

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

Bimal K.Kanth and Parashuram Mishra\*

*Bioinorganic and Materials Chemistry Research Lab.M.M.A.M.Campus,Biratnagar,,Tribhuvan University,Nepal*

---

### ABSTRACT

The present work deals with the *ab initio* structure determination and study the crystal chemistry of the heavy metal framework in  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$ . 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  $a=6.3458(\text{\AA})$ ,  $b=7.9400(\text{\AA})$ ,  $c=9.1040(\text{\AA})$ ,  $\alpha=77.3239^\circ$   $\beta=81.0395^\circ$   $\gamma=70.6732^\circ$  The refinement values are  $R_{wp} = 0.0680$ ,  $R_p = 0.030$  and  $GOF=0.031$  the structure factors  $F_0 = 3024$  and  $F_c = 3024$  and the volume =420.132 and particle size 80.124nm.

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

---

Date of Submission: 29-08-2020

Date of acceptance: 14-09-2020

---

### 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 favorite 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-ray 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 descanted 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  $\text{PbO}_2$  contained mixed valence as the starting materials in the molar ratio of 1 : 1 : 1 of 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  $1000^\circ\text{C}$  in air for 30h with several intermediate grindings. Finally the product was pressed into pallets and sintered at 100 K/h. Powder X-ray diffraction (XRD) data were collected at room temperature in the angular range of  $2\theta = 10$  to  $90$  with scan step width of  $0.02^\circ$  and a fixed containing time of 15 s using Philips powder diffractometer with graphite monochromatic  $\text{CuK}\alpha$  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  $1000^\circ\text{C}$ . The refinement values are  $R_{wp} = 0.0680$ ,  $R_p = 0.030$  and  $\text{GOF} = 0.031$  the structure factors  $F_0 = 3024$  and  $F_c = 3024$ . The density is determined by Archimedes principle.

### RESULTS AND DISCUSSIONS

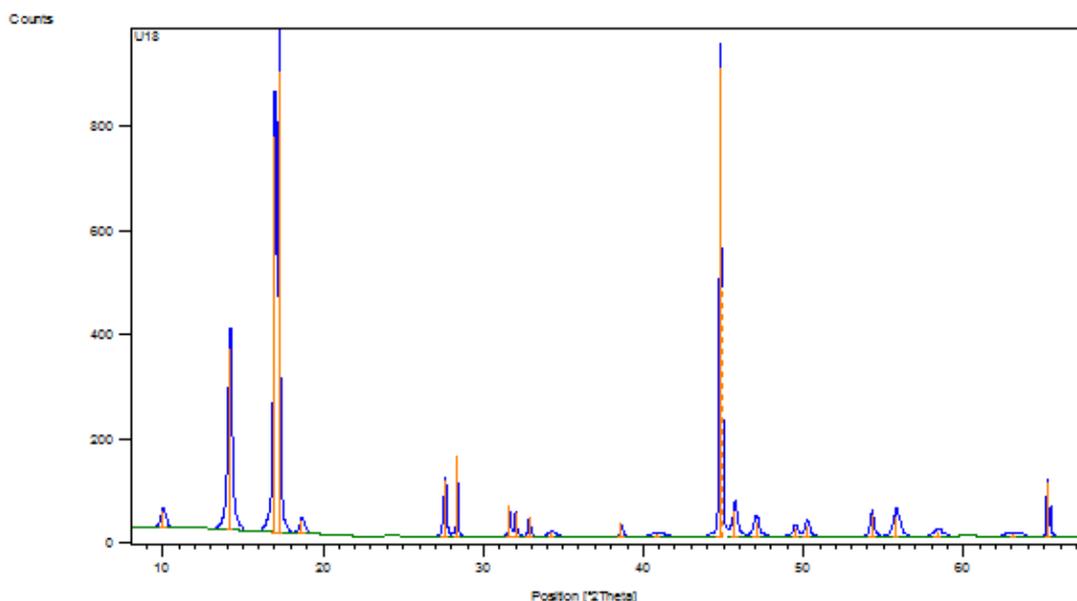
Indexation. at first, a Search–Match procedure was launched using the in-house XRD pattern No.1 with X'pert Highscore Plus9 without providing any phase identification. Consequently, an autoindexation procedure was applied on in-house HQ XRD data. Note that HRPD data from ESRF had not yet been collected at this stage of the study. The auto-indexation programs implemented in HighScore Plus were 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 maximum intensity was observed for the 30th peak at  $45.278^\circ 2\theta$ , 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  $a=6.3458(\text{\AA})$ ,  $b=7.9400(\text{\AA})$ ,  $c=9.1040(\text{\AA})$ ,  $\alpha=77.3239^\circ$   $\beta=81.0395^\circ$   $\gamma=70.6732^\circ$   $R_p=0.0112$ ,  $R_{wp}=0.01639$ , volume  $420.59 \text{\AA}^3$  and  $\text{GOF}=0.014$ . 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  $hk0$ ,  $h + k \neq 2n$ . 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  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$ . By considering the presence of possible anionic vacancies, we started with  $Z = 2$ , leading to the global formula  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$ . 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<sup>15</sup> implemented in JANA16 and the real space Monte Carlo method implemented in Espoir.<sup>17</sup> Both methods provided the same cationic solution for  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$ : 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<sub>Bragg</sub> ≈ 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/Kα1) of the copper radiation and to the high density of Bragg peaks starting from 10°-67° 2θ ranges. Attempts to find a consistent anionic structural arrangement with XRD data is successfully obtained.

