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Critical Role of Wet Milling for the Synthesis of Single-Phase $Pr_2Ru_2O_7$ and Evaluation of Its Crystallite Size

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ABSTRACT

Pyrochlore oxides, such as $Pr_2Ru_2O_7$, have attracted a lot of interest due to their unique magnetic properties and possible applications in technology. However, conventional synthesis techniques are often complicated and expensive. In this work, the significant role of the wet milling method in synthesizing single-phase $Pr_2Ru_2O_7$ was evaluated together with the determination of the crystallite size. Two types of samples were synthesized: Sample-1 via manual hand grinding and Sample-2 using wet ball milling. X-ray diffraction (XRD) was used to characterize the structural properties of samples, followed by Rietveld refinement analysis. Furthermore, the crystallite size was estimated using the Debye–Scherrer equation. Sample-1 showed multiphase with 8.6% of RuO_2 as secondary phase, whereas Sample-2 exhibited a single-phase $Pr_2Ru_2O_7$ structure with space group Fd-3m. The crystallite size of Sample-2 was 36.50 ± 3.31 nm, comparable to that produced by more advanced synthesis techniques. From this result, wet ball milling significantly enhances phase purity and provides a feasible, low-cost alternative for synthesizing high-quality $Pr_2Ru_2O_7$ pyrochlore oxide.

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1. Introduction

Over the past few decades, pyrochlore compounds with the formula $A_2B_2O_7$, where *A* is a trivalent rare-earth ion and *B* is a tetravalent transition metal ion, have attracted attention due to their intriguing physical behaviors [1, 2]. In these systems, both *A* and *B* cations form interpenetrating networks of corner-sharing tetrahedra. The magnetic moments located at the corners of these tetrahedra can generate magnetic frustration, giving rise to a variety of emergent phenomena such as spin-glass states [3], spin-ice behavior [4], spin liquids [5], and metal-insulator transitions accompanied by magnetic ordering [6, 7]. Not only known for their unique magnetic properties, but pyrochlore oxides also hold significant potential for industrial applications, including as electrode materials, catalysts, and thick film resistors [8-10].

Pyrochlore oxides, especially Ru-based pyrochlores, were known as a candidate for electrocatalyst in the oxygen evolution reaction (OER) of hydrogen production [11]. They have been considered as a good candiate for electrocatalyst in OER reaction because they have good electronic conductivity, fast charge transfer through the oxygen vacancies, stable crystal structure, easy to tune down the composition, bond strength, and its electronic structure, as well as good durability in electrolyte solution [10-13]. One of the pyrochlore oxides that has attracted attention due to its excellent OER performance is $Pr_2Ru_2O_7$ [10]. This material is typically synthesized using some techniques, such as sol-gel assisted by amino acid as a chelating agent [10], hydrothermal synthesis [14], and conventional solid-state reaction [15].

Previous studies have shown that solid-state reactions combined with wet milling techniques can reduce particle size [16]. The reduction in particle size may increase the performace of the catalyst since it increases the active surface area that may enhance the electrocatalyst performance in OER reaction [17-19]. Besides that, this method offers several advantages over other methods, including: large-scale production, uniform sample, simplicity in production, and cost efficiency [11]. However, there have been no reported studies on the physical properties of $Pr_2Ru_2O_7$ synthesized through the wet milling method. Therefore, this study aims to investigate the importance of the wet milling technique in the synthesis of the pyrochlore oxide $Pr_2Ru_2O_7$ and to evaluate the crystallite size of the material obtained using this method, which is become the novelty of this work.

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2. Experimental Methods

The research method used in this research paper was an experimental method that consisted of the synthesis method of the material and the characterization procedure.

2.1 Synthesis Method

Polycrystalline $Pr_2Ru_2O_7$ was synthesized by using a solid-state reaction, where two solid reactants were involved in the chemical reaction through mechanical activation and requiring high temperatures. In the current study, two precursors used as raw materials were Pr_6O_{11} and RuO_2 powder from Furuuchi Chemical with a purity of 99.9%.

