

# Synthesis, Structure, and Electrical Properties of The Solid Solution of A Ternarymixed Valence $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$ by *Ab Initio* Method Via Powder XRD

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## Abstract

Since the first discovery and description of materials, whose structures are not periodic, enormous efforts have been made in studying a periodic structure. With these efforts including the development of super space group theory and structure solution algorithms, numerous incommensurately modulated structures which represent the vast majority of known a periodic structure have been determined with single crystal X-ray diffraction data. However, the determination of modulated structures remains very difficult for polycrystalline materials. Powder X-ray diffraction yield remarkable information for polycrystalline materials. By this method, modulated structures of polycrystalline materials that impede solution by conventional methods can be determined. The power of these methods is illustrated with the examples of the determination of modulated structures of polycrystalline materials' by powder X-ray diffraction method has made enormous progress over the last decade. The determination of some structures using X-ray technique or in combination with powder X-ray diffraction (PXRD) has now become convenient. However, the analysis of complex structures is far from routine even with high-quality single crystal X-ray diffraction (SXRD) data, and the structure analysis of complex structures from PXRD data is more popular technique. For the structure determination a novel polycrystalline has been synthesized with followed stoichiometric process compounds which have some interesting functions and developing routine PXRD method to simplify the determination of complex structures of these new compounds. In order to search for new ionic conductor materials exhibiting a columnar  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$  structural type, the syntheses of the solid solutions  $\text{Zr}(\text{NO}_3)_4$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $\text{Cd CO}_3$  have been undertaken .multi phases were obtained for the last composition with 0.4-0.5 homogeneity range. Moreover, a new oxide with  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$  composition has been obtained from the limit nominal stoichiometric  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$ . X-ray powder diffraction studies have shown that this oxide crystallizes in the triclinic crystal system, having space group *P-1* with unit-cell parameters  $a=2.0402 \text{ \AA}$   $b=3.1582 \text{ \AA}$   $c=9.3582 \text{ \AA}$   $\alpha=96.2273^\circ$   $\beta=94.9552^\circ$   $\gamma=94.7501^\circ$  and volume  $59.46 \text{ \AA}^3$  and refine factors are  $R_p=0.3123$ ,  $R_{wp}=0.422015$  and  $\text{GOF}=0.00119$ .

**Keywords:** Ionic, conductor, modulated, X-ray diffraction, polycrystalline, stoichiometry.**Copyright © 2020 The Author(s):** This is an open-access article distributed under the terms of the Creative Commons Attribution **4.0 International License (CC BY-NC 4.0)** which permits unrestricted use, distribution, and reproduction in any medium for non-commercial use provided the original author and source are credited.

## INTRODUCTION

Perovskite-like mixed oxides with the general formula  $\text{ABO}_3$  (where A is transition metals and B is main group metal ions) are of interest due to their high activity and stability as catalysts for various high temperature processes involving oxygen, such as complete and selective oxidation of hydrocarbons, decomposition of nitrogen oxides, oxidative dimerization metal ions, etc. The catalytic properties of perovskites in these reactions depend on the phase and surface compositions, structure defectiveness, mobility of the surface and bulk oxygen atoms. At present, composite catalysts with a certain microstructure and

consisting of various perovskite-like phases are of great interest for researchers. Therefore, the understanding of relationship between the composition, microstructure, and catalytic properties of a composite is a task of primary importance in a search for new efficient catalysts. Unlike the known physical and chemical methods of phase analysis, the method of differential dissolution (DD) makes it possible to solve simultaneously three problems of a chemical analysis, namely the detection, identification, and quantitative determination of the composition of multiphase solid substances without using the reference samples of individual phases. The DD method also makes it possible to analyze changes in the composition of the

composite in the particle depth and to make conclusions about the formation of phases with constant and variable compositions, as well as to reveal features of the particle microstructure. In some cases, it makes the DD method indispensable for solving problems of the phase analysis of multi-element multiphase materials [1]. 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 [2]. 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. The aim of this work is determine the structure of titled compound by ab initio method via powder XRD which is popular technique and electrical properties.

