Synthesis and the Study of Triclinic Crystal Structure a Novel Quaternary Bi$_{0.245}$Pb$_{2.351}$U$_{1.25}$Zr$_{0.8}$O$_{4.5}$ Oxide Contained Mixed Valence by Ab Initio Method via Powder XRD

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ABSTRACT
The present work deals with the ab initio structure determination and study the crystal chemistry of the heavy metal framework in Bi$_{0.245}$ Pb$_{2.351}$ U$_{1.25}$ Zr$_{0.8}$ O$_{4.5}$ from precession X-ray diffraction intensities. The metal framework of the compound was solved in this investigation via direct methods by ab initio method from precession XRD diffraction intensities recorded with a Philips EM400 at 100 kV. A subsequent (kinematical) least-squares refinement with X-ray intensities yielded slightly improved co-ordinates for the 11 heavy atoms in the structure. Chemical analysis of several crystallites by EDX is in agreement with the formula Bi$_{0.245}$Pb$_{2.351}$U$_{1.25}$Zr$_{0.8}$O$_{4.5}$. Moreover, the structure was independently determined by Rietveld refinement from X-ray powder data obtained from a multi-phasic sample using JANA computer software programme. The compound crystallizes in the triclinic crystal system and space group P-1 with refined lattice parameters $a=6.3458$(Å), $b=7.9400$(Å), $c=9.1040$(Å), $\alpha=77.3239^\circ$, $\beta=81.0395^\circ$, $\gamma=70.6732^\circ$. The refinement values are $R_p=0.0680$, $R_p=0.030$ and $GOF=0.031$ the structure factors $F_0=3024$ and $F_c=3024$ and the volume $=420.132$ and particle size $=80.124$nm.

Key Words: X-ray, powder, triclinic Rietveld, refinement, structure, analysis

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I. INTRODUCTION
Our understanding of the properties of materials is almost always based on structural information on the atomic scale. Such information is commonly obtained by the wide spread method of X-ray crystallography. However, due to the relatively weak interaction of matter with X-rays, this method is insufficient to investigate extremely small volumes or individual crystals at the atomic scale. Materials with pronounced twinning or new compounds that only exist as part of a complex multi-phase powder sample are thus extremely difficult to treat with this standard method for structure determination. It should be noted that these problem cases also include many technologically relevant products such as small precipitates in a metallic matrix, catalysts, pharmaceuticals, pigments and thin films, which a priori exist only in small quantities or rarely grow as large crystals. Hence, ample motivation exists to develop alternative approaches capable for structural analysis of extremely small volumes and crystallites. However, the only real alternative to X-rays is fast electrons, since their interaction with matter is several orders of magnitude stronger than that of X-rays. Electron diffraction structure analysis (EDSA) makes it, thus, possible to obtain structural information at the atomic level even for the steadily growing number of nanocrystalline materials. On the other hand, structure analysis with electron data is rarely straightforward and fully automated, as it is the case with X-ray data. In particular, the non-kinematical nature of the diffracted intensities is a great concern for structure analysis with electron diffraction data and has hindered EDSA from becoming very popular since its foundation in Russia more than 65 years ago. While a large number of light-atom structures have been investigated by electron diffraction in the past [1–4], it has only succeeded in a few cases to solve structures with heavier atoms directly from electron diffraction spot patterns (see Table 1). In order to avoid these problems, an alternative approach was developed for such non-light-atom structures. This approach exploits the low-order structure factor phases extracted from high-resolution electron microscopy (HREM) images, to assign phases to the higher-order electron diffraction amplitudes [5–9]. In the most favorable case when the scattering power of the elements in the structure is not too different, the complete structure can be solved from X-ray powder pattern images and subsequently refined with electron diffraction data [10, 11]. Despite such hybrid methods proved very efficient, it is still highly desirable to also develop methods which allow solving heavy-atom structures directly from the measured electron diffraction amplitudes. As mentioned earlier, the non-kinematical (dynamical) nature of the electron intensities is the main concern in this endeavor because its influence on the diffracted intensities is very difficult to control in the
diffraction experiment. However, today it is generally believed that the precession X-ray diffraction via powder pattern is most popular technique of structure determination of mixed metal oxide method. In this method a small focused or parallel X-beam is scanned at a constant angle around the optic axis to produce a hollow-cone illumination of the sample. Those electron beams leaving the specimen exit-plane are then desected in such a way that a stationary spot diffraction pattern is formed. Thus, this method is, in principle, equivalent to the precession technique known from X-ray crystallography, where a crystal is turned (tilted) through a small angle about an axis perpendicular to the (stationary) beam [13]. Due to this geometry, the X-ray diffraction pattern consists of many reflections far out in reciprocal space with intensities that are integrated over the excitation error. The most important effect for quantitative work is, however, that this integration considerably limits the non-systematical dynamical interactions which are most pronounced under on-zone axis conditions [14–16]. On the other hand, structure analysis with electron data is rarely straightforward and fully automated, as it is the case with X-ray data because now-a-days powder X-ray diffraction has been routinely used a non-destructive fingerprinting technique. It has also been used in studies related to structural phase transitions at variable temperature and pressure. Hence, the present study aims at the preparation of \( \text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5} \) through the solid state reaction method and the determination of the structure of \( \text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5} \) powders through powder X-ray diffraction technique. The extensive search for novel inorganic materials with open frameworks formed of tetrahedral and octahedral delimiting inter-layer spaces (2D), tunnels (3D) or cages (1D) where cations are housed, represent currently a field of intense activity including several disciplines: solid-state chemistry, physics, mechanics, and mainly ionic conductivity properties and their use as battery materials. Chloride of transition and nontransition metals contained mixed valence ions are well known for their thermal stability and the simplicity of synthesis. The aim of this work is determine structure of titled compound by ab initio method with the help of powder XRD and the study of morphology as well as electrical property as well as crystal chemistry [17, 18].

