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"Pellet-Based XRD: A Simplified Approach to Phase Purity Determination in Solid-State Materials"

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Abstract

Phase purity determination is an essential step in the characterization of solid-state materials, typically conducted through powder X-ray diffraction (XRD). However, the preparation of powder samples is often time-consuming, can lead to material wastage, and risks altering the structural properties of the sample. In this study, we present an alternative method that involves the direct use of pelletized samples for XRD analysis, bypassing the need for powdering. Our investigation, conducted on 2 series of compounds or 6 samples of oxygen-deficient perovskite oxides, demonstrates that diffraction patterns from pellet samples are sufficiently distinct to confirm phase purity, offering a faster, more efficient alternative to traditional powder XRD methods.

This method not only reduces the time and effort involved in sample preparation but also preserves the material's structural and physicochemical integrity. By minimizing the mechanical manipulation and thermal exposure of the samples, the direct pellet method allows for subsequent

property measurements—such as electrical conductivity, magnetic behavior, thermoelectric behavior, catalytic activity, and electrode performance—without risking sample degradation. Our results show that this approach provides reliable phase purity assessment while conserving materials, making it an attractive option for researchers working with oxygen-deficient perovskite oxides and other complex materials.

Keywords: XRD, solid-state reaction, perovskite oxides, oxygen deficiency

Introduction

The determination of phase purity in solid crystalline materials is a critical step in material synthesis and characterization. Traditionally, powder X-ray diffraction (XRD) has been the preferred method for identifying crystallographic phases due to its effectiveness in providing detailed structural information. Powdering a sample ensures uniform diffraction patterns, making it a reliable approach for phase analysis. However, the preparation of powder samples, especially for quick tests, involves several steps that can be time-consuming, potentially leading to sample loss, contamination, and wastage.

In this study, we propose an alternative approach to phase purity testing using pelletized samples directly in XRD analysis. Our findings demonstrate that diffraction peaks obtained from pellet samples are sufficiently distinct for phase identification, offering a viable method for phase determination without the need for extensive sample preparation. The use of pellet samples can significantly reduce the time, effort, and material wastage associated with powdering, making it an attractive option for rapid phase purity assessments in material synthesis workflows.

Moreover, repeated confirmation of phase purity is often required, even when the synthesis process is known to reliably reproduce the desired phase. This step is crucial prior to subsequent material characterizations such as electrical conductivity[1], thermoelectric behavior[2], magnetic properties[3], catalytic activity[4, 5], and electrode behavior[6]. Utilizing the pellet form for XRD testing directly, followed by other characterization techniques, presents a significant advantage—it eliminates the need for multiple physicomechanical manipulations and thermal treatments that can degrade the sample or alter its intrinsic properties. By preserving the structural and physical

integrity of the material, this method allows for more accurate assessment of its properties without introducing variations caused by unnecessary handling or sample destruction.

This paper aims to highlight the practical advantages of using pellets directly for XRD analysis, focusing on the method's potential to enhance efficiency, conserve samples, and reduce experimental artifacts during material characterization.

2. Experimental

2.1. Synthesis

The perovskite oxides compounds containing Ca, Sr, Fe, and Mn metals were synthesized using a solid-state reaction method. Stoichiometric amounts of high-purity starting materials, including calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), iron oxide (Fe_2O_3), gallium oxide and manganese oxide (MnO_2), were carefully weighed and thoroughly mixed. The mixtures were ground using an agate mortar and pestle to achieve homogeneous powders.

The resulting powders were pressed into pellets and subjected to a two-step thermal treatment. Initially, the samples were calcined at 1000°C for 24 hours, with a ramping rate of 100°C per hour to ensure controlled heating. After cooling, the samples were reground, pressed again into pellets, and heated at 1200°C for an additional 24 hours under the same ramping conditions. Following the final heat treatment, the samples were allowed to cool to room temperature naturally inside the furnace.