## MATERIALS AND METHODS

All chemicals used were analytical grade. A polycrystalline sample of  $\text{Cd}_{0.21}\text{Zr}_{2.54}\text{Pb}_{1.251}\text{N}_{0.531}\text{O}_{0.561}$  was synthesized by a standard solid state reaction using a mixture of high purity reagents of solutions  $\text{Zr}(\text{NO}_3)_4$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $\text{CdCO}_3$  contained mixed valence as the starting materials in the molar ratio of 1 : 1 : 1. 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  $2\theta = 10$  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 CuK $\alpha$  radiation. The powder was rotated during the data collection to minimize preferred Orientation effect if any. The program TREOR in CRYSFIRE was used to index the powder pattern which give orthorhombic cell 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.  $R_{wp} = 0.0680$ ,  $R_p = 0.030$  and  $\text{GOF} = 0.31$  the structure factors  $F_0 = 2023$

and  $F_c = 3022$ . The density is determined by Archimedes principle.

## RESULTS AND DISCUSSIONS

In terms of crystal chemistry, under certain thermodynamic conditions, the layered perovskite structure type tends to pass into a more stable structure either of perovskite or a layered structure with a greater number of perovskite layers [3]. With regard to the noted above, layered perovskite of the  $\text{Cd}_{0.21}\text{Zr}_{2.54}\text{Pb}_{1.251}\text{N}_{0.531}\text{O}_{0.561}$  type with the ratio 1:1:1 is stable. It may be supposed that under certain conditions of the dynamic mode of dissolution, the structure of layered perovskite of the  $\text{NO}_4\text{P}_7\text{Q}_3\text{R}_3$  formula type.  $\text{NO}_4\text{P}_7\text{Q}_3\text{R}_3$  can become unstable during DD and can decompose into structurally related forms:  $\text{ZrO}_2$  and  $\text{PbO}$ . Moreover, perovskite formed after the decomposition of the layered structure can differ in stability from perovskite obtained during the synthesis due to its defectiveness, and can undergo further leaching out of CdO until the formation of the cited oxide. Meanwhile In materials chemistry, the crystal structure determination is the first step to understand and interpret physical properties of an unknown material. Moreover, it also guides people on how to modify the material and hence improve the performance [4]. Nowadays, the most successful technique for structure determination is through single crystal X-ray diffraction, from which a sufficient number of independent reflections against the structural parameters can be extracted in 3D reciprocal space. Several mature analysis methods, such as the direct method,<sup>1</sup> Patterson method,<sup>2</sup> charge-flipping algorithm<sup>3</sup> and maximum entropy method<sup>4</sup> can be applied to accurately solve the structure. This technique requires synthesizing a high quality single crystal at a micrometer. Experimentally, the chance to get polycrystalline materials is generally larger than to get single crystals. In this case, powder X-ray diffraction (PXRD) becomes a popular technique but with this technique, the possibility to determine an unknown structure dramatically decreases, because 3D reflections are compressed into 1D with an inevitable overlapping problem, especially when the unit cell is big. The situation will become worse when the PXRD is collected on a multi-phase sample, which is not uncommon in the preliminary stage of searching new materials, especially in the cases of hydrothermal (or solvothermal) syntheses of zeolitic or MOF materials' XRD data for the sample of  $\text{Cd}_{0.21}\text{Zr}_{2.54}\text{Pb}_{1.251}\text{N}_{0.531}$  synthesized at its nominal composition is shown in Figure-1. All peaks could be indexed to a triclinic unit cell with P-1 symmetry, analogous to the  $\text{Cd}_{0.21}\text{Zr}_{2.54}\text{Pb}_{1.251}\text{N}_{0.531}$  structure using CRYSFIRE PACKAGE [5]. In the diffraction pattern there is a slight anisotropic peak broadening moving to higher angles. This slight peak broadening could be caused by ordering within the cationic layers but relative disorder of the cations between layers. The sloping background observed in XRD at low angles out to  $\sim 30^\circ 2\theta$  is qualitatively

indicative of stacking faults, a common feature of honeycomb oxides. In an ideal layered mixed-metal oxide, all the cationic planes are stacked along the *c*-axis by a unique translational stacking vector. However it has been shown that two other stacking vectors with very similar energy (1-4 meV) can occur in a structure, leading to so called “stacking faults”. Stacking faults in

the honeycomb oxides occur due to the relatively weak coupling between the layers. In practice, the cationic layers are never perfectly stacked along the *a*-axis when a layered structure has the P-1 space group, although higher temperature thermal treatment during synthesis can decrease the frequency of stacking faults [6].

