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Polymorphism in $PbBiOXO_4$ compounds ($X = V$, P, As): Part II—$PbBiOPO_4$ and $PbBiOAsO_4$ structures and characterization of related solid solutions

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ABSTRACT

Reinvestigation of $PbBiOXO_4$ ($X = V$, P, As) thermal behaviour revealed a phase transition for V- and P-compounds, but no transition for the As-compound. As shown by single-crystal X-ray diffraction and high-resolution neutron powder diffraction, α-$PbBiOVO_4$ transforms to β-$PbBiOVO_4$ at 550 °C. The two $PbBiOPO_4$ varieties are isomorph to the vanadate forms, while $PbBiOAsO_4$ adopts the β-type structure whatever the temperature. $PbBiP_{1-x}OAs_xO_4$ and $PbBiV_{1-x}OM_xO_4$ ($M = As$, P, Cr, Mn) solid solutions display both triclinic and monoclinic domains, and the $\alpha \rightarrow \beta$ transition temperature is a function of the substitution rate. The ionic conductivity of these compounds was investigated by impedance spectroscopy. The analysis of free space in the β-$PbBiOVO_4$ structure allows to propose a one-dimensional oxygen diffusion pathway along [010] when the temperature increases.

1. Introduction

In a survey of nPbO–BiXO_4 ($X = V$, P, As) compounds, phases corresponding to $n = 1$, i.e. $PbBiOVO_4$, $PbBiOPO_4$ and $PbBiOAsO_4$, have been described [1–3].

A reinvestigation of $PbBiOXO_4$ ($X = V$, P, As) thermal behaviour (DSC, HTXRD) showed the occurrence of a similar phase transition in the vanadate and phosphate compounds, while no transition was evidenced for the arsenate. At room temperature, $PbBiOPO_4$ and $PbBiOAsO_4$ were considered to be isomorph to the $PbBiOVO_4$ low-temperature form and the high-temperature form, respectively [2,3]. So far their crystal structures have not been described.

In a previous part of this study, a new approach to prepare $PbBiOVO_4$ single crystals was successfully conducted, allowing an X-ray single-crystal diffraction reinvestigation of the structural transformation. Combined with high-resolution neutron powder diffraction, both room (25 °C) and high (550 °C) temperature forms were structurally characterized. Subsequently this paper is dealing with various cationic substitutions for vanadium and phosphorus in $PbBiOXO_4$ ($X = V$, P), which have been tested, and related solid solutions characterized in order to investigate the relationship between the substituent nature and the phase transition temperature.

2. Experimental

2.1. Syntheses

$PbBiOVO_4$, $PbBiOPO_4$ and $PbBiOAsO_4$ powder samples were prepared by solid-state reaction of stoechiometric amounts of the starting reagents PbO (Riedel de Haën, 99%), Bi_2O_3 (Aldrich, 99.9%), V_2O_5 (Aldrich, 99.6%), $(NH_4)_2HPO_4$ (Sigma, 99%) and As_2O_5 (Janssen, 99.5%). Compositions were weighed, mixed in an agate mortar, fired at temperatures in the 600–800 °C range for a week, with intermediate grindings in order to obtain the desired single-phase material. The phosphate samples were initially preheated at 300 °C to allow $(NH_4)_2HPO_4$ decomposition.

Substituted powder samples $PbBiOP_{1-x}As_xO_4$ and $PbBiOV_{1-x}X_xO_4$ ($X = As$, P, Cr, Mn) were also synthesized; the two later elements were introduced, respectively, as Cr_2O_3 (Probabo, 99.0%) and MnO_2 (Aldrich, 99%) oxides.

2.2. Characterization methods

The powder and single-crystal samples characterization by X-ray diffraction and their thermal behaviour were conducted as described in the part I of this paper. Their electrical conductivity properties were investigated by impedance spectroscopy, on pellets of 5 mm in diameter and 2–3 mm in thickness, sintered at 850 °C for 48 h. The relative density of the sample was about 90%. Gold electrodes were sputtered on both flat faces and measurements were carried out in air, by impedance spectroscopy in the 1–10^6 Hz frequency range, using a Schlumberger 1170

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frequency response analyser from 290 to 800 °C, with a step of 10 °C, with 1 h of stabilization at each temperature before measurement.