In this work, two batches of pyrochlore $Pr_2Ru_2O_7$ were synthesized by using two methods, one is the commonly used or traditional solid-state reaction, using a manual hand-grinding technique in the mixing process. Meanwhile, the second technique used for synthesizing the material is by engaging a wet-milling technique. Based on the previous study, the wet ball milling technique has been proven effective in reducing the particle size of Niobium (Nb) to the nanometer scale [16]. This work employed the wet milling method using ethanol to facilitate the mixing of powders and enhance the collision between the precursors with the milling container walls and the zirconium balls. Furthermore, the importance of using the wet-milling method with ethanol as a mixing enhancer in the synthesis of pyrochlore $Pr_2Ru_2O_7$ is also investigated in this study.

The chemical reaction involved in the formation of $Pr_2Ru_2O_7$ follows the reaction equation as follows:

$$Pr_6O_{11_{(s)}} + RuO_{2_{(s)}} \rightarrow 3Pr_2Ru_2O_{7_{(s)}} + O_{2_{(g)}}$$

Based on the chemical reaction above, the stoichiometric calculation of the mass of precursors can be determined by using equations (1) and (2) as follows:

$$m_{Pr_6O_{11}} = \frac{1}{3} \times \frac{m_{Pr_2Ru_2O_7}}{Mr_{Pr_2Ru_2O_7}} \times Mr_{Pr_6O_{11}} \quad (1)$$

$$m_{RuO_2} = \frac{6}{3} \times \frac{m_{Pr_2Ru_2O_7}}{Mr_{Pr_2Ru_2O_7}} \times Mr_{RuO_2} \quad (2)$$

The targeted sample $Pr_2Ru_2O_7$ was made with a total mass of 1.5 grams for each batch. Accordingly, the masses of Pr_6O_{11} and RuO_2 are 0.8578 g and 0.6705 g, respectively.

The flowchart of the $Pr_2Ru_2O_7$ sample preparation is shown in Fig. 1. The sample was prepared through the following detailed procedure.

(1) The precursor materials were weighed according to the previously calculated stoichiometric ratio;
(2) The weighed precursors were mixed and manually hand-grinded using a mortar and pestle for 1 hour to ensure homogeneity;
(3) The mixed powder was then transferred into a milling container along with zirconium balls of three different sizes, as shown in Fig. 2. These balls served

as milling media to enhance the collision surface area and improve the mixing efficiency;

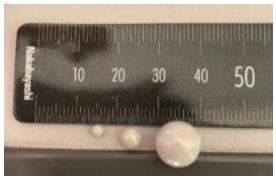

Figure 2. The different sizes of Zirconium balls used in the milling process

(4) Ethanol was added as a process-controlling agent to ensure thorough dispersion of the powder and to prevent any adhesion of the powder to the container walls or milling balls. The volume of ethanol was adjusted to fully submerge the powder and balls;

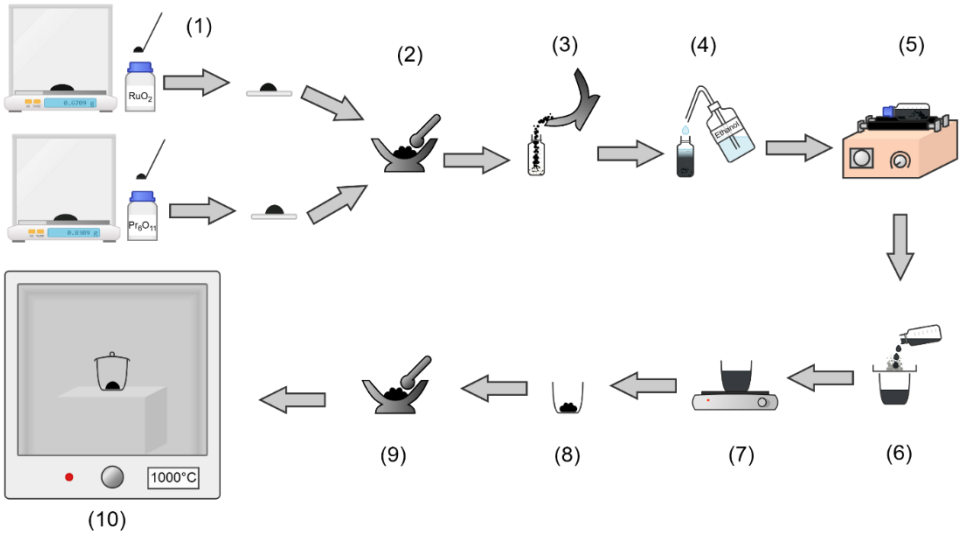

Figure 1. Synthesis method of $Pr_2Ru_2O_7$

(5) The mixture underwent wet ball milling for 12 hours;