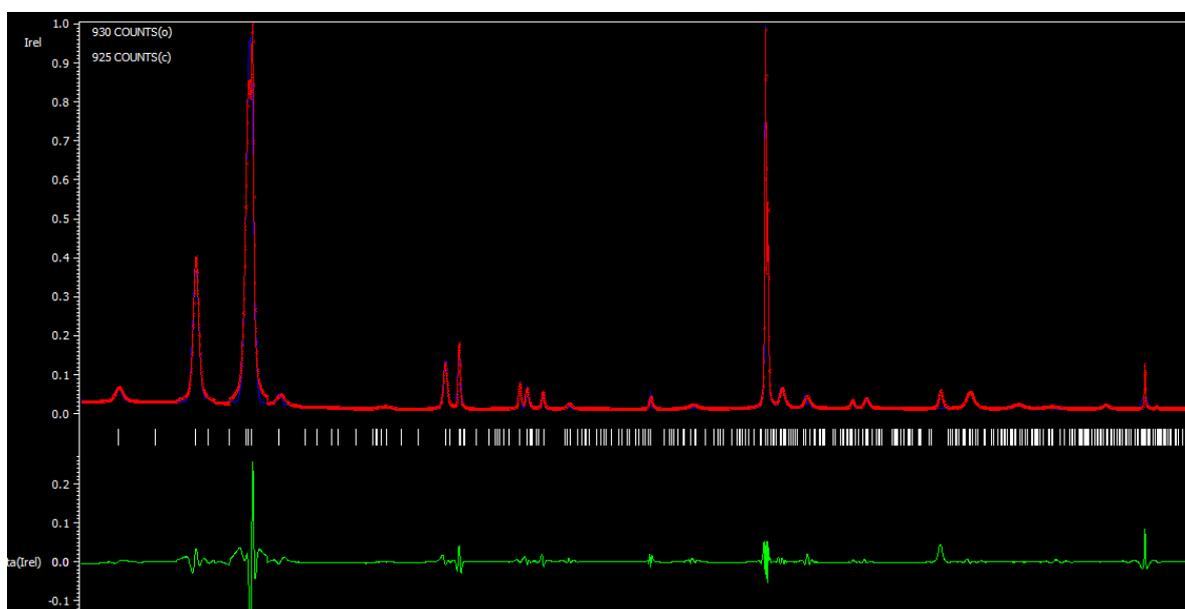
#### CRYSTAL CHEMISTRY AND STRUCTURE DETERMINATION

The framework structure of  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  was first examined by ab initio structure determination method using the powder XRD data. The initial lattice parameters were determined to be  $a = 15.347 \text{ \AA}$ ,  $b = 3.753 \text{ \AA}$ ,  $c = 9.149 \text{ \AA}$ , and  $\beta = 99.441^\circ$  by an indexing procedure using the program N-TREOR15 in EXPO2004.<sup>16</sup> The most probable space group was suggested to be P-1. Next, the integrated intensities were extracted by the Le Bail and pseudo-Voigt method using the program Jana2006.<sup>14</sup> A profile function and background function of the Le Bail method used in the present study were pseudo-Voigt function and 20th order Legendre function, respectively. An initial structure model was then obtained by the charge flipping (CF) method<sup>17</sup> 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  $(\text{BiO}^{3-})$  was successfully determined. In this stage, the lattice parameters of  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  was refined to be  $a = 15.3244(2) \text{ \AA}$ ,  $b = 3.74847(2) \text{ \AA}$ ,  $c = 9.1429(1) \text{ \AA}$ , and  $\beta = 99.419(1)^\circ$  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  $R_{wp} = 0.0680$ ,  $R_p = 0.030$  and  $\text{GOF} = 0.031$  the structure factors  $F_0 = 3024$  and  $F_c = 3024$ . 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  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  was previously reported in the literature,<sup>[10,11]</sup> the atomic displacement parameters have not been clarified. In addition, the reported reliability value was relatively large ( $R = 111.1\%$ )<sup>[1]</sup> Therefore, we first reinvestigated the crystal structure of  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  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 Jana2006.<sup>14</sup> The framework structure of  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  was first analyzed by ab initio structure determination method using the powder XRD data. The calculation was performed using the computer program N-TREOR15 in EXPO2004,<sup>16</sup> Jana2006,<sup>14</sup> and Superflip.