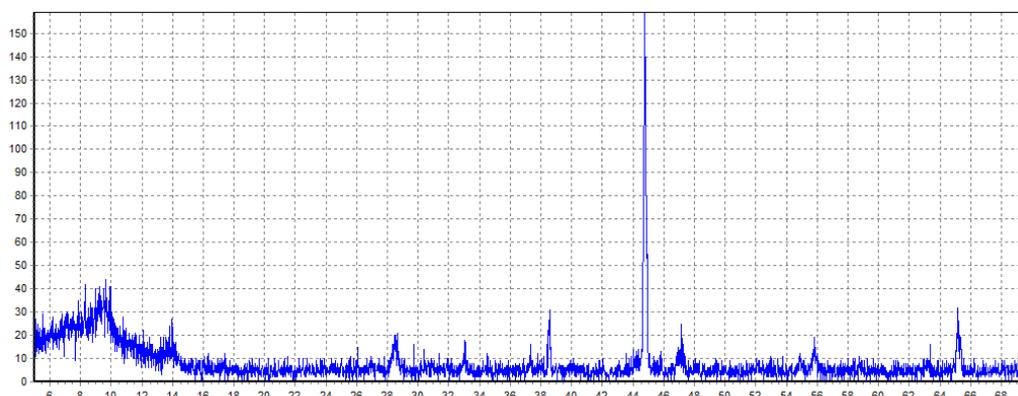


Fig-1: Powder XRD graphical spectra of of  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$

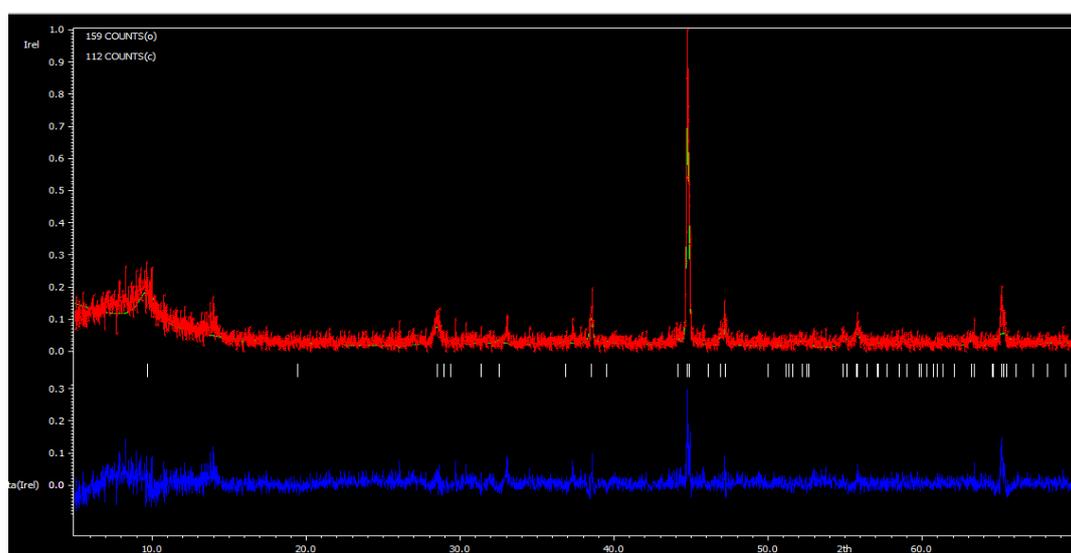


Fig-2: Graphical representation of the result from Rietveld refinement with X-ray powder data. Vertical bars indicate positions of the Bragg reflections for of  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$  dots mark the observed intensities and the solid line gives the calculated intensity curve. The deviations between the observed and the calculated intensities from the refined model are shown by the difference plot in the lower part of the diagram