II. MATERIALS AND METHODS

All chemicals used were analytical grade. A polycrystalline sample of \( \text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5} \) was synthesized by a standard solid state reaction using a mixture of high purity reagents of \( \text{UO}_{2}, \text{Bi}_{2} \text{O}_{3}, \text{ZrO}_{2} \) and \( \text{PbO} \) contained mixed valence as the starting materials in the molar ratio of 1 : 1 : 10\( \text{'} \) parent materials. The mixture was ground carefully, homogenized thoroughly with methanol (99%) in an agate mortar and then packed into an alumina crucible and calcined at 1000°C in air for 30h with several intermediate grindings. Finally the product was pressed into pellets and sintered at 100 K/h. Powder X-ray diffraction (XRD) data were collected at room temperature in the angular range of \( 2θ = 10 \) to 90 with scan step width of 0.02\( \text{'} \) and a fixed containing time of 15 s using Philips powder diffractometer with graphite monochromatic CuKa radiation. The powder was rotated during the data collection to minimize preferred orientation effect if any. The program TREOR in CRYSFIRE [19] was used to index the powder pattern which give triclinic system. SIRPOW92 was used to locate the positional parameters of constituent atoms. The full pattern is fitting and peak decomposition in the space group P-1 using check cell program. The structural parameters were refined by the Reitveld method using the JANA program which gave at 1000°C. The refinement values are \( R_{wp} = 0.0680, R_p = 0.030 \) and \( GOF=0.031 \) the structure factors \( F_0 = 3024 \) and \( F_c = 3024 \). The density is determined by Archimedes principle.