2.2. X-ray Diffraction measurement

The phase purity of the synthesized compounds was confirmed using Bruker D2 phaser X-ray diffractometer (XRD) with Cu Kα1 (λ = 1.54056 Å), employing a direct analysis of the pellet samples without further grinding into powder and their respective powders. Rietveld refinements were conducted using GSAS software[7] and the EXPEGUI interface[8].

For the measurement of the powder XRD, we followed the usual method as instructed by the Brucker D2 series: the amount, thickness of the powder and the circular area filling. For the measurement of Pellet XRD, the pellet size is made 13 mm to 25 mm of diameter and thickness of the deft of the sample holder. Incase if the sample thickness becomes thicker than the deft or

the diameter becomes bigger, the sample height is adjusted to fit the level required by the instrument.

Results and Discussion

The X-ray diffraction (XRD) patterns of six oxygen-deficient perovskite-derived compounds — $Ca_2Fe_2O_{6-\delta}$, $CaSrFe_2O_{6-\delta}$, $Sr_2Fe_2O_{6-\delta}$, $Ca_2FeMnO_{6-\delta}$, $CaSrFeMnO_{6-\delta}$, and $Sr_2FeMnO_{6-\delta}$ — were measured for both pelletized and powdered samples. These compounds have been well-documented in the literature, with their structures derived from perovskite oxides and displaying characteristic oxygen deficiencies.[1, 9, 10] In this study, the XRD patterns of the pellet samples were directly compared to those of their powdered counterparts to assess the viability of using pellets for phase purity determination.

The diffraction peaks for all six compounds were consistent with previously reported structures, confirming that the synthesized materials retained their expected crystallographic phases. Specifically, the $Ca_2Fe_2O_{6-\delta}$, $CaSrFe_2O_{6-\delta}$, and $Sr_2Fe_2O_{6-\delta}$ series exhibited the orthorhombic structure typically associated with oxygen-deficient brownmillerite phases.[1, 10] These phases are characterized by alternating layers of FeO_6 octahedra and FeO_4 tetrahedra, with ordered oxygen vacancies. The Mn-substituted series, $Ca_2FeMnO_{6-\delta}$, $CaSrFeMnO_{6-\delta}$, and $Sr_2FeMnO_{6-\delta}$, also displayed diffraction patterns in line with those expected for oxygen-deficient perovskites.[9] These structures adopt a similar framework with a mixed-valence state of Fe and Mn, contributing to oxygen vacancy ordering and associated lattice distortions.

Comparison of the XRD patterns from pellets and powders showed that the major diffraction peaks were in excellent agreement, indicating that the structural integrity of the compounds was preserved during the pelletization process. The diffraction peak positions, intensities, and profiles were nearly identical, confirming that pellet XRD provides reliable phase purity information without the need for powdering the sample. Notably, the sharpness and clarity of the peaks from the pellet samples were sufficient to identify the phases, ruling out any significant differences in phase identification between pelletized and powdered samples.

The ability to directly analyze pellets using XRD eliminates the time and material waste associated with powdering while preserving the structural integrity of the sample for further

testing. This is particularly advantageous for materials like oxygen-deficient perovskites, where repeated physicomechanical manipulation may affect their delicate structures and properties. By maintaining phase purity and preventing sample degradation, the use of pellet XRD proves to be a practical alternative for researchers engaged in the synthesis and characterization of complex oxide materials.

For the XRD measurements of both the pelletized and powdered samples, certain requirements were met to ensure accurate phase purity determination. The powder XRD measurements were performed following the standard method as outlined by the Bruker D2 series, including careful control over the amount of sample, the thickness of the powder layer, and the proper filling of the circular area on the sample holder. In the case of pellet XRD measurements, pellets were prepared with diameters ranging from 13 mm to 25 mm and thicknesses corresponding to the depth of the sample holder. If the pellet exceeded the required thickness or diameter, the sample height was adjusted to match the level required by the instrument to ensure correct alignment and measurement accuracy. The pellet position adjustments are shown in the 2-6. This adjustment was crucial for obtaining consistent and reliable diffraction patterns from the pellet samples, confirming their phase purity. By adhering to these guidelines, we ensured that both pellet and powder XRD data could be directly compared, demonstrating that pellet XRD is a valid and efficient alternative for phase purity analysis.