(6) Following the milling process, the resulting slurry was transferred into a crucible, and a sieve was employed to separate the zirconium balls from the ethanol-containing sample;

(7) The ethanol was evaporated by heating the crucible on a hot plate at 150 °C until the sample was completely dry;

(8) The resulting dried powder was collected;

(9) A second manual hand-grinding step was performed using a mortar and pestle for 1 hour;

(10) The powder was then sintered at 1000 °C for 12 hours in a crucible to obtain the $Pr_2Ru_2O_7$ compound in powder form. A final manual grinding was carried out to ensure there was no agglomerated powder prior to further characterization.

For the first batch, the synthesis process only involved steps (1), (2), and (10), without

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undergoing the wet ball milling process, and the resulting sample was referred to as Sample-1. Meanwhile, the second batch sample was prepared by following all the synthesis procedures and was referred to as Sample-2.

2.2 Characterization

After obtaining Sample-1 and Sample-2, both samples were characterized using an X-ray diffractometer (XRD) to investigate their phases, crystal structures, and crystallite sizes. The XRD characterization was carried out at RIKEN, Japan, using a Rigaku MiniFlex 600 with a Cu X-ray source having a wavelength of 1.5406 Å.

The obtained XRD pattern data were then analyzed using the Rietveld refinement method with the GSAS-II software [20]. Furthermore, the XRD patterns were also analyzed to determine the crystallite size of the $Pr_2Ru_2O_7$ sample. The crystallite size was calculated using the Debye-Scherrer equation, as shown in Eq. (3) below [21].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Where D is the crystallite size, λ is the wavelength of the X-ray source, θ is the diffraction angle, K is a constant whose value depends on the crystal shape and width factors, and β is the full width at half maximum (FWHM) of the diffraction peak observed from the XRD pattern [21].

3. Results and Discussions

3.1. Rietveld refinement of XRD Pattern

The synthesis and XRD characterization of Sample-1 and Sample-2 have been carried out. The XRD pattern of Sample-1 and Sample-2 is shown in Fig. 3 and Fig. 4, respectively. Figure 3 shows that Sample-1 contains two phases, namely $Pr_2Ru_2O_7$ and RuO_2 phases. Although the percentage of the $Pr_2Ru_2O_7$ phase is higher than that of RuO_2, as shown by the peaks in the XRD pattern that are dominated by the peaks of the $Pr_2Ru_2O_7$ phase, additional peaks from RuO_2 are still clearly observable.

The RuO_2 phase is expected to originate from unreacted RuO_2 precursor and thus remain in the resulting compound. In contrast, the XRD pattern of Sample-2 shows no indication of an additional phase. This suggests that Sample-2 consists of a pure single-phase $Pr_2Ru_2O_7$.

These results highlight the importance of the wet ball milling process in synthesizing single-phase $Pr_2Ru_2O_7$. In Sample-1, the manual hand grinding technique resulted in a powder mixture with low homogeneity, as the grinding energy and contact surface could not be well controlled. On the other hand, Sample-2, which was synthesized using wet ball milling, received greater and more uniformly distributed energy through the zirconium balls and ethanol medium, leading to a more uniform molecular distribution.

