystallographic characteristics, data collection conditions and various refinement parameters are gathered in Table II.

To facilitate the description of these structures, presented hereafter, the samples are labelled according to their nominal Pb/Bi ratio in the starting material: Pb_3Bi_{43} for x=0.7, Pb_6Bi_{40}-1 and Pb_6Bi_{40}-2 for the two crystals isolated from the composition x=0.4. Surprisingly, the Pb_6Bi_{40}-1 crystal obtained from the Pb richest nominal composition, displays a unit cell similar to $Bi_{46}V_8O_{89}$ [16], i.e. for the lead free composition.

Table II: Principal characteristics of $Pb_6Bi_{40}V_8O_{86}$-1, $Pb_6Bi_{40}V_8O_{86}$-2 and $Pb_3Bi_{43}V_8O_{87.5}$ structure determinations on the X-ray single crystal diffractometer.

Crystallographic data			
Nominal formula	$Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ (*x*=0.4) $\equiv Pb_6Bi_{40}V_8O_{86}$		$Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ (*x*=0.7) $\equiv Pb_3Bi_{43}V_8O_{87.5}$
Sample identification	$Pb_6Bi_{40}V_8O_{86}$ -1	$Pb_6Bi_{40}V_8O_{86}$ -2	
Refined formula	$Bi_{23}V_4O_{45}$	$Bi_{23}V_4O_{44}$	$Bi_{23}V_4O_{44}$
Symmetry	Monoclinic	Monoclinic	Orthorhombic
Space group	C 2/m (N°12)	C 2/m (N°12)	I mmm(N°71)
Cell parameters (Å)	a=20.0822(4) b=11.6351(2) c=21.0878(5) β=111.678(1)°	a=20.0874(4) b=11.6841(2) c=29.5629(6) β=98.816(1)°	a=12.1371(4) b=11.6935(4) c=16.0191(6)
Cell volume (Å³)	4578.8(2)	6856.5(2)	2273.5(1)
Relationship with δ-Bi_2O_3 cell	$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 3 \\ -\frac{3}{2} & \frac{3}{2} & 0 \\ -3 & -3 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_\delta$	$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & -3 \\ -\frac{3}{2} & \frac{3}{2} & 0 \\ \frac{5}{2} & \frac{5}{2} & 4 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_\delta$	$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{3}{2} & -\frac{3}{2} & 0 \\ \frac{3}{2} & \frac{3}{2} & 0 \\ 0 & 0 & 3 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_\delta$
Z	4	6	2
F000	9440	14112	4704
Intensity collection			
2θ range (°)	4.08 – 80.7	2.78 – 78.84	4.22 – 89.56
Data collected	-33≤ h ≤36 -20≤ k ≤17 -36≤ l ≤38	-35≤ h ≤35 -20≤ k ≤19 -48≤ l ≤52	-13≤ h ≤23 -22≤ k ≤23 -30≤ l ≤28
No. of reflections collected	63114	97783	29396
No. of reflections measured	14458	20474	4709
No. of independent (I>3σ(I))	7142	10425	2332
Redundancy	4.365	4.776	6.243
Completeness (%) /2θ(°)	96.71 /80.7°	96.80 /78.84°	95 /88.72°
μ_1 (Mo, Kα) mm^{-1}	94.929	95.089	95.59
Tmin/Tmax ratio	0.2416	0.263	0.248
$R(F^2)_{int}$ before absorption correction	0.2914	0.1934	0.2421
$R(F^2)_{int}$ after absorption correction	0.0719	0.0604	0.0811
Refinement			
No. of parameters	223	315	81
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
R(F) obs/all	0.0804 / 0.1767	0.0670 / 0.1528	0.0649 / 0.1442
wR(F) obs/all	0.0903 / 0.0982	0.0699 / 0.0767	0.0826 / 0.0887
ρmax, ρmin (e-/Å³)	3.59 / -7.61	7.84 / -8.14	4.42 / -4.75
Second extinction correction	0.011(1)	0.019(1)	0.029(2)