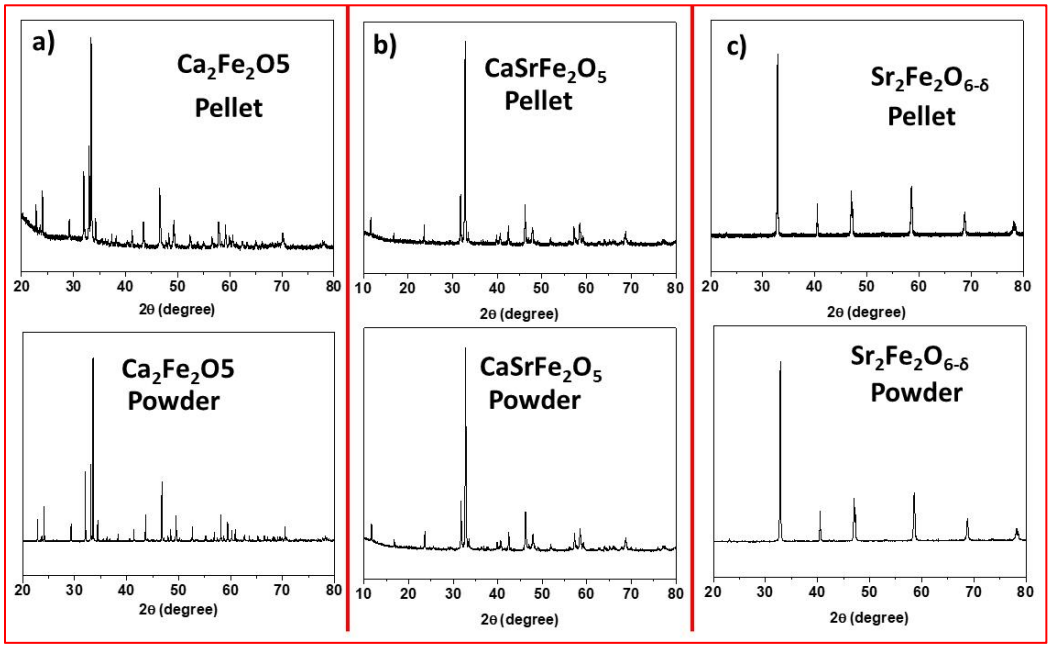

Figure 1a. comparative Pellet and powder XRD data of $Ca_2Fe_2O_{6-\delta}$, $CaSrFe_2O_{6-\delta}$ and $Sr_2Fe_2O_{6-\delta}$,