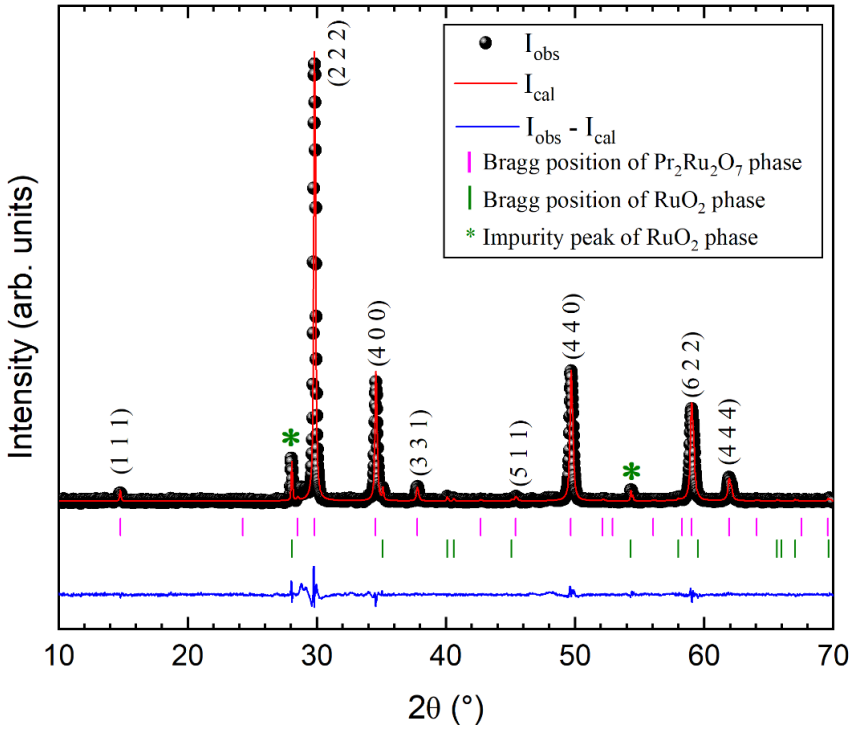

Figure 3. XRD pattern of Sample-1 synthesized with manual hand-grinding

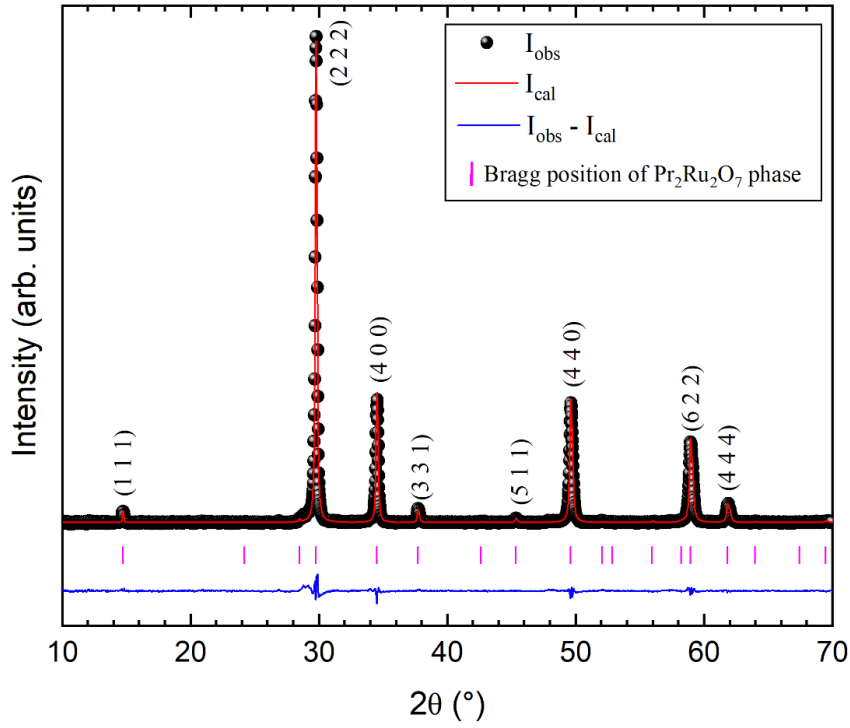

Figure 4. XRD pattern of Sample-2 synthesized with the wet ball milling method

This study further demonstrates the benefits of the wet ball milling technique. In addition to reducing particle size [16], wet ball milling also enhances the efficiency and effectiveness of pyrochlore oxide synthesis, leading to the formation of

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single-phase pyrochlore oxide material, $Pr_2Ru_2O_7$, in this work.