3. Results and discussion

3.1. PbBiOPO$_4$

As already described by Giraud et al. [2], PbBiOPO$_4$ has been previously identified as isostructural to PbBiOVO$_4$, but no single crystal of good quality could be obtained. DTA revealed an incongruent melting at 930 °C, with two peaks observed at 880 and 865 °C during the cooling process, leading to a polyphasic mixture containing PbBiOPO$_4$ back to room temperature. On heating, no thermal effect related to a phase transition was noticed.

As for PbBiOVO$_4$, a Guinier-Lenné pattern was collected from 20 to 850 °C in 40 h, and stopped just before reaching the melting temperature. It revealed a phase transition, with a drastic modification of the diffraction pattern occurring around 725 °C; the diffraction lines observed at 20 °C were indexed on the basis of the α-PbBiOVO$_4$ triclinic cell. The lattice parameters evolution is similar to PbBiOVO$_4$ and confirms the transformation to a β-PbBiOPO$_4$ form isomorph to the high temperature form of PbBiOVO$_4$.

In an attempt to prepare good quality single crystals, a powder sample of PbBiOPO$_4$ was melted at 1000 °C; the cooling process was similar to that used for the vanadate homologous, with a first slow cooling step (1 °C/h) down to 850 °C, and finally the furnace switching off until RT. The obtained crystals were quenched at room temperature. Several phases were found, i.e. Pb$_4$Bi(PO$_4$)$_3$O, Pb$_3$Bi(PO$_4$)$_3$ and PbBiOPO$_4$ belonging to the PbO–Bi$_2$O$_3$–P$_2$O$_5$ ternary system. However, the selected PbBiOPO$_4$ crystals were not of sufficient quality and structural single-crystal studies failed. Consequently, an X-ray powder Rietveld analysis was conducted. Powder X-ray diffraction data were taken from 5° to 110° in 2θ, with a 0.02° step scan and an integration time of 11 s, on a Bruker D8 Advance diffractometer, Cu $K\alpha$ radiation, equipped with a SolX energy dispersive detector.

The PbBiOPO$_4$ structure refinement was made with the JANA2006 software [4], based on structural information from the PbBiOVO$_4$ crystal data: a *pattern matching* allowed fixing a number of parameters (full-width at half-maximum, background, lattice parameters, etc.). The atomic positions from PbBiOVO$_4$ were then introduced, and refined. Isotropic phosphorus and oxygen thermal factors were given a common value, and the lead and bismuth corresponding anisotropic factors were refined. The Rietveld agreement factors were $R_p = 6.03\%$, $R_{wp} = 7.90\%$, $R_{exp} = 3.31\%$, $R_w(\text{obs}) = 4.33\%$ (Fig. 1).

3.2. PbBiOAsO$_4$

3.2.1. Thermal evolution

At room temperature, PbBiOAsO$_4$ was first prepared by Giraud et al. [3]. Its diffraction lines could be indexed on the basis of β-PbBiOXO$_4$ (X = V, P) high temperature form lattice parameters. Consequently, at ambient temperature, PbBiOAsO$_4$ is monoclinic. DTA, DSC and Guinier-Lenné X-ray thermodiffraction experiments did not show any phase transition. On the other hand, a thermal analysis down to −173 °C was performed using a 141 Setaram DSC and a Panalytical powder diffractometer equipped with a nitrogen cooled Anton Paar TTK450 device. Again, neither accident on the DSC curve, nor any modification of the diffraction lines were observed, thus eliminating any hypothetical low-temperature phase transition from the β form to the α one, at least down to −173 °C.

3.2.2. Single-crystal structural study

PbBiOAsO$_4$ powder was sampled in a gold tube, heated at 1000 °C for 1 h, then slowly cooled at 1 °C/h until reaching 850 °C, and finally the furnace was disconnected. Single crystals of various shapes were obtained; a crystal sample was selected and the diffraction data collected on a Bruker X8 CCD 4K diffractometer. The refinement results are reported in Table 1.

