Ab Initio Structure Determination Of A Novel Mixed Valence Transition Oxide La0.5 $C_{d0.125}$ $Zr_{0.125S0.76}$ $N_{0.125}$ $O_{0.25}$ Via Powder X-Ray Diffraction And Study The Electrical Property

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Abstract

The present work deals with the ab initio structure determination of the heavy metal framework La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 from precession electron diffraction intensities The metal framework of the compound was solved in this investigation via direct methods from hk0 precession electron diffraction intensities recorded with a Philips EM400 at 100 kV. A subsequent (kinematical) least-squares refinement with electron intensities yielded slightly improved co-ordinates for the 6 heavy atoms in the structure. Chemical analysis of several crystallites by EDX is in agreement with the formula La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125. Moreover, the structure was independently determined by Rietveld refinement from X-ray powder data obtained from a multi-phasic sample. The compound having orthorhombic crystal system space group Pcnb with refined lattice parameters a=10.3617,b=10.3124,c=10.5490, and v=1192.64 Å3. Comparison of the framework structure from electron diffraction with the result from Rietveld refinement shows an average agreement for the heavy atoms within 0.09A ˚ . The titled compound was prepared from mixture of La2(CO3)3, Zr(NO)2,andCdSO4 by solid state reaction with full thermal decomposition at 1000°C. Rwp = 0.0417, Rp = 0.032 and Rp = 0.082. The structure factors F0=3032 and Fc=3031. The morphology of the crystal has been determined by SEM.

Keywords: Crystal structure, powder XRD, orthorhombic, space group, SEM, morphology, Electron crystallography

Introduction

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. 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,1 Patterson method,2 charge-flipping algorithm3 and maximum entropy method4 can be applied to accurately solve the structure. This technique requires synthesizing a high quality single crystal at a micrometre level, which might be difficult in some fields, for example in ceramic chemistry. Experimentally, the chance to get polycrystalline materials is generally larger than to get singlecrystals. 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. The difficulty could further increase when the target phase is not the highly dominant one in the composition. To determine the structure of an unknown phase in a multi-phase polycrystalline sample would be very helpful for the researchers, saving time to optimize the

syntheses conditions. 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 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[3]. 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[4-7]. 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 structure of titled compound by ab initio method with the help of powder XRD [1].

Materials and Methods

All chemicals used were analytical grade. A polycrystalline sample of La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 was synthesized by a standard solid state reaction using a mixture of high purity reagents of La2(CO3)3, Zr(NO3)4,andCdSO4 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 pallets and sintered at 100 K/h. Powder X-ray diffraction (XRD) data were collected at room temperature in the angular range of 2q =10 to 90 with scan step width of 0.02° 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 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 Pcnb using check cell program. The structural parameters were refined by the Reitveld method using the GSAS program which gave Rwp = 0.0417, Rp= 0.032, Rp = 0.082. The density is determined by Archimedes principle. The morphology of titled compound was determined using AFM (Nanoscope III, Digital Instruments, Santa Barbara) [2].

Results and Discussions

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 oxides of metals and alkaline cations are well known for their thermal stability and the simplicity of syntheses , which is important for many practical applications lithium batteries. Calcium oxide powder was dried and decarbonated at 10000C over night prior to use. The oxides were weighed in stoichiometric proportions and ground together in an agate mortar. The prepared composition was heated upto14000C for over night in an alumina crucible, no particular condition was used in order to cool down the samples. This procedure was applied at least twice in order to etastabilized compound as verified by X-ray powder diffraction. The final compound is white in color.In the course materials science, the crystal structure determination is the first step to understand and interpret physical properties of an unknown material. Moreover, it also suggested to people on how to modify the material and hence improve the performance. At present the most successful technique for structure determination is through powder 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, 1 Patterson method,2 charge-flipping algorithm3 and maximum entropy method4 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 La0.5.Cd0.125.Zr0.125.S. 0.76.O 0.25.N 0.125 synthesized at its nominal composition is shown in Figure 1. All peaks could be indexed to a orthorhombic unit cell with Pcnb symmetry, analogous to the La0.5.Cd0.125.Zr0.125.S. 0.76.O 0.25.N 0.125 structure using CRYSFIRE PACKAGE11]. 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 ~30° 2θ 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 (1-2 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 c-axis when a layered structure has the Pcnb space group, although higher temperature thermal treatment during synthesis can decrease the frequency of stacking faults.
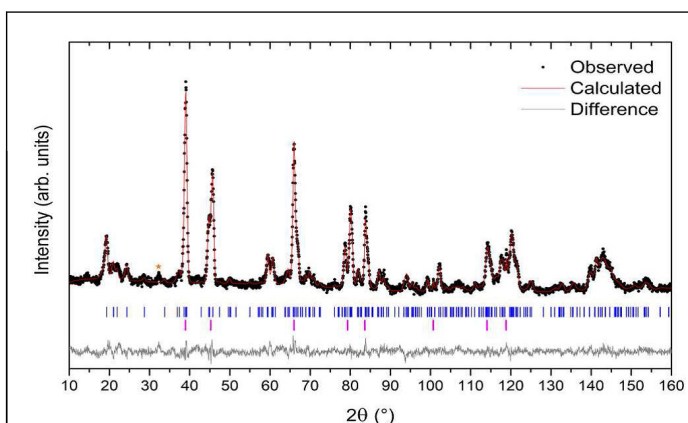

Figure 1: Powder XRD data (Cu Kα, λ = 1.5418 Å) for the sample of La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 at room temperature. Note that the Rietveld fit shown is to the structural model subsequently obtained.