The XRD patterns were further analyzed using the Rietveld refinement method to extract detailed crystallographic information. In this study, the refinement was conducted using the crystallographic database for $Pr_2Ru_2O_7$ obtained from the Crystallographic Open Database (COD) with reference code 1531107 of $Ho_2Ru_2O_7$, which has a similar crystal structure and space group [22]. The Rietveld analysis provided key parameters related to the crystal structures, including the phase percentage, space group, crystal structure type, lattice parameter, unit cell volume, and also the reliability factors of refinement as summarized in Table 1.

Quantitative analysis revealed that the $Pr_2Ru_2O_7$ phase accounted for 91.4% of the Sample-1, significantly higher than the RuO_2 phase, which is only 8.6%. Furthermore, the Rietveld refinement confirmed that the synthesized $Pr_2Ru_2O_7$ possessed a cubic structure with a space group of Fd-3m. The lattice parameters of Sample-1 (10.3725 Å) and Sample-2 (10.3815 Å) showed no significant difference in the range of 10.35 – 10.38 Å, consistent with previous studies [10, 14, 23].

Table 1. Parameters obtained from the Rietveld refinement analysis of XRD pattern data for Sample-1 and Sample-2

	Sample-1 (Hand-grinding)	**Sample-2 (Wet-milling)**
Structure Parameters		
Phase of $Pr_2Ru_2O_7$	91.4% (8.6% is the RuO_2 phase)	100%
Space Group	Fd-3m	Fd-3m
Structure	Cubic	Cubic
Lattice parameter $a = b = c$ (Å)	10.3725 ±0.0002	10.3815 ±0.0002
V (Å^3)	1115.96 ±0.05	1118.87 ±0.04
Reliability Factors		
Rwp %	6.43	6.29
Goodness of Fit (GoF)	2.20	2.37

3.2. Evaluation of the Crystallite Size

A further analysis was performed on the XRD pattern of Sample-2 to determine the crystallite size of the $Pr_2Ru_2O_7$ phase. The crystallite size was calculated using the Debye-Scherrer equation, as shown in Eq. (3). In this study, the X-ray source has a wavelength of λ = 1.5406 Å, and the Scherrer constant was taken as K = 0.9 [21].

Based on the diffraction pattern displayed in Fig. 3 and Fig. 4, eight diffraction peaks were clearly observed, each with corresponding Miller indices

(hkl) and 2θ values summarized in Table 2. The FWHM of each observable diffraction peak is also listed in Table 2, initially expressed in degrees. Prior to calculation, the FWHM values were converted from degrees to radians. The crystallite size (*D*) was then determined for each of the diffraction peaks.

Table 2. Calculation of Crystallite Size of Sample-2 using the Debye-Scherrer Method

Miller Indices (hkl)	**2θ (°)**	**FWHM (°)**	**D (nm)**
111	14.745	0.153	52.36
222	29.780	0.182	45.17
400	34.520	0.228	36.49
331	37.746	0.229	36.66
511	45.361	0.217	39.68
440	49.650	0.288	30.39
622	58.991	0.343	26.61
444	61.894	0.376	24.64

Therefore, based on those calculations, the average crystallite size from Sample-2 can be determined, yielding a value of D = 36.50 ± 3.31 nm.

The crystallite size obtained in this study is similar to the value reported by Pawar et al., which is approximately 31.38 [23]. The wet ball milling method employed in this work produced a slightly larger crystallite size compared to the co-precipitation technique. Nevertheless, wet ball milling presents a promising alternative for synthesizing $Pr_2Ru_2O_7$ pyrochlore oxide due to its simpler procedures and lower cost compared to sol-gel and co-precipitation methods. While the current work demonstrated the feasibility of the wet milling method, the influence of milling duration has not yet been explored. Further investigation is necessary to evaluate how variations in milling time affect both the crystallite size and particle size of the resulting material.