Even if the crystal was not of high quality, the structure refinement was possible down to a sufficient level to show unambiguously that the structure is identical to the high-temperature PbBiOVO$_4$ polymorph. The Pb1 coordination

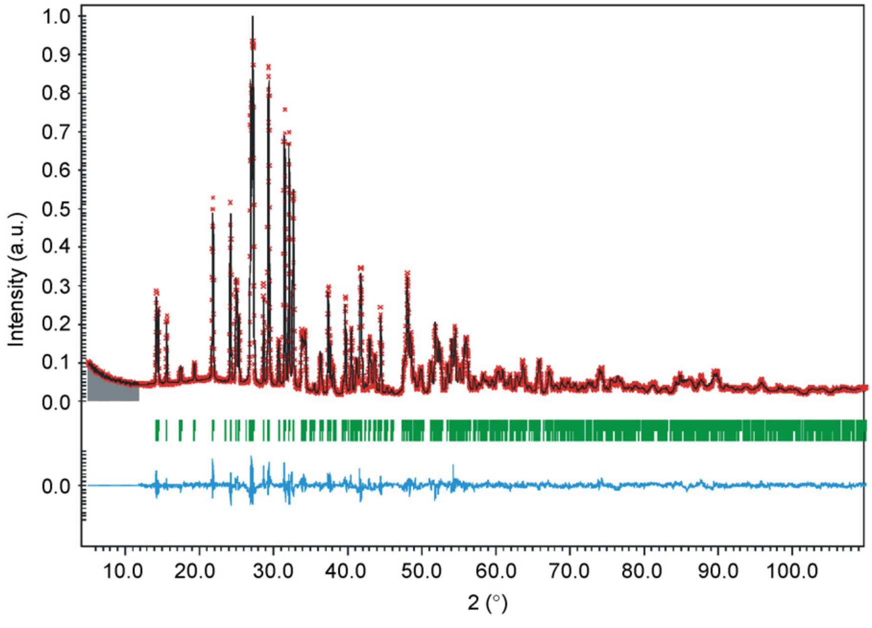

Fig. 1. PbBiOPO$_4$ X-ray powder diffraction pattern: experimental (red), calculated (black) and difference (blue).

Table 1
Principal characteristics of $PbBiOXO_4$ crystal structure determinations from X-ray powder ($X = P$) or single-crystal ($X = As$) data

Crystallographic data		
Radiation type	X-ray	X-ray
Chemical formula	$PbBiOPO_4$	$PbBiOAsO_4$
Formula weight (g)	527.1	571.1
Temperature (°C)	25	25
Form	α	β
Cell setting	Triclinic	Monoclinic
Space group	$P-1$ (N°2)	$C2/m$ (N°12)
a (Å)	5.6158(1)	$a = 13.528(2)$
b (Å)	6.8706(1)	$b = 5.576(1)$
c (Å)	7.1189(1)	$c = 7.068(1)$
α (deg)	109.982(1)	–
β (deg)	109.817(1)	$\beta = 114.054(5)$
γ (deg)	96.897(1)	–
V (Å^3)	234.04(1)	486.9(1)
Z	2	4
Dx (g/cm^3)	7.478	7.79
Data collection		
Wavelength (Å)	1.5418 (Cu $K\alpha$)	0.71073 (Mo $K\alpha$)
2θ range (deg)	5.00–110.00	6.32–78.64
2θ step (deg)	0.02	–
Data collected	–	$-23 \leqslant h \leqslant 23$
–		$-9 \leqslant k \leqslant 7$
–	–	$-12 \leqslant l \leqslant 11$
Collected reflections Nb	–	6538
Measured reflections Nb	–	1495
Independent reflections Nb ($I > 3\sigma(I)$)	–	1156
Redundancy	–	4.157
μ_1/mm (Mo, $K\alpha$)	–	79.74
$R(F^2)_{int}$	–	0.0738
Diffractometer	Bruker D8	Bruker X8
Monochromator	–	Graphite
Detector	Energy dispersive (Sol-X)	CCD 4K
Refinement		
$R(F)$ obs/all	–	0.0876/0.1039
$wR(F)$ obs/all	–	0.1063/0.1077
Second extinction	–	0.024(3)
Background	10 Legendre polynomial terms combined with manual background	
R_p	0.0603	–
wR_p	0.0790	–
wR_{obs}	0.0433	–
GOF	2.40	–
Nb of used parameters	38	29
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$
Profile	Pseudo-Voigt	–
Computer programs	Jana 2006—β version	Jana 2006—β version

polyhedron is built from a pseudo-rectangular basis O1O4O3O4, and the five remaining oxygen atoms belong to different AsO_4 tetrahedra: i.e. three O3 on one side, two of them being one AsO_4 edge, and O1, O2 from an other AsO_4 on the other side. As described previously for $PbBiOVO_4$ polymorphs (part I of this paper) lone pair coordinates and distances (Å) from nuclei were determined: 0.325, 0.000, 0.865 and 0.272 for lead, and 0.029, 0.000, 0.322 and 0.343 for bismuth, respectively. Again, the Bi lone pair L is oriented opposite to the square basis, towards the missing corner of a pseudo-cubic environment.