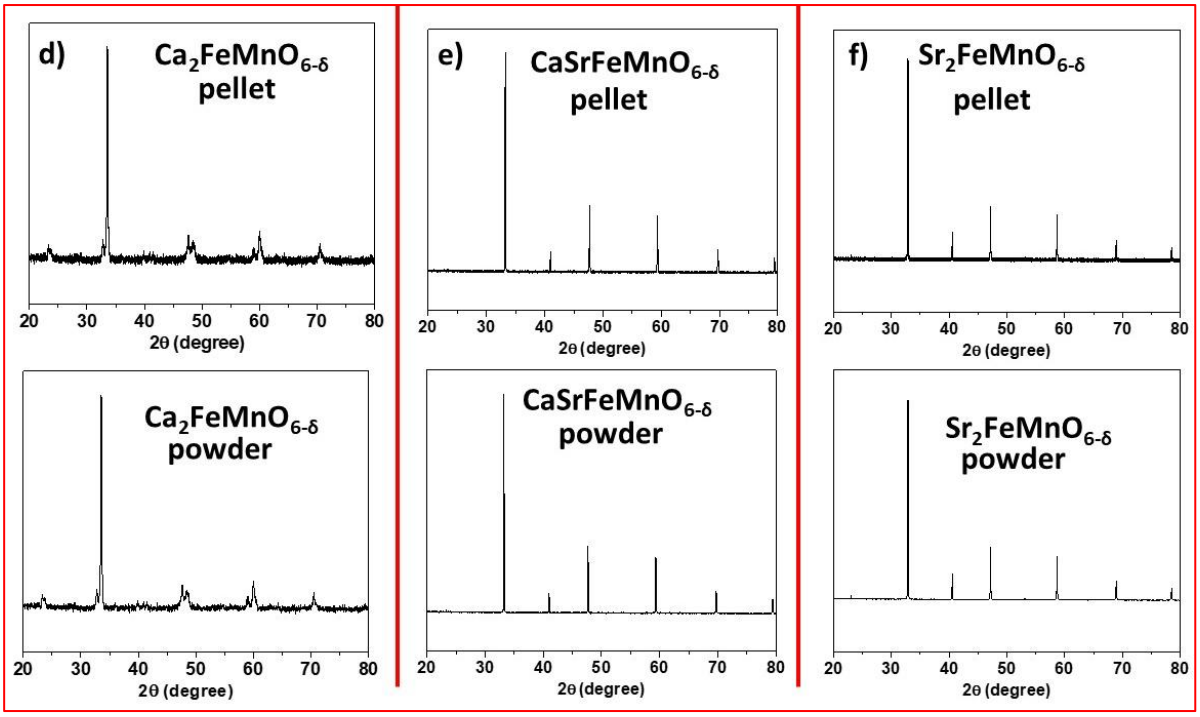

Figure 1b. comparative Pellet and powder XRD data of $Ca_2FeMnO_{6-\delta}$, $CaSrFeMnO_{6-\delta}$, and $Sr_2FeMnO_{6-\delta}$.

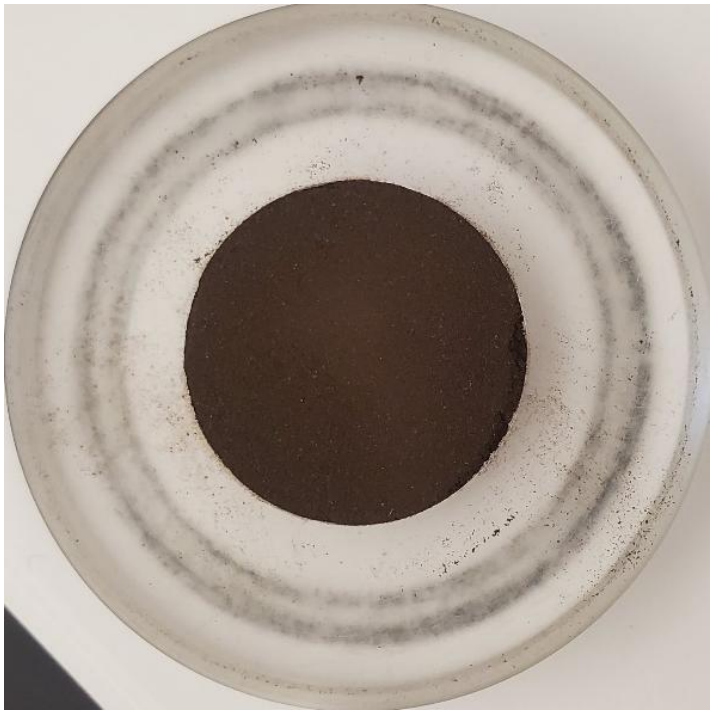

Figure 2. Powder sample spread in the well of the sample holder with the required height alignment.

Figure 3. Sample Pellet thicker than the sample holder depth where sample goes.