RESULTS AND DISCUSSIONS

Indexation. at first, a Search−Match procedure was launched using the in-house XRD pattern No.1 with X'pert Highscore Plus9 without providing any phase identification. Consequently, an autoindexation procedure was applied in-house HQ XRD data. Note that HRPD data from ESRF had not yet been collected at this stage of the study. The auto-indexation programs implemented in HighScore Plus were not run using the angular positions of the first 25 peaks observed in the pattern, which all have small to tiny relative intensities ranging from 0.1 to 4.7\( \% \). Let us notice that the minimum intensity was observed for the 30th peak at 45.278\( ^{\circ} \) 2\( θ \), which was therefore not included in the data set used for auto indexation Shown in figure 1 which is spectra of \( \text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5} \). The auto indexation programs Treor,10 Dicvol,11 and McMaille12 gave the same result in the TRICLINIC system with \( a=6.3458(\text{Å}), b=7.9400(\text{Å}), c=9.1040(\text{Å}), α=77.3239^{\circ}, β=81.0395^{\circ}, γ=70.6732^{\circ} \). \( R_p=0.0112, R_{wp}=0.01639, \) volume 420.59 \( \text{Å}^3 \) and \( GOF=0.014 \). and a factor of merit ranging from 20 to 30. All the 30 peaks were indexed. Because of the rather high value of the unit-cell volume a challenging ab initio structural resolution was expected. With the help of the diffraction mode in TEM, the reciprocal lattice was successfully reconstructed with the presence of the basis plane (001)* thus confirming the cell parameters above (Figure 1)[20]. The Bravais lattice C of the structure was not only observed in the reciprocal lattice reconstruction but also deduced from the peak systematic absences in the basis plane (Figure 2) with the extinction condition for h0k0, h + k \( \neq 2n \). In order to confirm definitively the validity of the Bravais lattice C, a Le Bail refinement13 was launched on XRD pattern No.1 in space group P-1 using the JANA software. All the Bragg peaks are perfectly indexed (Figure 3), and no other extinction condition and search for Atomic Positions. The first proposition of the number Z[21] of chemical formula units per unit cell was deduced from
the final formula Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5}. By considering the presence of possible anionic vacancies, we started with Z = 2, leading to the global formula Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.4}. The determination of the cationic structure was primarily conducted with the XRD pattern No.1 using the intensities of the 189 first Bragg peaks extracted by the Le Bail procedure. Two methods were employed: 1) the Superflip method\textsuperscript{15} implemented in JANA\textsuperscript{16} and the real space Monte Carlo method implemented in Espoir\textsuperscript{17}. Both methods provided the same cationic solution for Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5}; seven crystallographic sites were identified, one site for Bi atom and six sites for Zr atoms labeled from Zr1 to Zr6 in Table 3. The Rietveld refinement with JANA based on this cationic arrangement yielded an acceptable result (R_{Bragg} \approx 25\%). Several sequences of Fourier difference and Rietveld refinement using JANA were then carried out to locate oxygen atomic positions to make CIF data.. However, a clear and consistent crystallographic solution was difficult to obtain from in-house XRD data, owing to the medium resolution of the in-house diffractometer largely due to the presence of the doublet (Cu/Kα) of the copper radiation and to the high density of Bragg peaks starting from 10°-67° 20 ranges. Attempts to find a consistent anionic structural arrangement with XRD data is successfully obtained.

CRYSTAL CHEMISTRY AND STRUCTURE DETERMINATION

The framework structure of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was first examined by ab initio structure determination method using the powder XRD data. The initial lattice parameters were determined to be a = 15.347 Å, b = 3.753 Å, c = 9.149Å, and β = 99.441_ by an indexing procedure using the program N-TREOR\textsuperscript{15} in EXPO2004.16 The most probable space group was suggested to be P-1. Next, the integrated intensities were extracted by the Le Bail and pseudo-voight method using the program Jana\textsuperscript{2006.14} profile function and background function of the Le Bail method used in the present study were pseudo-Voight function and 20thorder Legendre function, respectively. An initial structure model was then obtained by the charge flipping (CF) method\textsuperscript{17} using the extracted integrated intensities. Although the Li site could not be clearly determined by the CF method using the powder XRD data, the framework structure of (BiO\textsuperscript{+}) was successfully determined. In this stage, the lattice parameters of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was refined to be a = 15.3244(2) Å, b = 3.74847(2) Å, c = 9.1429(1) Å, and β = 99.419(1) by the Rietveld method using the powder XRD data. The resultant reliability values, which were relatively large because of the preferred orientation of the sample, were Rwp = 0.0680, Rp = 0.030 and GOF=0.031 the structure factors F0 =3024 and Fc = 3024. The obtained lattice parameters and the framework structure were well consistent with the structure parameters values. The frame and layer type of structure shown in figure 5.