3.3. *Solid solutions*

3.3.1. *Identification of crystalline forms*

Introduction of various doping elements into $PbBiOVO_4$ was carried out via cationic substitution for vanadium. As indicated in XRD analysis, a triclinic solid solution was obtained for $PbBiOV_{1-x}P_xO_4$ samples, whatever the P for V substitution rate.

Introduction of As was performed via cationic substitution for M^{5+} element in $PbBiOVO_4$ or $PbBiOPO_4$. Both structural types (triclinic and then monoclinic) were successively observed.

As noted during the high-temperature X-ray diffraction study (Fig. 3), the modification of the γ angle of the triclinic phase, resulting from the As for V substitution, is characteristic of the triclinic $\leftrightarrow$ monoclinic crystal structure evolution. The closer is the γ angle value to 90°, the closer it gets to the triclinic$\rightarrow$ monoclinic transition (Fig. 2—top); when γ reaches 90°, the phase transition occurs. Along with the P for V substitution, γ increases far from this value; both $PbBiOPO_4$ and $PbBiOVO_4$ are triclinic at room temperature and in $PbBiOPO_4$, the transition temperature, observed at 750 °C, is higher than for $PbBiOVO_4$. Substituting As for V (Fig. 2—bottom) leads to an opposite evolution of γ.

While doping $PbBiOVO_4$ with chromium and manganese, the resulting solid solutions $PbBiOV_{1-x}Cr_xO_{4\pm y}$ and $PbBiOV_{1-x}Mn_xO_{4\pm y}$ were observed, respectively, until $x = 0.15$ and 0.06; above these limits, some extra peaks characterizing Cr_2O_5 and Pb_2MnO_4, were always detected in the corresponding powder X-rays patterns.

Fig. 3 shows the composition dependence of $PbBiOV_{1-x}X_xO_4$ unit formula volume for the different investigated triclinic domains. The significant decrease of this volume for As or P doping agent is in good agreement with the X^{5+} ionic radii of these elements, smaller than V^{5+} radius. Mn or Cr which exhibits an ionic radius higher than V^{5+}, induced a very limited expansion of the unit cell volume, linked to their narrow compositional domain.

3.3.2. *Conduction properties*

Conductivity measurements were performed on $PbBiOVO_4$ and substituted materials, during two heating–cooling cycles between 280 and 800 °C. The measurements carried out during the first heating run are generally erroneous because of the evolution of the sample–electrodes–cell interfaces, and cannot be trusted. The results corresponding to the first cooling run, which are reproducible during the subsequent thermal cycles, are presented on conductivity Arrhenius plots (Fig. 4).

Quite logically, a single pseudo-linear Arrhenius domain characterizes the $PbBiOAsO_4$ compound, which is monoclinic in the temperature range of significant measurements (below 500 °C, the conductivity values are too low and cannot be measured). An analogous pseudo-linear domain is also observed, over the whole investigated temperature range for $PbBiOPO_4$, and below 700 °C for $PbBiOVO_4$, although the $\beta \rightarrow \alpha$ phase transition occurs for both compounds; the small accident which can be observed around 440 °C for $PbBiOVO_4$, cannot be correlated to the phase transition identified near 450 °C by several other techniques, since similar anomalies in $\log \sigma$ evolution are observed for $PbBiOPO_4$ (550 °C) or $PbBiOAsO_4$ (460 °C), where no phase transition occurs. The oxyvanadate compound is a better conductor than its phosphate or arsenate homologous, although the latter is under the “stabilized” high-temperature form, in the whole investigated temperature range.