## STRUCTURE SOLUTIONS

### X-Ray powder diffraction and Rietveld refinements

X-Ray powder diffraction (XRD) patterns were collected on a PANalytical X'Pert-MPD diffractometer using graphite-monochromated  $\text{Cu-K}\alpha$  radiation. The data were collected at 40 kV, 30 mA with a step size of  $0.02^\circ$  in the  $2\theta$  range of  $10\text{--}90^\circ$  and spectra in Figure-1. Rietveld refinements of the XRD patterns were performed using JANA computer package. The backgrounds were fit with Chebyshev function, and Bragg-Brentano was selected as diffractometer type. Lattice constants, instrument parameters, atomic coordinates, thermal parameters, and peak profile functions were refined in order to achieve a simulated diffraction pattern that matched the

experimental data. The crystallographic data obtained refinement shown in Table-1 as well as Rietveld spectra shown in Figure-2. The completed refinements provided phase quantification and lattice parameter determination. The observed, difference and calculated patterns of the newly synthesized novel oxide obtained by Rietveld refinement has been shown in Fig-2. The structure in packing from shown in Figure-2. In the structure Bi is bonded with Cd-Zr bonded with Cd-Zr-Pb with O and N) each forming closed type structure. The bonding between different constituent atoms has been discussed in more details in Table-2. In conclusion, the structure of  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251} \text{N}_{0.531} \text{O}_{0.561}$  has been solved by the ab initio approach using powder X-ray diffraction data. of  $\text{Cd}_{0.21} \text{Zr}_{2.54} \text{Pb}_{1.251}$

$N_{0.531}O_{0.561}$  was found to crystalline in orthorhombic crystal system with space group P-1 which displays an unusual spiral chain structure along the c-axis and packing form on three-dimensional axis. The data were analyzed using Diamond package with help of CIF file. Rietveld refinement of triclinic crystal system of  $Cd_{0.21}Zr_{2.54}Pb_{1.251}N_{0.531}O_{0.561}$  against XRD data for structural determination proved difficult, due to a combination of preferred orientation of the plate-like crystallites in flat-plate geometry [5]. In other words, the extracted peak intensities for phase 1 could be reliable. Note that if the relative intensities differed a lot from the simulated patterns of the known phases, additional manual partitioning of those overlapping peaks would be necessary to get reliable intensities for the unknown phase 1. After considering the multiplicity and Lorentz-polarization correction, the intensities of phase 1 were used for the structure solution. Moreover, the reflection conditions indicated possible space groups P-1. The initial structure model was obtained using a charge flipping algorithm with the program Superflip. 8 from

Jana package [6-10]. Random phases were used at the beginning of the charge-flipping interaction, and overlapping peaks were re-partitioned using a histogram match to improve the convergence. The iteration converged with an R factor of 20 % and the final electron density shows a P-1 symmetry with a 5% error. The program of EDMA was then used to automatically assign atomic positions. Four unique heavy atomic positions were found and the heaviest one was assigned as Cd while the others were considered as Pb and Zr. Due to the existence of heavy atoms, all oxygen positions were ambiguous in the electron density map of this stage [11]. To locate the oxygen atoms, a Monte-Carlo based simulated annealing process with the program TOPAS was applied. For each annealing process, various atomic coordinates were randomly assigned as the initial positions of the oxygen atoms [12]. The annealing process was restarted after finding a few oxygen positions, until all oxygen positions were found to be reasonable.

**Table-1: Crystallographic Data**

Phase data	
Formula sum	$Cd_{0.21}Pb_{1.251}Zr_{2.54}N_{0.531}O_{0.561}$
Formula weight	530.9 g/mol
Crystal system	triclinic
Space-group	P -1 (2)
Cell parameters	$a=2.0402 \text{ \AA} \quad b=3.1582 \text{ \AA} \quad c=9.3582 \text{ \AA} \quad \alpha=96.2273^\circ \quad \beta=94.9552^\circ \quad \gamma=94.7501^\circ$
Cell ratio	$a/b=0.6460 \quad b/c=0.3375 \quad c/a=4.5869$
Cell volume	$59.46 \text{ \AA}^3$
Z	2
Calc. density	$29.6515 \text{ g/cm}^3$
Meas. density	$29.5967 \text{ g/cm}^3$
Pearson code	aP81
Formula type	NO4P7Q32R37
Wyckoff sequence	i39hgc