As in the $(M,Bi)_{46}V_8O_y$ family (M=Sr, Ca, Cd, $Bi_{0.5}Na_{0.5}$) reported in the precedent paragraph, the three crystal structures can be described as a stacking of 2 types of cationic layers containing either bismuth/lead/vanadium, or bismuth/lead. Vanadium is located in two third of the layers; a "slab" structural model can be seen from a stacking of triple layer blocks, where the vanadium is systematically located in both "external" layers. A sequence of 6 layers in Pb_3Bi_{43} or Pb_6Bi_{40}-1 (Fig. 4) and 9 layers in Pb_6Bi_{40}-2 (Fig. 5) can be identified along the c axis, corresponding respectively to a stacking of 2 slabs and 3 slabs, thus describing each structure from a common structural feature. As previously indicated, the lead atom cannot be distinguished from bismuth by X-ray diffraction when using Mo Kα radiation. In order to try to localize the lead site, a tentative comparison of the crystal structures of $M_{10}Bi_{36}V_8O_{84}$ (M=Sr, Ca, Cd) and the structures of $Pb_{10}Bi_{36}P_8O_{84}$ ($\equiv Pb_5Bi_{18}P_4O_{42}$) and $Pb_{10}Bi_{34}P_{10}O_{86}$ ($\equiv Pb_5Bi_{17}P_5O_{43}$) [21, 23], where Pb and Bi atoms were unambiguously identified, was undertaken.

Figure 4: (010) projections of Pb_6Bi_{40}-1 structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons and two slabs stacking (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c).

Figure 5: (010) projections of Pb_6Bi_{40}-2 structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons and three slabs stacking (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c).

Unfortunately, it was unsuccessful, mainly due to the existence of Bi/M mixed sites and the numerous possibilities of Pb localization to consider. An electron microprobe elemental analysis on Bi-Pb containing single crystals, did not give any conclusive information on the sample formulation. As the presence of lead is confirmed, this analysis of the Pb_6Bi_{40}-1 crystal (with a cell identical to $Bi_{46}V_8O_{89}$) corresponds rather to a standard solid solution composition $Pb_\delta Bi_{46-\delta}V_8O_{89-\delta/2}$. A thorough structural comparison of the vanadates with the already known fluorite type structure was undertaken with the aim of understanding their similarities and differences, and to identify a general layer like structural model.

3.3. The electrical conductivity properties.

Investigation of materials conductivity was undertaken for $M_{10}Bi_{36}V_8O_{15}$ (M=Pb, Sr, Ca, Cd, $Na_{0.5}Bi_{0.5}$) nominal compositions. While preponderant oxide ion mobility can be reasonably presumed for Pb, Sr, Ca and Cd based materials, a Na^+ cationic conductivity component cannot be excluded in the Na based family member, and could even become preponderant. For this latter Na sample we could not prepare a pellet with stable dimensions, going through the necessary sintering process; this thermal instability is probably related to the high sodium content of the material which yields a significant hygroscopicity.

Conductivity measurements were carried out on ceramic pellets of the other materials; the temperature dependence of the conductivity was evidenced from Arrhenius plots log (σT) = f ($10^3 T^{-1}$). Representation of the 1st cooling (800-300°C) and of 2nd heating (300-840°C) runs overlap, and only the 2nd heating data are represented for clarity of the figure (Fig. 6). Table III regroups the significant values of this study for σ conductivity (500 and 800°C) and for Ea activation energy (500°C).

The manufactured materials display an Arrhenius type electrical conduction behaviour, i.e. a linear relationship between log (σT) and $1/T$. The absence of any break or jump in each graph (300-840°C) is in good agreement with the absence of any event occurring during the thermal behaviour samples examination (Guinier Lenné diffraction and differential thermal analyses). Only one phase is stable within the whole investigated temperature range. For a given temperature above 550°C, the conductivity level decreases in the order Pb, Sr, Ca and Cd. The $Ca_{10}Bi_{36}V_8O_{84}$ sample presents the weakest activation energy, clearly distinct from the three other samples at low temperature. At 300°C, the Ca and Pb based samples exhibit similar conductivity performances.