<sup>17</sup> The Rietveld refinement of  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  was performed by Jana2006 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  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  shown in Figure 3. The basic  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  framework in  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  is maintained nearly unchanged from that in the parent oxide. All three bismathate ions octahedral were strongly distorted, and the Zr-O distances were in the wide range of 2.52(1)-2.63(1) Å. These features for the ZrO<sub>2</sub> ions unit were very similar to those observed in  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$ . On the other hand, the most interesting feature of the  $\text{Bi}_{0.245} \text{Pb}_{2.351} \text{U}_{1.25} \text{Zr}_{0.8} \text{O}_{4.5}$  structure is the Bi occupation site in the tunnel space [22-27].



**Figure1.** Powder XRD spectra of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$



**Figure 2.** Observed, calculated, and difference pattern for the Rietveld refinement using the powderX-ray diffraction data of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_4$ . The short vertical lines below the profiles mark positions of all position Bragg reflections of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_4$ .

**Table 1 Crystallographic data**

<b>Formula sum</b>	$\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_4$
<b>Formula weight</b>	980.8 g/mol
<b>Crystal system</b>	triclinic
<b>Space-group</b>	P -1 (2)
<b>Cell parameters</b>	$a=6.3458 \text{ \AA}$ $b=7.9400 \text{ \AA}$ $c=9.1040 \text{ \AA}$ $\alpha=77.3239^\circ$ $\beta=81.0395^\circ$ $\gamma=70.6732^\circ$
<b>Cell ratio</b>	$a/b=0.7992$ $b/c=0.8721$ $c/a=1.4346$
<b>Cell volume</b>	$420.59 \text{ \AA}^3$

<b>Z</b>	2
<b>Calc. density</b>	7.74425 g/cm <sup>3</sup>
<b>Meas. density</b>	7.67586g/cm <sup>3</sup>
<b>Index</b>	0≤h≤2,-2≤k≤1,0≤l≤3
<b>Pearson code</b>	aP77
<b>Formula type</b>	NO2P6Q27R41
<b>Wyckoff sequence</b>	i37dba

**Atomic parameters**

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Å <sup>2</sup> ]
U1	+4	1d	-1		1/2	0	0	0.0380
Pb3	+2	2i	1		0.37590	0.03736	0.21210	0.0380
Zr1	+4	2i	1		0.48302	0.23384	0.05222	0.0380
Zr3	+4	2i	1		0.15867	0.05580	0.34065	0.0380
O1	-2	2i	1		0.17603	0.12261	0.04838	0.0380
O2	-2	2i	1		0.78850	0.43464	0.06763	0.0380
O3	-2	2i	1		0.01202	0.22500	0.07177	0.0380
O4	-2	2i	1		0.54448	0.24309	0.47121	0.0380
O5	-2	2i	1		0.18992	0.07424	0.05316	0.0380
O6	-2	2i	1		0.34616	0.58922	0.19284	0.0380
O7	-2	2i	1		0.59003	0.17090	0.24819	0.0380
O8	-2	2i	1		0.21509	0.01620	0.02306	0.0380
O9	-2	2i	1		0.81389	0.79639	0.29358	0.0380
O10	-2	2i	1		0.66418	0.37776	0.46437	0.0380
O11	-2	2i	1		0.06288	0.24578	0.68821	0.0380
O12	-2	1a	-1		1.00000	0	0	0.0380
O13	-2	2i	1		0.66024	0.09934	0.29221	0.0380