Substitution of vanadium, generally decreases the conductivity, except the Cr for V doping which leads to an enhancement of σ in the domain of the monoclinic β-form and shows two pseudo-linear domains, with a slope change likely corresponding to the $\beta \rightarrow \alpha$ phase transition. This specific positive effect of Cr-doping on the β-form σ could be attributed to the appearance of an electronic conductivity contribution due to chromium. These influences of the substituting elements are similar to that reported for cationic substitutions in Pb_2BiVO_6 [5]. While the

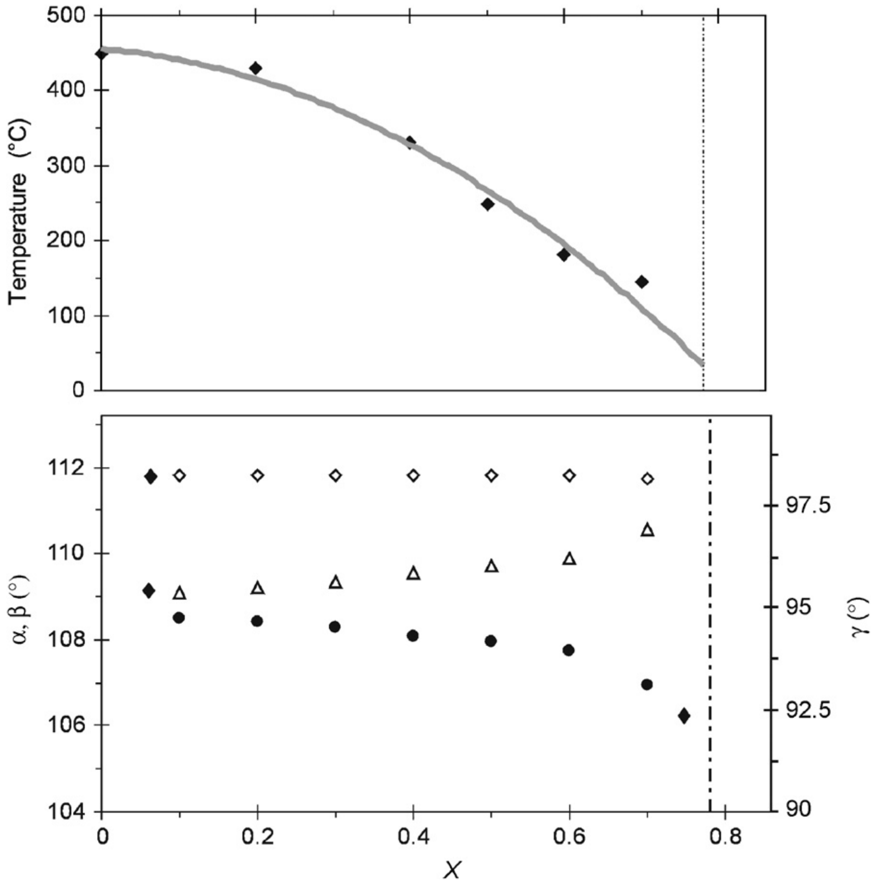

Fig. 2. Composition dependence of transition temperature (high part) and angles for triclinic $PbBiOV_{1-x}As_xO_4$ samples.

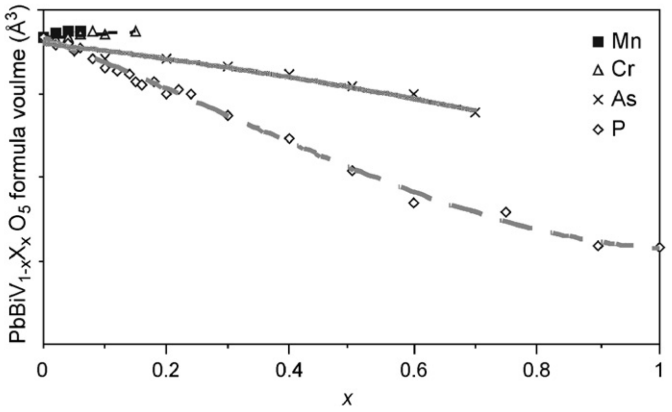

Fig. 3. Triclinic $PbBiOV_{1-x}X_xO_4$ formula volume versus composition for different doping elements ($X = P$, As, Cr, Mn).

highest conductivity performances are observed in the high-temperature domain for Cr-doped ($x = 0.06$) β-$PbBiOVO_4$, the unsubstituted α-$PbBiOVO_4$ variety remains the best conductor among the investigated compounds in the 20–450 °C temperature range.