4. Conclusion

$Pr_2Ru_2O_7$ samples were synthesized by the solid-state reaction method. Two different techniques were employed to produce Sample-1 and Sample-2. Sample-1 was made with the traditional solid-state method using manual hand grinding, whereas Sample-2 was made by involving the wet milling technique. The XRD patterns showed that Sample-2 has 100% $Pr_2Ru_2O_7$ phase, proving the critical role of the wet milling process in the production of single-phase $Pr_2Ru_2O_7$. Moreover, the crystallite size of Sample-2 is in the nanometer scale and gives a value of D = 36.50 ± 3.31 nm, similar to that obtained using other synthesis methods. The results support the potential of wet milling as a favorable synthesis method for $Pr_2Ru_2O_7$ pyrochlore oxide, attributed to its simplicity and lower processing costs.

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6. References

1. Gardner, J. S., Gingras, M. J. P., & Greedan, J. E. (2010). Magnetic pyrochlore oxides. *Reviews of Modern Physics*, *82*, 53-107.
2. Ku, S. T., Kumar, D., Lees, M. R., Lee, W. T., Aldus, R., Studer, A., Imperia, P., Asai, S., Masuda, T., Chen, S. W., Chen, J. M., & Chang, L. J. (2018). Low temperature magnetic properties of $Nd_2Ru_2O_7$. *Journal of Physics: Condensed Matter*, *30*(15), 155601.
3. Park, J. G., Jo, Y., Park, J., Kim, H. C., Ri, H. C., Xu, S., Moritomo, Y., & Cheong, S. W. (2003). Electrical and magnetic properties of $R_2Mo_2O_7$ (R= Nd, Sm, Gd and Dy). *Physica B: Condensed Matter*, *328*(1-2), 90-94.
4. Harris, M. J., Bramwell, S. T., McMorrow, D. F., Zeiske, T. H., & Godfrey, K. W. (1997). Geometrical frustration in the ferromagnetic pyrochlore $Ho_2Ti_2O_7$. *Physical Review Letters*, *79*(13), 2554-2557.
5. Nakatsuji, S., Machida, Y., Maeno, Y., Tayama, T., Sakakibara, T., Duijn, J. V., Balicas, L., Millican, J. N., MacAluso, R. T., & Chan, J. Y. (2006). Metallic spin-liquid behavior of the geometrically frustrated Kondo lattice $Pr_2Ir_2O_7$. *Physical Review Letters*, *96*(8), 087204.
6. Matsuhira, K., Wakeshima, M., Hinatsu, Y., & Takagi, S. (2011). Metal–insulator transitions in pyrochlore oxides $Ln_2Ir_2O_7$. *Journal of the Physical Society of Japan*, *80*(9), 094701.
7. Asih, R., Adam, N., Mohd-Tajudin, S. S., Sari, D. P., Matsuhira, K., Guo, H., Wakeshima, M., Hinatsu, Y., Nakano, T., Nozue, Y., Sulaiman, S., Mohamed-Ibrahim, M. I., Biswas, P. K., & Watanabe, I. (2017). Magnetic moments and ordered states in pyrochlore iridates $Nd_2Ir_2O_7$ and $Sm_2Ir_2O_7$ studied by Muon-spin relaxation. *Journal of the Physical Society of Japan*, *86*(2), 024705.