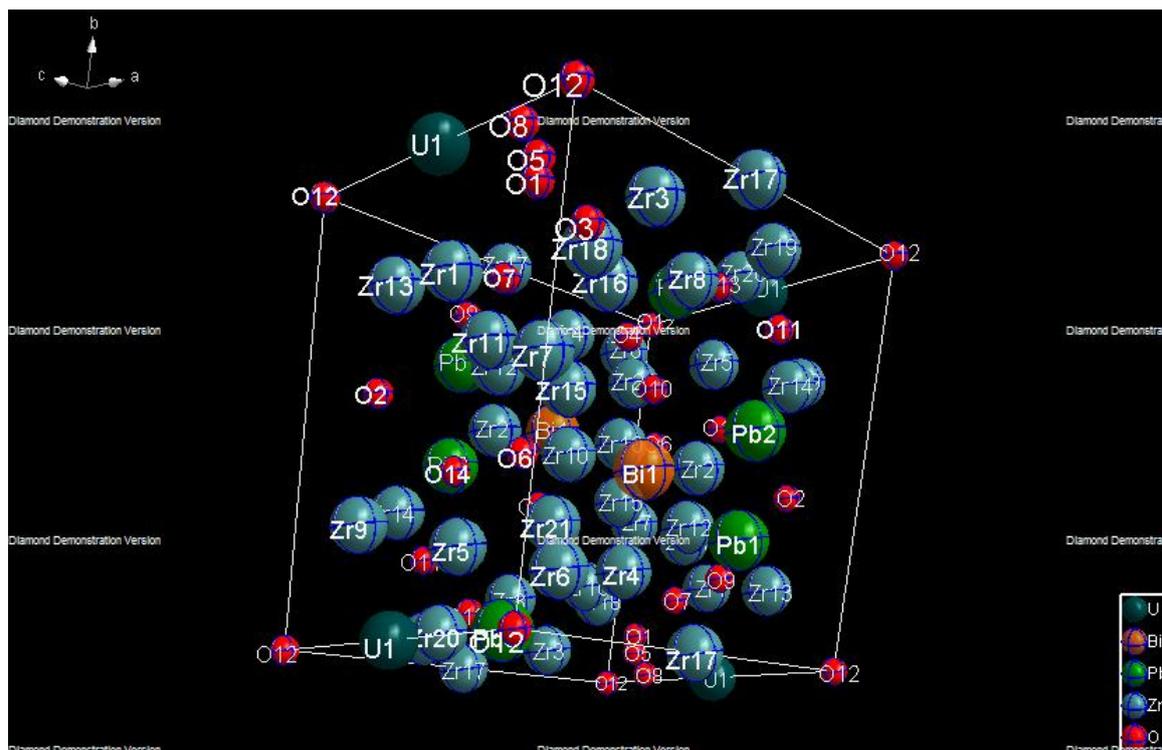


Figure 3. Triclinic structure with 3D of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$

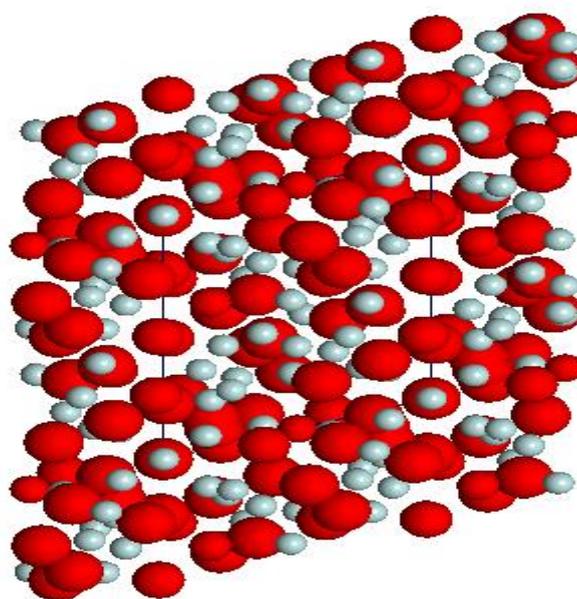


Figure 4. The framework structure in closed packed with O atoms layer structure of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$