Table 2 reports the significant values (activation energy: E_a and conductivity: σ) at 700 °C, which correspond in all cases to the monoclinic structure, and at 300 °C (conductivity: σ) which, depending on the composition, corresponds to one or the other structure.

In contrast to the other compositions, the vanadium compound exhibits a sudden increase of conductivity at 710 °C while no evident phase transition was observed by X-ray thermodiffractometry. A significant curvature of the Arrhenius plot above 600 °C was also observed by Sinclair et al. [6] for this composition and could not be associated with any phase transition. However, a tentative interpretation of this phenomenon can be proposed on the basis of what occurs in $Bi_{26}Mo_{10}O_{69}$ oxide ion conductors [7]. An increase of the conductivity could be explained by possible motion of oxygen vacancy at temperature higher than 750 °C. Indeed if we consider the cationic lattice of $PbBiOVO_4$, its crystal structure can also be viewed as a superstructure of the fluorite-type to which the highly conductive form δ-Bi_2O_3 belongs. Writing the studied compound formula as $Pb_4Bi_4V_4O_{20}$, clearly shows that a super cell originating from stacking three fluorite-type unit cells (i.e. $Ca_{12}F_{24}$) would introduce four anionic vacancies, or show one oxide vacant site per formula unit, i.e. $PbBiOVO_4\square_1$.

A rapid analysis of available free space in the β-polymorph revealed a cavity at 0.196 1/2 0.584, located in between two VO_4 along [010], at 2.17 and 2.19 Å from O(3) and O(2), respectively, and at 2.36 Å from Bi(1). At 550 °C, the centre of this cavity is too close to O(2) and O(3) sites to allow oxygen diffusion, but one can expect an expansion of the cavity size due to thermal motion when the temperature increases. This would allow the possibility of oxygen motion with a diffusion pathway along [010].

4. Conclusion

This reinvestigation of $PbBiOXO_4$ ($X = V$, P, As) phases revealed a phase transition for V- and P-compounds, but no transition for the As-compound. The two $PbBiOPO_4$ varieties are isomorph to the vanadate forms, while $PbBiOAsO_4$ adopts the β-type structure