Figure 6: Conductivity Arrhenius plots of $M_{10}Bi_{36}V_8O_{84}$ materials (M=Pb, Sr, Ca, Cd).

Table III: σ total conductivity (ohm.cm)$^{-1}$ at 500 and 800°C and Ea activation energy (eV) for $M_{10}Bi_{36}V_8O_{84}$ (M=Pb, Sr, Cd, Ca) samples.

Ionic radii of $M^{2+}_{(VIII)}$ (Å)	Sample	σ (ohm.cm)$^{-1}$		Ea (eV)
		500°C	800°C	500°C
1.29	$Pb_{10}Bi_{36}V_8O_{84}$	$8,91.10^{-5}$	$4,57.10^{-3}$	0,92
2.26	$Sr_{10}Bi_{36}V_8O_{84}$	$3,75.10^{-5}$	$1,87.10^{-3}$	1,01
1.12	$Ca_{10}Bi_{36}V_8O_{84}$	$3,73.10^{-5}$	$1,05.10^{-3}$	0,79
1.10	$Cd_{10}Bi_{36}V_8O_{84}$	$4,27.10^{-6}$	$2,52.10^{-4}$	0,93

3.4. Discussion

In a previous paper about the $M\text{Bi}_6\text{V}_2\text{O}_{15}$- family type [26], we have described three isomorphous members (M=Sr, Ca and Cd), in the same space group C2/c. A methodology, based on structural results, allowed us to plot for the different (Bi, M) mixed site compositions, the mean cationic radius versus the unit cell volume. The dependence between the mean cationic radius and the cell volume for this series permitted us to construct a calibration curve that we used as a "standard chart", and consequently, we were able to evaluate the Pb/Bi radii for the corresponding mixed sites of the isostructural lead containing sample. From these radii, the Bi/Pb occupancy factors were estimated and a chemical formula was proposed. The same approach was tried for the materials reported in the present paper, i.e. the $(M,\text{Bi})_{46}\text{V}_8\text{O}_y$ family, which crystallizes with closely related structures, but with various space groups. Unfortunately, no correlation between the mixed site cationic radii could be evidenced.

Examining successively the various members of the series $(M,\text{Bi})_{42}\text{V}_{12}\text{O}_y$ independently of the changes of space group (respectively C2, Cm ou C2/m for $\text{Bi}_{42}\text{V}_{12}\text{O}_{93}$ [17], C2/c or C121 for $(M,\text{Bi})_{42}\text{V}_{12}\text{O}_y$ with M=Pb, Sr, Ca, Cd or $\text{Na}_{0.5}\text{Bi}_{0.5}$) a linear correlation can be identified between the cell volume and the ions volume for the corresponding formula units (calculated from M^{2+}, Bi^{3+}, V^{5+} and O^{2-} ionic radii $_{(VI)}$ [27, 28]–Fig. 7; correlation factor r^2=0.94). M for Bi substitution, even when $r\text{M}^{2+}$>$r\text{Bi}^{3+}$ (M=Sr, Pb), leads to a decrease of the cell volume. This tendency is resulting from the decrease of the oxygen content when compared to $\text{Bi}_{42}\text{V}_{12}\text{O}_{93}$. An analogous cell contraction is observed for $(M,\text{Bi})_{46}\text{V}_8\text{O}_y$ crystalline materials obtained from substitutions in $\text{Bi}_{46}\text{V}_8\text{O}_{89}$ using smaller elements than bismuth ($\text{Na}_{0.5}\text{Bi}_{0.5}$, Ca, Cd; linear correlation factor r^2=0.91), whereas a dilatation of the lattice is observed with Sr.

Figure 7: Cell volume – ions volume correlation for $(M\text{Bi})_{46}\text{V}_8\text{O}_y$ and $(M\text{Bi})_{42}\text{V}_{12}\text{O}_y$ families.