Table 2. Selected Bond angles( $^{\circ}$ )

U1	O8	O8	180.00
O8	O5	Bi1	162.883
Bi1	Pb2	Zr10	136.659
Pb2	Zr21	O9	139.27
Pb2	O11	Zr5	63.431
Pb2	Zr2	Bi1	169.228
Zr2	O11	Zr12	111.116
Bi1	O11	Zr10	62.102

Bi1	Pb1	O7	136.501
O1	O5	O8	21.696
O2	O3	O14	145.005
O3	Zr13	Pb4	52.953

**Table 3. Selected bond lengths**

Number	Atom1	Atom2	Length(A)
1	U1	Pb3	1.9663
2	U1	Zr1	1.9809
3	U1	O5	1.8747
4	U1	Pb3	1.9663
5	U1	Zr1	1.9809
6	U1	O5	1.8747
7	Bi1	Pb2	1.6958
8	Bi1	Zr2	3.5119
9	Bi1	O6	2.1440
11	O4	Bi1	2.8602
12	O6	Zr1	2.6468
13	U1	Pb3	1.9663
14	Pb3	Zr1	2.5500
15	Pb3	O5	1.8838
16	Zr1	O5	2.5722
17	Zr2	O4	2.6359
18	Zr2	O4	2.6359

correlation terms. 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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$ , and 1.5 au for the Bi atom, 1.8 au for the U atom, and 1.7 au for the O atom in  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$ . 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]. Self-consistency was carried out on a 400 k-points mesh in the full Brillouin zone. The energy criterion for self-consistency was set to less than 0.001 eV per formula unit. The present structural parameters for  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  by ab initio method via powder XRD.

### ELECTROCHEMICAL MEASUREMENTS.

Electrochemical Pb insertion/ extraction experiments for  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  in a 50:50 mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) by volume (analytical grade) was used as the 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<sup>-1</sup>, between 1.0 and 3.0 V at 25 °C after standing 6 h under an open circuit condition. AC impedance measurements for  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  was successfully prepared and structure determined by ab ignition methods from starting material as a parent compound via  $\text{UO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{PbO}_2$  to 1100°C. The phase purity and chemical composition of the ion-exchanged samples were well characterized. The crystal structure of  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  was refined by Rietveld refinement using the powder X-ray diffraction data. The basic ( $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$ ) framework in  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$ . 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

affect the good lead conduction property even at room temperature among lead-ziconate 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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  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  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_4$ , hexagonal in  $\text{Bi}_{0.245}\text{Pb}_{2.351}\text{U}_{1.25}\text{Zr}_{0.8}\text{O}_{4.5}$  has been found for the first time by using cited compound can be used as super conductor materials by ion-exchange reaction.