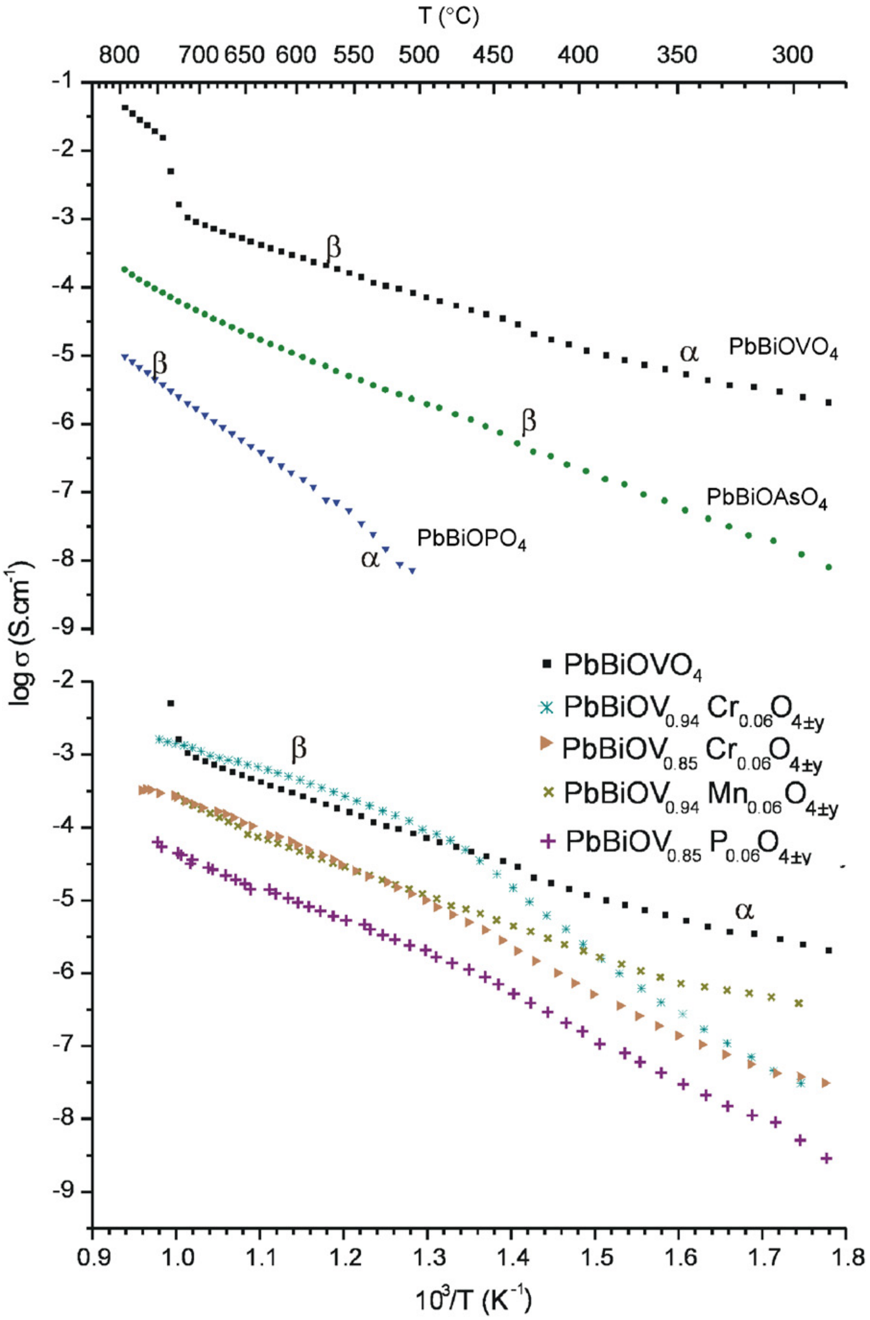

Fig. 4. Conductivity Arrhenius plots of $PbBiOXO_4$ ($X = V$, P, As) compounds (upper part) and of $PbBiOVO_4$-related solid solutions (lower part).

Table 2
Activation energy and conductivity values at 700 and 300 °C

Material	Ea (eV)	$\sigma_{700\,^{\circ}C}$ $(\Omega\,cm)^{-1}$	$\sigma_{300\,^{\circ}C}$ $(\Omega\,cm)^{-1}$
$PbBiOVO_4$	0.75	9.3×10^{-4}	2.64×10^{-6}
$PbBiOPO_4$	1.67	1.68×10^{-6}	5.34×10^{-10}
$PbBiOAsO_4$	1.06	4.69×10^{-5}	1.98×10^{-8}
$PbBiOV_{0.94}Cr_{0.06}O_{4\pm y}$	0.79	1.05×10^{-3}	3.11×10^{-8}
$PbBiOV_{0.85}Cr_{0.15}O_{4\pm y}$	1.01	1.8×10^{-4}	2.15×10^{-8}
$PbBiOV_{0.94}Mn_{0.06}O_{4\pm y}$	0.76	1.77×10^{-4}	3.88×10^{-9}
$PbBiOV_{0.85}P_{0.15}O_4$	1.07	2.83×10^{-5}	5.12×10^{-9}

whatever the temperature. $PbBiOP_{1-x}As_xO_4$ and $PbBiOV_{1-x}X_xO_4$ ($X = As$, P, Cr, Mn) solid solutions display both triclinic and monoclinic domains, and the $\alpha \rightarrow \beta$ transition temperature is a function of the substitution rate. The ionic conductivity of these compounds was investigated by impedance spectroscopy: β-$PbBiOVO_4$ displays an interesting conductivity jump at 710 °C, without any noticeable structural change. An analysis of the available free space in the structure of the β-$PbBiOVO_4$ allows to propose a one-dimensional oxygen diffusion pathway along [010] when the temperature increases. Neutron diffraction above 710 °C will be performed to verify this assumption.

Supplementary materials

Crystal Structure Data for the various phases gathered in Tables 1 and 2, 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, as supplementary material CSD nos. 419124 for PbBiOAsO4-RT-XC (room temperature structure of $PbBiOAsO_4$ determined on single crystal using X-ray diffraction), 419125 for PbBiOPO4-RT-XP (room temperature structure of $PbBiOPO_4$ determined on powder using X-ray diffraction). Copies of this information can be obtained by contacting the FIZ (quoting the article details and the corresponding CSD number).

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