Rietveld refinement of orthorhombic La0.5.Cd0.125.Zr0.125.S. 0.76.O 0.25.N 0.125 against XRD data for structural determination proved difficult, due to a combination of preferred orientation of the plate-like crystallites in flat-plate geometry[13].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 themultiplicity and Lorentz-polarization correction, the intensities of phase 1 were used for the structure solution as below [3]. Moreover, the reflection conditions indicated possible space groups Pcnb . The initial structure model was obtained using a charge flipping algorithm with the program Superflip.8 Random phases were used at the beginning of the charge-flipping iteration, and overlapping peaks were re-partitioned using a histogram match to improve the convergence. The iteration converged with an R
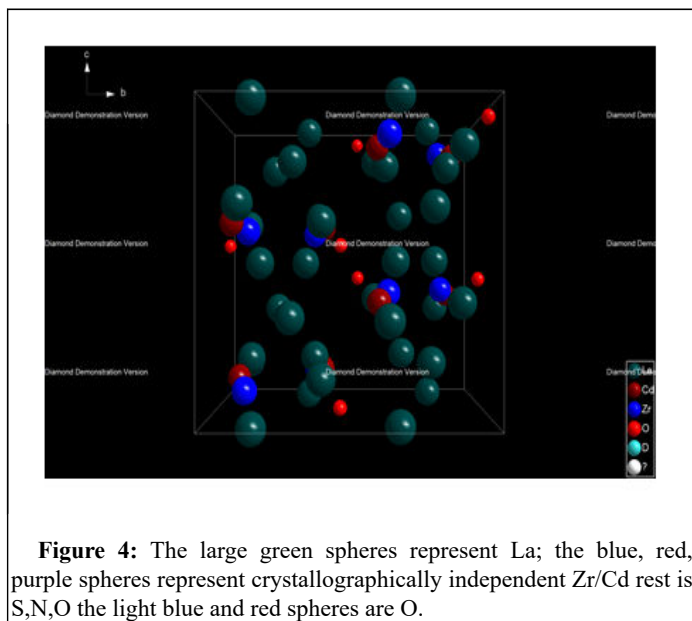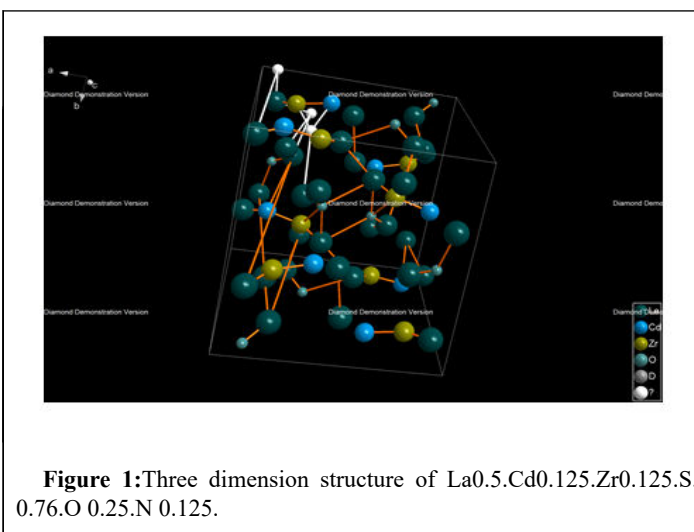
factor of 29% and the final electron density shows a Pcnb symmetry with a 5% error. The program of EDMA was then used to automatically assign atomic positions. Four unique heavy atomic positions were found and the heaviest one was assigned as La while the others were considered as Zr nd Cd. Due to the existence of heavy atoms, all oxygen positions were ambiguous in the electron density map of this stage. 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. The annealing process was restarted after finding a few oxygen positions, until all oxygen positions were found to be reasonable [4].

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 Cu-Kα radiation. The data were collected at 40 kV, 30 mA with a step size of 0.02° in the 2θ range of 5–80°. Rietveld refinements of the XRD patterns were performed using GSAS-II The backgrounds were fit with Chebyschev 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 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 Figure 1. The structure in packing. In the structure La is bonded with Cd . Zr bonded with Cd-O,,La with N) each forming closed type structure. The bonding between different constituent atoms has been discussed [5].

In conclusion, the structure of La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 has been solved by the ab initio approach using powder X-ray diffraction data. La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 was found to crystalline in orthorhombic crystal system with space group Pcbn which displays an unusual spiral chain structure along the c-axis and packing form on three-dimensional axis.The data were analyse Diamond package with help of CIF file (Figure 1).

Figure 1: Three dimension structure of La0.5.Cd0.125.Zr0.125.S. 0.76.O 0.25.N 0.125.

Figure 4: The large green spheres represent La; the blue, red, purple spheres represent crystallographically independent Zr/Cd rest is S,N,O the light blue and red spheres are O.

Conclusion

The determination of crystal structure from powder X-ray diffraction data appears to hold promise for the future especially in materials science and drugs and drugs and pharmaceuticals fields where the growth the o diffraction quality crystals becomes a serious rate limiting step. La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 has been successfully synthesized by high temperature solid state reaction in open air atmosphere for the first time.. Its structure features an intricate 3D framework composed of 1D neodymium oxygen chains connected with Cd cations located in the internal space. The phase purity was verified by XRD measurement coupled with Rietveld refinement. Preliminary structural work on the new La0.5.Cd0.125.Zr0.125.S.0.76.O 0.25.N 0.125 phase leads to the orthorhombic system, space group Pcnb with unit-cell parameters Unit cell dimensions a = 10.3617 Å,b =10.9111, c = 10.5490 Å,Cell volume 1192.64 Å3 Z=8 , and experimental density by Archimedes principle is 1.495 g/cm3Density, calculated 1.545 g/cm3. In summary, this work shows how the substitution of La for Zr and Cd in columnar structural-type oxides is progressively carried out with a simplification of the structure. At the same time, the oxygen ion conduction is improved.

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