**Table-2**

Atomic parameters							
Atom	Ox.	Wyck.	Site	x/a	y/b	z/c	U [ $\text{\AA}^2$ ]
Pb1	+2	1c	-1	0	1/2	0	0.0380
Cd1	+2	2i	1	0.03227	0.07501	0.15984	0.0380
Cd2	+2	2i	1	-0.29195	0.54510	0.16602	0.0380
Zr1	+4	2i	1	0.14882	0.08384	0.10329	0.0380
Zr2	+4	2i	1	0.00357	0.52631	0.19758	0.0380
Zr3	+4	2i	1	-0.07828	0.54098	0.24173	0.0380
Zr4	+4	2i	1	0.16975	0.27745	0.41284	0.0380
O1	-2	2i	1	-0.17180	0.51637	0.41686	0.0380
O2	-2	2i	1	0.27148	0.31860	0.25474	0.0380
O3	-2	2i	1	-0.23906	0.00194	0.49832	0.0380
O4	-2	2i	1	-0.14613	0.10534	0.08038	0.0380
O5	-2	2i	1	-0.43827	-0.14002	0.25225	0.0380
O6	-2	2i	1	-0.76477	-0.21344	0.33467	0.0380
O7	-2	2i	1	-0.07133	-0.15673	-0.00388	0.0380
N1	-3	2i	1	-0.36832	-0.24743	0.49407	0.0380
N2	-3	2i	1	-0.07211	0.04524	0.32251	0.0380
N3	-3	1h	-1	-1/2	1/2	1/2	0.0380
N4	-3	2i	1	0.03102	-0.17985	0.25486	0.0380

**Table-3: Selected bond angles**

Atom1	Atom2	Atom3	Angles
Pb1	O7	O7	180.000
	O7	Zr12	87.939
	O7	Zr12	92.061
Cd	O7	Zr18	42.365
	O7	Zr18	137.635
	O7	Cd13	45.637
	O7	O13	134.363
	O7	Zr12	108.635
	O7	Zr12	71.365
Zr	O7	Zr4	145.190
	O7	O4	34.810
	O7	Zr17	90.059
Pb	O7	Cd1	136.504
	O7	Cd1	43.496
	O7	O13	38.950
	O7	O13	141.050
	O7	Cd1	136.052
N1	O7	O4	43.639
	O7	O8	82.543
	O7	O8	97.457
	O7	O16	145.157
Zr3	O7	O16	34.843
	O7	Zr1	63.972
	O7	Zr1	116.028
	O7	Zr9	119.401
	O7	Zr9	60.599
Pb	O7	N4	73.965
	O7	N4	106.035
	O7	O4	54.699
	O7	O4	125.301
	O7	Zr12	92.061
	O7	Zr12	87.939
	O7	Zr18	137.635
O12	O7	Zr18	42.365
	O7	O13	134.363
	O7	O13	45.637
	O7	Zr12	71.365
Pb12	O13	Zr1	96.198
	O13	Zr9	41.122
	O13	Zr9	138.878
	O13	N4	105.776
	O13	N4	74.224
Cd	O13	O4	93.593
	O13	O4	86.407
	O13	Zr1	45.820
	O13	Zr1	134.180

## CRYSTAL CHEMISTRY

The framework structure of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  was first examined by ab initio structure determination method using the powder XRD data. The initial lattice parameters were determined to be  $a=2.0402 \text{ \AA}$   $b=3.1582 \text{ \AA}$   $c=9.3582 \text{ \AA}$   $\alpha=96.2273^\circ$   $\beta=94.9552^\circ$   $\gamma=94.7501^\circ$ , and volume= $59.46 \text{ \AA}^3$  by an indexing procedure using the program N-TREOR15 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-Voigt method using the program Jana2006.14 A profile function and background function of the Le Bail method used in the present study were pseudo-Voigt function and 20<sup>th</sup> 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 (ZrO ion was successfully determined. In this stage, the lattice parameters of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  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  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  was previously reported in the literature,[10,11] the atomic displacement parameters have not been clarified. In addition, the reported reliability value was relatively large ( $R = 111.1\%$ ). Therefore, we first reinvestigated the crystal structure of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  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  $\text{Cu}/\text{K}\alpha$  radiation (operating condition: 50 kV, 40 mA) at 295 K. The structure refinement was carried out using a computer program Jana2006.14 The framework