8. Lee, K. S., Seo, D. K., & Whangbo, M. H. (1997). Structural and Electronic Factors Governing the Metallic and Nonmetallic Properties of the Pyrochlores $A_2Ru_2O_{7-y}$. *Journal of Solid State Chemistry*, *131*, 405-408.
9. Horowitz, H. S., Longo, J. M., Horowitz, H. H., & Lewandowski, J. T. (1985). The synthesis and electrocatalytic properties of nonstoichiometric Ruthenate pyrochlores. *ACS Symposium Series: Solid State Chemistry in Catalysis*, *279*, 143-163.
10. Matsumoto, A., Cai, Z. X., & Fujita, T. (2022). Synthesis of pyrochlore oxides containing Ir and Ru for efficient oxygen evolution reaction. *Materials*, *15*(17), 6107.
11. Widyaiswari, U., Putri, G. N., & Risdiana. (2025). Ru-based pyrochlore oxide as a candidate for electrocatalyst in hydrogen production: A systematic literature review. *International Journal of Hydrogen Energy*, *106*, 444-453.
12. Kim, M., Jinho, P., Kang, M., Kim, J. Y., & Lee, S. W. (2020). Toward efficient electrocatalytic oxygen evolution: Emerging opportunities with metallic pyrochlore oxides for electrocatalysts and conductive supports. *ACS Central Science*, *6*(6), 880-891.
13. Galyamin, D., Torrero, J., Rodriguez, I., Kolb, M. J., Ferrer, P., Pascual, L., Salam, M. A., Gianolio, D., Celorrio, V., Mokhtar, M., Sanchez, D. G., Gago, A. S., Friedrich, K. A., Pena, M. A., Alonso, J. A., Calle-Vallejo, F., Retuerto, M., & Rojas, S. (2023). Active and durable R2MnRuO7 pyrochlores with low Ru content for acidic oxygen evolution. *Nature Communications*, *14*(2010), 1-12.
14. Yao, L., Wang, D., Peng, W., Hu, W., Yuan, H., & Feng, S. (2011). Hydrothermal synthesis and characterization of rare-earth ruthenate pyrochlore compounds $R_2Ru_2O_7$ (R = Pr3+, Sm3+, Ho 3+). *Science China Chemistry*, *54*, 941-946.
15. Tachibana, M., Kohama, Y., Atake, T., & Takayama-Muromachi, E. (2007). Heat capacity of pyrochlore $Pr_2Ru_2O_7$. *Journal of Applied Physics*, *101*(9).
16. Eze, A. A., Sadiku, E. R., Kupolati, W. K., Snyman, J., Ndambuki, J. M., Jamiru, T., Durowoju, M. O., Ibrahim, I. D., Shongwe, M. B., & Desai, D. A. (2021). Wet ball milling of niobium by using ethanol, determination of the crystallite size

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e- ISSN 2549-1989

and microstructures. *Scientific Reports*, *11*(1), 22422.

17. Rao, R. R., Bucci, A., Corby, S., Moss, B., Liang, C., Gopakumar, A., Stephens, I. E. L., Lloret-Fillol, J., & Durrant, R. (2024). Unravelling the role of particle size and nanostructuring on the oxygen evolution activity of Fe-doped NiO. *ACS Catalysis*, *14*(15), 11389-11399.
18. Yu, J., He, Q., Yang, G., Zhou, W., Shao, Z., & Ni, M. (2019). Recent advances and prospective in Ruthenium-based materials for electrochemical water splitting. *ACS Catalysis*, *9*(11), 9973-10011.
19. Abbott, D. F., Pittkowski, R., Macounova, K. M., Nebel, R., Marelli, E., Fabbri, E., Castelli, I. E., Krtil, P., & Schmidt, T. J. (2019). Design and synthesis of Ir/Ru pyrochlore catalysts for the oxygen evolution reaction based on their bulk thermodynamic properties. *ACS Applied Materials & Interfaces*, *11*(41), 37748-37760.
20. Toby, B. H., & Von Dreele, R. B. (2013). GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography*, *46*(2), 544-549.
21. Holzwarth, U., & Gibson, N. (2011). The Scherrer equation versus the 'Debye-Scherrer equation'. *Nature Nanotechnology*, *6*(9), 534.
22. Bansal, C., Kawanaka, H., Bando, H., & Nishihara, Y. (2002). Structure and magnetic properties of the pyrochlore $Ho_2Ru_2O_7$: A possible dipolar spin ice system. *Physical Review B*, *66*(5), 052406.
23. Pawar, R. A., Nikumbh, A. K., Bhange, D. S., Karale, N. J., Nighot, D. V., & Khanvilkar, M. B. (2017). Chemical synthesis and characterization of nano-sized rare-earth ruthenium pyrochlore compounds $Ln_2Ru_2O_7$ (Ln = rare earth). *Bulletin of Materials Science*, *40*(7), 1335-1345.