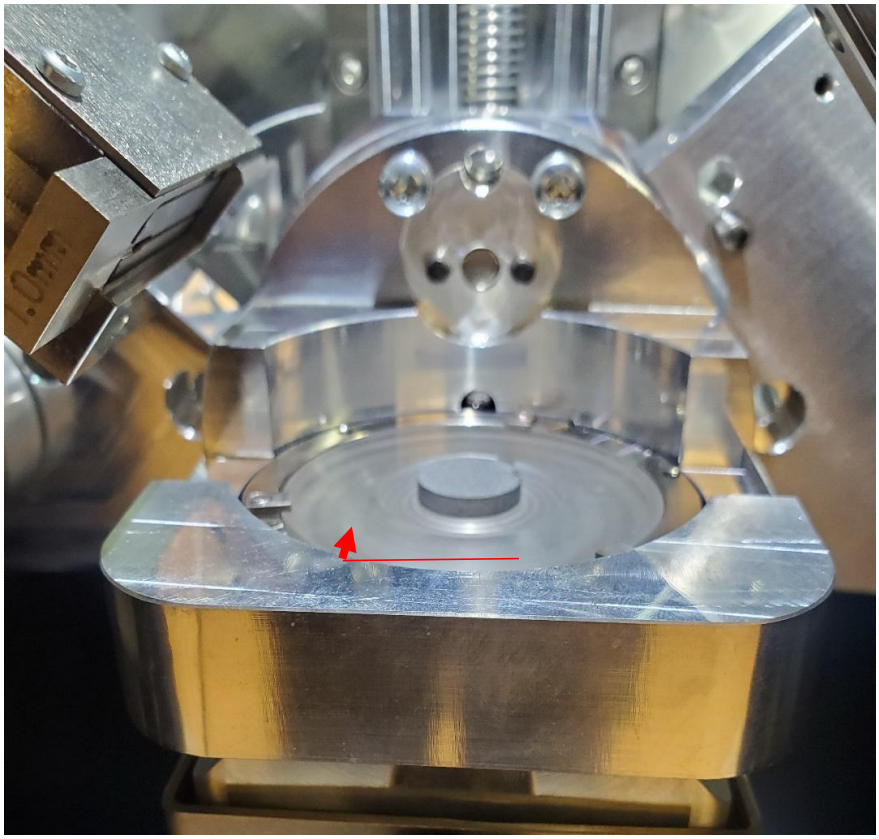

Figure 4. Sample height is coming above the level in the machine during measurement. The required level is shown by a line while the raised height is shown by the arrow. This position is wrong for the stage during measurement.

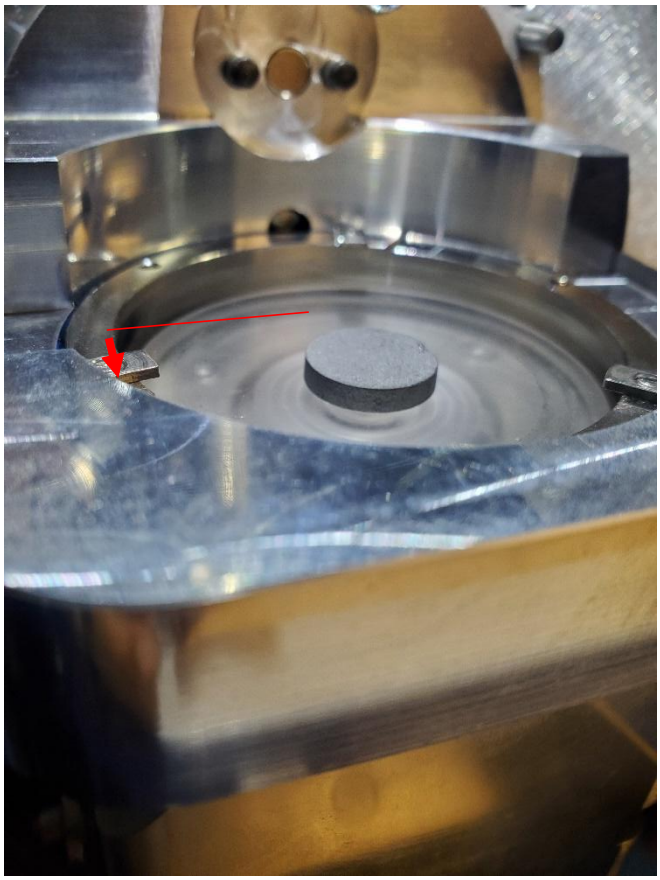

Figure 5. Sample height is going below the level in the machine during measurement. The required level is shown by a line while the unreached height is shown by the arrow. This position is wrong for the stage during measurement.