structure of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  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 EXPO2004,16 Jana2006,14 and Superflip.17 The Rietveld refinement of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  was performed by Jana2006 using powder X-ray diffraction data measured at room temperature with wavelength=1.556  $\text{ \AA}$ . 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 be  $a=2.0402 \text{ \AA}$   $b=3.1582 \text{ \AA}$   $c=9.3582 \text{ \AA}$   $\alpha=96.2273^\circ$   $\beta=94.9552^\circ$   $\gamma=94.7501^\circ$ , shown in Figure 3. The basic  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  framework in be  $a=2.0402 \text{ \AA}$   $b=3.1582 \text{ \AA}$   $c=9.3582 \text{ \AA}$   $\alpha=96.2273^\circ$   $\beta=94.9552^\circ$   $\gamma=94.7501^\circ$ , is maintained nearly unchanged from that in the parent oxide. All three lead ions octahedral were strongly distorted, and the Zr-O distances were in the wide range of 1.52(1)-2.63(1)  $\text{ \AA}$ . These features for the ZrO<sub>2</sub> ions unit were very similar to those observed be  $a=2.0402 \text{ \AA}$   $b=3.1582 \text{ \AA}$   $c=9.3582 \text{ \AA}$   $\alpha=96.2273^\circ$   $\beta=94.9552^\circ$   $\gamma=94.7501^\circ$ , On the other hand; the most interesting feature of the  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  structure is the Pb occupation site in the tunnel space [13]. The structure of cited oxide was obtained as shown in Figure-4.

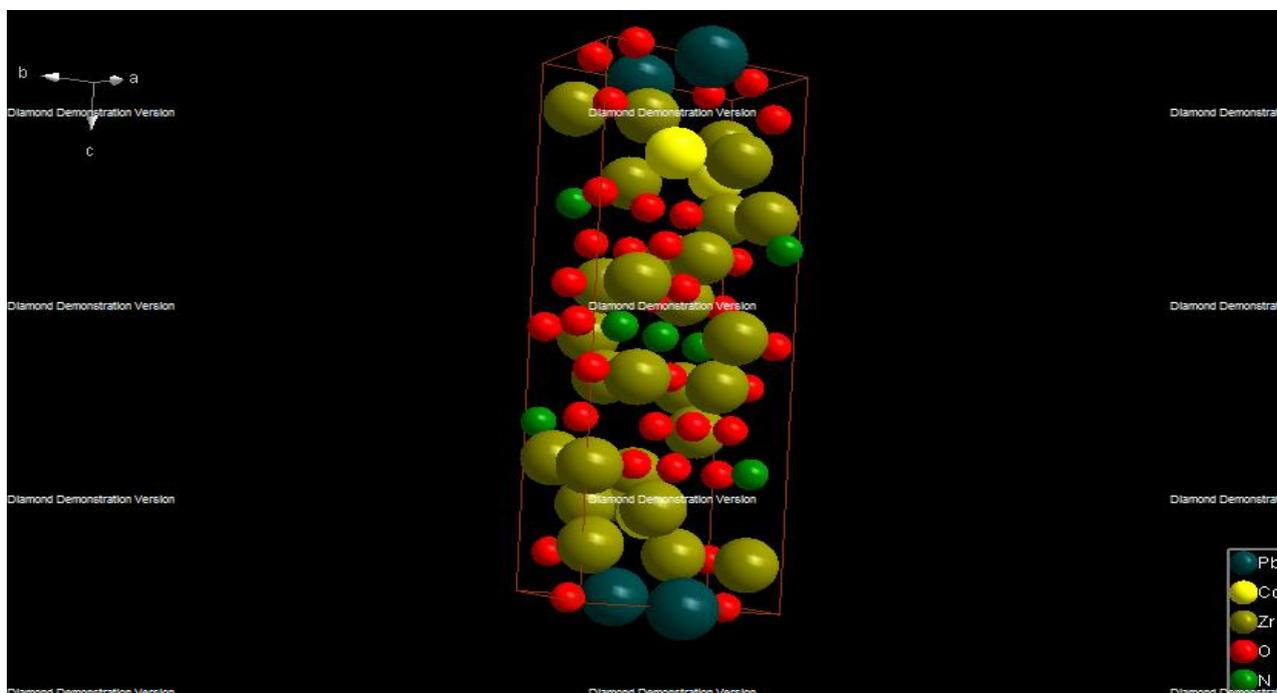


Fig-4: Perovskite-like mixed oxides structure of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$