### REFERENCES

- [1]. Thomas E. Weiricha, Joaquim Portillo, Gerhard Cox, Hartmut Hibste, Stavros Nicolopoulos, , Ultramicroscopy 106 (2006) 164–175
- [2]. Zhengyang Zhou, Lukáš Palatinus and Junliang Sun, Inorganic CHEMISTRY Frontiers Cite this: DOI: 10.1039/c6qi00219f
- [3]. Palatinus, L.; Chapuis, G. J. Appl. Crystallogr. 2007, 40, 786–790.
- [4]. Ohoyama, K.; Kanouchi, T.; Nemoto, K.; Ohashi, M.; Kajitani, T.; Yamaguchi, Y. Jpn. J. Appl. Phys. 1998, 37, 3319–3326.
- [5]. Izumi, F.; Dilania, R. A. Recent Research Developments in Physics,
- [6]. II; Transworld Research Network: Trivandrum, 2002; pp 699\_726.
- [7]. Momma, K.; Izumi, F. J. Appl. Crystallogr. 2008, 41, 653–658.
- [8]. Blaha, P.; Schwarz, K.; Madsen, G.; Kvasnicka, D.; Luitz, J. WIEN2k, Augmented Plane Wave þ Local Orbitals Program for Calculating Crystal Properties; Technische Universität Wien: Vienna, 2001.
- [9]. Perdew, P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.
- [10]. Shanon, R. D. Acta Crystallogr. 1976, A32, 751–767
- [11]. Kripasindhu Sardar,† Helen Y. Playford,† Richard J. Darton,†,‡ Emma R. Barney,§ Alex C. Hannon,§ David Tompsett, Janet Fisher, Reza J. Kashtiban,^ Jeremy Sloan,^ Silvia Ramos, X Giannantonio Cibin, X and Richard I. Walton\* Chem. Mater. 2010, 22, 6191–6201 DOI:10.1021/cm1025848
- [12]. Giordano, F.; Trovarelli, A.; de Leitenburg, C.; Giona, M. J. Catal. 2000, 193, 273.
- [13]. Monte, R. D.; Ka\_spar, J. Catal. Today 2005, 100, 27. Monte, R. D.; Ka\_spar, J. J. Mater. Chem. 2005, 15, 633.
- [14]. Baidya, T.; Hegde, M. S.; Gopalakrishnan, J. J. Phys. Chem. B 2007, 111, 5149.
- [15]. Sasikala, R.; Gupta, N. M.; Kulshreshtha, S. K. Catal. Lett. 2001, 71, 69.
- [16]. Baidya, T.; Gupta, A.; Deshpandey, P. A.; Madras, G.; Hegde, M. S. J. Phys. Chem. C 2009, 113, 4059. Gupta, A.; Hegde, M. S.; Priolkar, K. R.; Waghmare, U. V.; Sarode, P. R.; Emura, S. Chem. Mater. 2009, 21, 5836.
- [17]. Wang, D. Y.; Park, D. S.; Griffith, J.; Nowick, A. S. Solid State Ionics 1981, 2, 95.
- [18]. Balazs, G. B.; Glass, R. S. Solid State Ionics 1995, 76, 155.
- [19]. Yamashita, K.; Ramanujachary, K. V.; Greenblatt, M. Solid State Ionics 1995, 81, 53.
- [20]. Baidya, T.; Gayen, A.; Hegde, M. S.; Ravishankar, N.; Dupont, L. J. Phys. Chem. B 2006, 110, 5262.
- [21]. Dutta, G.; Waghmare, U. V.; Baidya, T.; Hegde, M. S.; Priolkar, K. R.; Sarode, P. R. Chem. Mater. 2006, 18, 3249.
- [22]. Li, G.; Smith, R. L.; Inomata, H. J. Am. Chem. Soc. 2001, 123, 11091.
- [23]. Roy, S.; Hegde, M. S. Catal. Commun. 2008, 9, 811.
- [24]. Yabe, S.; Yamashita, M.; Momose, S.; Tahira, K.; Yoshida, S.; Li, R. X.; Yin, S.; Sato, T. Int. J. Inorg. Mater. 2001, 3, 1003.
- [25]. Yabe, S.; Sato, T. J. Solid State Chem. 2003, 171, 7.
- [26]. Feng, X. D.; Sayle, D. C.; Wang, Z. L.; Paras, M. S.; Santora, B.; Sutorik, A. C.; Sayle, T. X. T.; Yang, Y.; Ding, Y.; Wang, X. D.; 26. Her, Y. S. Science 2006, 312, 1504. (16) Fu, X. Q.; Wang, C.; Yu, H. C.; Wang, Y. G.; Wang, T. H. Nanotechnology 2007, 18, 145503.
- [27]. Dikmen, S.; Shuk, P.; Greenblatt, M. Solid State Ionics 1998, 112, 299.
- [28]. Li, G. S.; Mao, Y. C.; Li, L. P.; Feng, S. H.; Wang, M. Q.; Yao, X. Chem. Mater. 1999, 11, 1259.
- [29]. Zhao, H.; Feng, S. H. Chem. Mater. 1999, 11, 958.
- [30]. Zhao, H.; Feng, S.; Xu, W. Mater. Res. Bull. 2000, 35, 2379.

Paper ID:AG98005

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

Name: Parashuram Mishra

Full Address: Bioinorganic and Materials Chemistry Research

Laboratory, M.M.A.M. Campus, Biratnagar, Nepal

District: Morang

State: Koshi

Country: Nepal

Pin code: 60005

Mobile No: +9779742129647