Although the structure of the parent Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was previously reported in the literature,\textsuperscript{10,11} the atomic displacement parameters have not been clarified. In addition, the reported reliability value was relatively large (R = 111.1%)[\textsuperscript{43}] Therefore, we first reinvestigated the crystal structure of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} using the powder crystal X-ray diffraction data. Integrated intensity data were collected powder X-ray diffractometer with an imaging plate (Philips R-AXIS RAPID-II) using graphite-monochromatized Cu/Kα radiation (operating condition: 50 kV, 40 mA) at 295 K. The structure refinement was carried out using a computer program Jana\textsuperscript{2006.14} The framework structure of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was first analyzed by ab initio structure determination method using the powder XRD data. The calculation was performed using the computer program N-TREOR\textsuperscript{15} in EXPO2004.16 Jana\textsuperscript{2006.14} and Superflip\textsuperscript{17} The Rietveld refinement of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was performed by Jana\textsuperscript{2006} using powder X-ray diffraction data measured at room temperature with wavelength=1.556 Å. The powder XRD spectra shown to determine the index value and rietveld refinement spectra is shown in figure 2 for crystallographic and atomic parameters with CIF to obtain crystal structure and visualization of the structure obtained from Diamond computer software programme. The crystal structure of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} shown in Figure 3. The basic Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} framework in Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} is maintained nearly unchanged from that in the parent oxide. All three bismuthate ions octahedral were strongly distorted, and the Zr–O distances were in the wide range of 2.52(1)-263(1) Å. These features for the ZrO2 ions unit were very similar to those observed in Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5}; On the other hand, the most interesting feature of the Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} structure is the Bi occupation site in the tunnel space [22-27].
Figure 1. Powder XRD spectra of Bi$_{0.245}$Pb$_{2.351}$U$_{1.25}$Zr$_{0.8}$O$_{4.5}$

Figure 2. Observed, calculated, and difference pattern for the Rietveld refinement using the powder X-ray diffraction data of Bi$_{0.245}$Pb$_{2.351}$U$_{1.25}$Zr$_{0.8}$O$_{4}$. The short vertical lines below the profiles mark positions of all position Bragg reflections of Bi$_{0.245}$Pb$_{2.351}$U$_{1.25}$Zr$_{0.8}$O$_{4}$.

Table 1 Crystallographic data

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### Synthesis and the Study of Triclinic Crystal Structure a Novel Quartenary

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#### Atomic parameters

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Figure 3. Triclinic structure with 3D of $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$

Figure 4. The framework structure in closed packed with O atoms layer structure of $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$

Table 2. Selected Bond angles (°)

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The atomic spheres used were 2.4 au for the Pb atom, 1.9 au for the Zr atom, and 1.7 au for the O atom in Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5}. The plane-wave cutoff was 7.0, where RMT is the smallest atomic sphere radius in the unit cell and Kmax is the magnitude of the largest k vector[28].

**ELECTROCHEMICAL MEASUREMENTS.**

Electrochemical Pb insertion/extraction experiments for Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} were performed using lead/coin-type cells. The working electrode was prepared by mixing 62% active material, 31% acetylene black, and 7% polytetrafluoroethylene (PTFE) powder in weight by pressing the mixture onto an Al mesh having a diameter of 15 mm under a pressure of 20 MPa. The counter electrode was a Pb foil having a diameter of 20 mm[29]. The separator was a microporous polypropylene sheet. A solution of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} in a 50:50 mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) by volume (analytical grade) was used as electrolyte. Cells were constructed in an argon-filled glove box, and electrochemical measurements were carried out with a constant current density per unit of mass of the active material, 10 mA g^{-1}, between 1.0 and 3.0 V at 25 °C after standing 6 h under an open circuit condition. AC impedance measurements for Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was conducted using a Solartron 1260 impedance analyzer operating at 10 mV applied ac amplitude at 13 MHz-10 Hz frequencies at room temperature[30].