This Sr specific behaviour can be explained by the more important defective character of the $\text{Bi}_{46}\text{V}_8\text{O}_{89}$ oxide sublattice compared to $\text{Bi}_{42}\text{V}_{12}\text{O}_{93}$; thus the influence of the oxygen content decrease, during the Sr^{2+} for Bi^{3+} substitution, is minor when compared to the dilatation effect due to the increase of the cationic radius. The absence of "cell volume-ions volume" correlation in $(M,\text{Bi})_{46}\text{V}_8\text{O}_y$ series, while a linear correlation is observed for the

$Bi_{42}V_{12}O_{93}$ related family, is not clear at present. These observations led us to renounce to Pb evaluation in the here investigated corresponding materials.

The organization in cationic layer triplets (hereafter slabs) is a common structural character to numerous phases in this system. The mixed oxide phases with the rhombohedral Bi-Sr-O-type [29], containing bismuth - alkaline-earth, or bismuth - rare earth can be so described. In this case, the number of slabs is specific to each variety: a single slab determines the ε-variety, whereas a stacking of three slabs is necessary to describe β_2 or β_1 variety.

The cationic planes correspond to (111) crystallographic planes of a distorted cubic standard fluorite cell. In the $M_6Bi_{36}V_{12}O_{90}$ series [24], it consists of a crushing of the fluorite type lattice perpendicularly to these planes, thus leading, in each plane, to increased inter cationic distances compared to their initial location in a truly cubic cell. This type of crushing is also observed for the rhomboedral Bi-Sr-O type structures [29]. In the $(M,Bi)_{46}V_8O_y$ series considered in the present paper, the fluorite lattice is stretched. The reference thickness unit, i.e. "slab + inter-slab", which corresponds in all cases to the main diagonal $(a_F\sqrt{3})$ of a standard fluorite cell, is here longer than the diagonal of a truly cubic fluorite cell (maximum of inequality for Ca based sample).

Another representation of these structures consists in layer like arrangements of $O(Bi,M)_4$ anti-tetrahedrons (M=Pb, Bi, Sr, Ca, Cd, $Bi_{0.5}Na_{0.5}$) and VO_4 tetrahedrons, as presented in the $MBi_6V_2O_{15}$-type family [24] where a stacking of disconnected slabs has been identified; on the contrary, the slabs of $(M,Bi)_{46}V_8O_y$ materials are linked by $O(Bi,M)_4$ anti-tetrahedrons. There exists a relationship between the number of oxygen of the lateral slab layers and the inter-slab distance, since a slight dilatation of inter-slab space is observed between $Bi_{50}V_4O_{85}$ and $Bi_{46}V_8O_{89}$: as 4 vanadium atoms substitute for bismuth atoms, a contraction of the layers should appear (bismuth ionic radius being larger than the vanadium one); however, this is negligible compared to dilatation. The influence of the cationic size is thus counterbalanced by the major influence of introduced oxygen atoms. On the other hand, increasing the vanadium content ratio (from $(M,Bi)_{46}V_8O_y$ materials to $MBi_{36}V_{12}O_{90} \equiv MBi_6V_2O_{15}$) induces the trapping of interslab oxygen atoms, towards the slabs, to form vanadate anions. So the slabs are more easily distinguished. The presence of the oxygen ratio in the interslab spaces leads to the formation of "bridging" $O(Bi,M)_4$ entities between the slabs.

It is worth to note that the conductivity performances of $M_{10}Bi_{36}V_8O_{84}$ materials in the high temperature domain increase in the order Cd→Ca→Sr→Pb. This order corresponds to

the regular increase of the unit cell volume and to decrease of the inter layer distances within the slab therefore producing an expansion of the interlab space. This space can be reasonably presumed as the host sublattice for the mobile ions, considering the analogy of these structures with the rhombohedral Bi-Sr-O type conductors [29]. The latter as well as the $M_{10}Bi_{36}V_8O_{84}$ materials are slightly more conductive than the $MBi_6V_2O_{15}$ ($\equiv M_6Bi_{36}V_{12}O_{90}$) family. It is difficult to identify the parameters responsible for these better conductivity properties: both the ionic compactness of the structure and the oxide ions number are lower for $M_{10}Bi_{36}V_8O_{84}$, and when the first characteristic favours the conductivity, the second one would diminish it. In fact $M_{10}Bi_{36}V_8O_{84}$ series, contrarily to $MBi_6V_2O_{15}$-one, exhibits oxygen ions in the interslab space, with OBi_4 and $O(Bi,M)_4$ environments. It is reasonable to think that these ions are responsible for the conductivity enhancement.