Figure 6. Adjustment of the sample height in the machine for alignment. The sample holder is lowered to align the sample surface (height) with the required surface or height as shown by red lines.

Conclusion

This study demonstrates the feasibility of using pelletized samples directly for X-ray diffraction (XRD) analysis as a quick and reliable method for phase purity determination in oxygen-deficient perovskite oxides. The XRD patterns of the pellet samples were consistent with those obtained from traditional powdered samples, confirming that the pellet method provides accurate structural information without the need for extensive sample preparation. By using pellets, researchers can save time, reduce sample wastage, and preserve the material's physical integrity for further characterization, such as electrical, magnetic, and catalytic property measurements. Additionally, adherence to proper pellet size and sample height adjustments during measurement ensures accurate diffraction data. This approach presents a practical alternative to powder XRD, offering significant advantages for researchers working with complex solid-state materials, particularly in situations where rapid phase purity confirmation is required.

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References

[1] Hona, R. K.; Huq, A.; Mulmi, S.; Ramezanipour, F., Transformation of Structure, Electrical Conductivity, and Magnetism in AA′Fe2O6−δ, A = Sr, Ca and A′ = Sr. *Inorg. Chem.* **2017,** *56* (16), 9716-9724.

[2] Zhang, Y.; Yao, Q.; Qian, J.; Zhao, X.; Li, D.; Mi, Q., Thermoelectric properties of all-inorganic perovskite $CsSnBr_3$: A combined experimental and theoretical study. *Chem. Phys. Lett.* **2020,** *754*, 137637.

[3] Yang, F.; Yang, X.; Su, K.; Lin, J.; He, Y.; Lin, Q., Structural and Magnetic Properties of Perovskite Functional Nanomaterials $La_{(1-x)}R_{(x)}FeO_{(3)}$ (R = Co, Al, Nd, Sm) Obtained Using Sol-Gel. *Molecules (Basel, Switzerland)* **2023,** *28* (15).

[4] Hona, R. K.; Karki, S. B.; Cao, T.; Mishra, R.; Sterbinsky, G. E.; Ramezanipour, F., Sustainable Oxide Electrocatalyst for Hydrogen- and Oxygen-Evolution Reactions. *ACS Catalysis* **2021,** *11* (23), 14605-14614.

[5] Hona, R. K.; Karki, S. B.; Ramezanipour, F., Oxide Electrocatalysts Based on Earth-Abundant Metals for Both Hydrogen- and Oxygen-Evolution Reactions. *ACS Sustainable Chemistry & Engineering* **2020,** *8* (31), 11549-11557.

[6] Hona, R. K.; Thapa, A. K.; Ramezanipour, F., An Anode Material for Lithium-Ion Batteries Based on Oxygen-Deficient Perovskite Sr2Fe2O6−δ. *ChemistrySelect* **2020,** *5* (19), 5706-5711.

[7] C.Larson, A.; Dreele, R. B. V., General Structure Analysis System (GSAS). *Los Alamos National Laboratory Report LAUR, 1994*, p. 86 - 748.

[8] Toby, B., EXPGUI, a graphical user interface for GSAS. *J. Appl. Crystallogr.* **2001,** *34* (2), 210-213.

[9] Mulmi, S.; Hona, R. K.; Jasinski, J. B.; Ramezanipour, F., Electrical conductivity of Sr2-xCaxFeMnO5 (x = 0, 1, 2). *J. Solid State Electrochem.* **2018,** *22* (8), 2329-2338.

[10] Hona, R. K.; Dhaliwal, G. S.; Thapa, R. Investigation of Grain, Grain Boundary, and Interface Contributions on the Impedance of Ca_2FeO_5 *Appl. Sci.* [Online], 2022.