### III. CONCLUSIONS

In the present study, quaternary Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was successfully prepared and structure determined by ab initiation methods from starting material as a parent compound via UO_{2}, Bi_{2}O_{3}, ZrO_{2}, and PbO_{2} to 1100°C. The phase purity and chemical composition of the ion-exchanged samples were well characterized. The crystal structure of Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was refined by Rietveld refinement using the powder X-ray diffraction data. The basic (Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5}) framework in Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} was maintained nearly unchanged from that in the parent materials. The Pb occupation site in the tunnel space shifted to the y = 0.5 position, and the moving resulted in the tetrahedral coordination with oxygen atoms planar coordination in Bi_{0.245} Pb_{2.351} U_{1.25} Zr_{0.8} O_{4.5} U is coordinated with octahedral arrangement along with Zr is also coordinated with oxygen atoms by hexagonal. In all respect the crystal of cited oxide is triclinic having P-1 space group. The structural validity was confirmed by bond valence sums calculation, with situ XRD measurements, and the results of the present first-principles calculation by the FLAPW method. This unusual Pb-O coordination may

---

**Table 3. Selected bond lengths**

<table>
<thead>
<tr>
<th>Number</th>
<th>Atom1</th>
<th>Atom2</th>
<th>Length(A)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>U1</td>
<td>Pb3</td>
<td>1.9663</td>
</tr>
<tr>
<td>2</td>
<td>U1</td>
<td>Zr1</td>
<td>1.9809</td>
</tr>
<tr>
<td>3</td>
<td>U1</td>
<td>O5</td>
<td>1.8747</td>
</tr>
<tr>
<td>4</td>
<td>U1</td>
<td>Pb3</td>
<td>1.9663</td>
</tr>
<tr>
<td>5</td>
<td>U1</td>
<td>Zr1</td>
<td>1.9809</td>
</tr>
<tr>
<td>6</td>
<td>U1</td>
<td>O5</td>
<td>1.8747</td>
</tr>
<tr>
<td>7</td>
<td>Bi1</td>
<td>Pb2</td>
<td>1.6958</td>
</tr>
<tr>
<td>8</td>
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</tr>
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<tr>
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<tr>
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<td>Zr1</td>
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<tr>
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<td>O4</td>
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<tr>
<td>17</td>
<td>Zr2</td>
<td>O4</td>
<td>2.6359</td>
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affect the good lead conduction property even at room temperature among lead-zincate ion compounds. On the other hand, the electrochemical Pb insertion/ extraction experiments revealed that the Pb insertion reaction led to the degradation of the host Bi$_{0.245}$ Pb$_{2.351}$ U$_{1.25}$ Zr$_{0.8}$ O$_{4.5}$ structure. The low-temperature synthetic techniques such as ion-exchange reaction called "chimie douce" have resulted in major developments in the field of the solid-state chemistry of transition and non transition metal oxides. In many cases, the framework structures of the parent compounds were maintained nearly unchanged; however, the local structural changes around transition and non-transition atoms were recently revealed by the precise structural studies. In the present study, an unusual Bi$_{0.245}$ Pb$_{2.351}$ U$_{1.25}$ Zr$_{0.8}$ O$_{4.5}$ hexagonal in Bi$_{0.245}$ Pb$_{2.351}$ U$_{1.25}$ Zr$_{0.8}$ O$_{4.5}$ has been found for the first time by using cited compound can be used as super conductor materials by ion-exchange reaction.

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