On the other hand, to the $Ca_{10}Bi_{36}V_8O_{84}$ material which exhibits the lowest activation energy, is associated the structure characterized by the most stretched fluorite type lattice. This high stretching rate is likely responsible of the opening of migration pathways for the oxide ions, and consequently to a decrease of the activation energy.

4. Conclusion

The cationic slab model built out of [(Bi/M, V) / Bi/M /(Bi/M, V)] triple layers where the vanadium atoms are systematically located in the external layers, appears to be adapted to the whole family of phases highlighted in this work, but fits also other fluorite related structural types, i.e. vanadates or phosphates reported in the literature: $Bi_{50}V_4O_{85}$ [18], $Bi_{46}X_8O_{89}$ (X=V, P) [16], $Pb_{10}Bi_{36}P_8O_{84}$ ($\equiv Pb_5Bi_{18}P_4O_{42}$) [21], $Bi_{42}P_{12}O_{93}$ ($\equiv Bi_{14}P_4O_{31}$) [18]. The crystal structure investigation of $Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ solid solution samples has shown the existence of two kinds of triple layer stacking (6 cationic layers organized in 2 slabs, or 9 cationic layers in 3 slabs). The lead atoms could not be located and specifically identified from Bi.

5. Supplementary material.

Crystal Structure Data for the various phases gathered in Table I and Table IV, have been sent to the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany

(fax: (+49)7247-808-666; e-mail: crystaldata@fiz-karlsruhe.de;

http://www.fiz-karlsruhe.de/ecid/Internet/en/icsd/depot_anforderung.html),

as supplementary material CSD Nos. 418365 ($Ca_{10}Bi_{36}V_8O_{84}$), 418366 ($Cd_{10}Bi_{36}V_8O_{84}$), 418367 ($Na_5Bi_{41}V_8O_{84}$), 418368 ($Pb_3Bi_{43}V_8O_{87.5}$), 418369 ($Pb_6Bi_{40}V_8O_{86}$ -1), 418370 ($Pb_6Bi_{40}V_8O_{86}$ -2), 418371 ($Sr_{10}Bi_{36}V_8O_{84}$). Copies of this information can be obtained by contacting the FIZ (quoting the article details and the corresponding CSD number).

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Fig. 1: (010) projections of $Sr_{10}Bi_{36}V_8O_{84}$ related structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c). For clarity, only one configuration of tetrahedrons is presented.

Fig. 2: Evidence of VO_4 disordering in $Sr_{10}Bi_{36}V_8O_{84}$ related structure.

Fig. 3: Evolution of $Pb_{10(1-x)}Bi_{36+10x}V_8O_{84+5x}$ X-ray diffractograms versus x.

Fig. 4: (010) projections of Pb_6Bi_{40}-1 structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons and two slabs stacking (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c). For clarity, only one configuration of tetrahedrons is presented.

Fig. 5: (010) projections of Pb_6Bi_{40}-2 structure: cationic arrangement, crystalline cell and related fluorite sub-cell (a); viewing of VO_4 tetrahedrons and three slabs stacking (b); long range network from VO_4 and $O(Bi,M)_4$ assembly (c). For clarity, only one configuration of tetrahedrons is presented.

Fig. 6: Conductivity Arrhenius plots of $M_{10}Bi_{36}V_8O_{84}$ materials (M=Pb, Sr, Ca, Cd).

Fig. 7: Cell volume – Ions volume correlation for $(MBi)_{46}V_8O_y$ and $(MBi)_{42}V_{12}O_y$ formulas.