**Table-3: Selected bond angles**

Atom1	Atom2	Atom3	Angles
Pb1	O7	O7	180.000
	O7	Zr12	87.939
	O7	Zr12	92.061
Cd	O7	Zr18	42.365
	O7	Zr18	137.635
	O7	Cd13	45.637
	O7	O13	134.363
	O7	Zr12	108.635
	O7	Zr12	71.365
Zr	O7	Zr4	145.190
	O7	O4	34.810
	O7	Zr17	90.059
Pb	O7	Cd1	136.504
	O7	Cd1	43.496
	O7	O13	38.950
	O7	O13	141.050
	O7	Cd1	136.052
N1	O7	O4	43.639
	O7	O8	82.543
	O7	O8	97.457
	O7	O16	145.157
Zr3	O7	O16	34.843
	O7	Zr1	63.972
	O7	Zr1	116.028
	O7	Zr9	119.401
	O7	Zr9	60.599
Pb	O7	N4	73.965
	O7	N4	106.035
	O7	O4	54.699
	O7	O4	125.301
	O7	Zr12	92.061
	O7	Zr12	87.939
	O7	Zr18	137.635
O12	O7	Zr18	42.365
	O7	O13	134.363
	O7	O13	45.637
	O7	Zr12	71.365
Pb12	O13	Zr1	96.198
	O13	Zr9	41.122
	O13	Zr9	138.878
	O13	N4	105.776
	O13	N4	74.224
Cd	O13	O4	93.593
	O13	O4	86.407
	O13	Zr1	45.820
	O13	Zr1	134.180

Metal ions are coordinated as Zr with tetrahedral coordination number (C.N.) 4 similarly coordinated with tetrahedral having coordination number 4 having bond angle  $109.25^\circ$  and Cd coordinated octahedral with C.N.6 having bond angle  $90.13^\circ$ . All the probable angles are shown in Table-3.

## ELECTROCHEMICAL MEASUREMENTS

Electrochemical Pb insertion/ extraction experiments for  $Cd_{0.21} Pb_{1.251} Zr_{2.54} N_{0.531} O_{0.561}$  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 25 MPa. The counter electrode was a Pb foil having a diameter of 20 mm [14-16]. The separator was a micro porous polypropylene sheet. A solution of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.5615}$  in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (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,  $10 \text{ mA g}^{-1}$ , between 1.0 and 3.0 V at 25 °C after standing 6 h under an open circuit condition. AC impedance measurements for  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  MHz-10 Hz frequencies at room temperature [17] particle size is 55.351nm was found.

## CONCLUSIONS

In the present study, ternary  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  oxide was successfully prepared and structure determined by ab initio methods from starting material as a parent compound via  $\text{Zr}(\text{NO}_3)_4$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $\text{CdCO}_3$  to 1100°C. The phase purity and chemical composition of the ion-exchanged samples were well characterized. The crystal structure of  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  was refined by Rietveld refinement using the powder X-ray diffraction data. The basic  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  framework in  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  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  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  coordinated with octahedral arrangement along with Zr is also coordinated with oxygen and N 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-zirconate 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  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  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, as particle size 55.351 nm an unusual  $\text{Cd}_{0.21} \text{Pb}_{1.251} \text{Zr}_{2.54} \text{N}_{0.531} \text{O}_{0.561}$  triclinic has been found for the first time by using cited compound can be used as super conductor materials as nanoparticle by ion-exchange reaction.

## Compliance with ethical standards

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## Author's Short Biography

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Parashuram Mishra is a senior researcher and did Postdoc from University of Delhi, India. He involved in teaching and research more than 25 years and awarded by Science and Technology Award from Govt. of Nepal as well as Outstanding International Scientist Award also.

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