



---

## Synthesis and study the physical properties of perovskite $(\text{Sr}_{2-x}/\text{Gd}_x)(\text{Co}_{1-y}/\text{Cu}_y)\text{O}_4$ that belongs to the series RUDDLESDEN-POPPER ( RP)

Dr. Ahmed Kelzyeh<sup>1</sup>, Dr. Manar Hassan<sup>2</sup>, Ola Ameer Alkhoja<sup>3</sup>

<sup>1</sup>Prof; Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria

<sup>2</sup>Lecturer; Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria

<sup>3</sup>Postgraduate Student (Master Degree), Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria

**Abstract** The search for the possibility of oxides possessing distinctive properties of superconductivity, ionic conductivity, and many insulating properties of great importance in microelectronics, wired and wireless communications is increasing. One of the most important of these oxides is perovskite oxides and compounds derived from layered perovskite structure called the Ruddlesden and Popper series.

New oxides from the Ruddlesden and Popper series  $(\text{A}_{n+1} \text{B}_n \text{O}_{3n+1})$  were synthesized, prepared using the ceramic and sol-gel methods. The physical properties of these oxides and the effect of partial cobalt substitution in the crystalline network with the copper transition element were studied and, at the same time, the partial substitution of strontium with gadolinium (a rare earth element) was studied.

The results of X-ray diffraction shows that the prepared oxides crystallize according to the tetragonal crystalline structure within the  $I4/mmm$  space group at  $n = 1$ , a decrease of the lattice constants  $a$  and  $b$ , an increase in  $c$ , and thus an increase in cell unit size when partial substitution of cobalt with copper and strontium with gadolinium where the oxygen atoms are settled in the vacant sites when moving from 2+ oxidation states of Strontium to 3+ oxidation states of Gadolinium and when adding the copper element, the resistance decreased, the conductivity increased, and this is due to the movement of oxygen. In contrast, the resistance increased clearly, and the conductivity decreased when the element Gadolinium was introduced due to the movement of the electrons.

**Keywords** perovskite; Ruddlesden-Popper; Solid-oxide fuel cells; conductivity; X-ray diffraction

---

### Introduction

The global demand for alternative, renewable and environmentally friendly energy sources is increasing, and one of the most important of these sources is the Solid Oxide Fuel Cells (SOFC). Stored in hydrogen in the form of electrical energy, so it is one of the modern technologies for direct generation of electric energy with high efficiency.

Attention is now turning to lower operating temperatures by vaccinating electrolytes with specific compounds that play an important role in new industries and research [1], as their physical properties vary from superconductivity, magnetic properties, and insulating properties. In addition, the elevator material is developed within the cell to give higher efficiency. [2]

There is growing search for the possibility of oxides possessing distinctive properties of superconductivity [3], ionic conductivity, and many insulating properties [4] of great importance in microelectronics and telecommunications [5]. Perovskite oxides are one of the most important oxides that attract a lot of attention due to The great variety in physical phenomena that it manifests as a solid object. Perovskite compounds have several important industrial applications in the field of renewable energies as they are used in electrical applications such as the photoelectric treatment of water to produce hydrogen [6], Also, they are the main component of solid oxide cells that use hydrogen to produce electricity, which recently has found an important application in electric car batteries.

The preparation of several cobalt oxides with a new crystalline structure belonging to the perovskite family leads to magnetic and electronic states by controlling the oxygen content giving important applications used in solid fuel cells [7]

### Perovskite structure

The term Perovskite is used to describe a class of compounds that share the same general formula for  $\text{CaTiO}_3$  [8].

The perovskite structure takes the general formula  $\text{ABO}_3$  where: A: Cations are located in the cell heads, which are mono-, di- or triple-oxidant elements. B positively charged metal ions are located in the center of the cell, and they are triple, quad or five oxidation elements.

O negative non-metallic ions Anions. The oxygen is often located in the center of the faces [9].

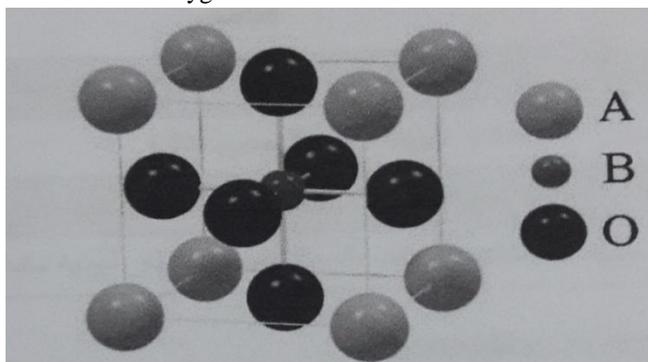


Figure 1: The cell unit of the  $\text{ABO}_3$  perovskite system [10]

There are compounds derived from the perovskite structure called the Ruddlesden and Popper series. Their general formula  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  has a lamellar structure that separates the plates from one another with layers of structure similar to the NaCl structure.

A and B are cations and n: denotes the number of separating layers  $n = 1, 2, 3$  [11].

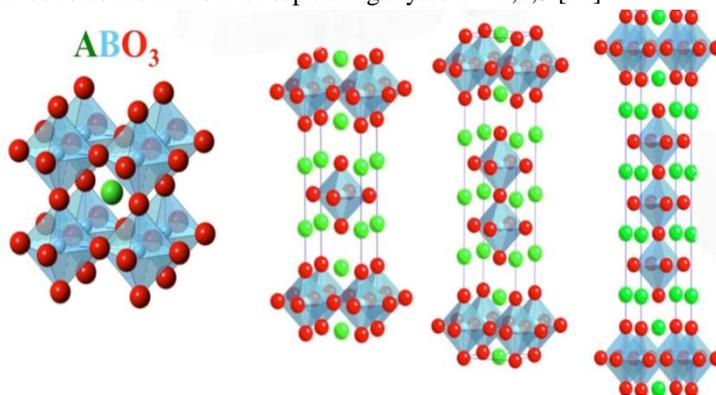


Figure 2: The structure of Ruddlesden and Popper for  $n = 1, 2, 3$  [12]

The structure of the compounds belonging to the Ruddlesden and Popper series was reached when  $n = 1$  for  $\text{K}_2\text{NiF}_4$  [13] and  $n = 2$  for  $\text{Sr}_3\text{Ti}_2\text{O}_7$  [14] and  $n = 3$  for  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ . [15].

### Materials and Methods



## Experimental

### Ceramic method

The solid state route is a method of synthesis at high temperatures (1000 °C), which consists of mixing oxides or other salts of the metals involved by grinding, followed by heat treatments necessary to give rise to diffusion to obtain the final compound. Because the mixture is produced on a macroscopic scale, very high temperatures and heating times allow the diffusion of chemical elements during the reaction process.

The advantage of this method is its extreme simplicity, and its use is essential for preparing new mixed oxides, such as perovskites with special morphologies, like monocrystals or thin layers.

The choice of reagents has been as follows; in the case of alkaline earths (strontium), the starting compounds chosen are carbonates. While in the case

transition metals and rare earths, they are based on their most stable oxides. All the reagents used are of high purity (99.99%). The reagents are mixed and homogenized by hand in an agate mortar. After that, we perform an initial heating process in the incineration furnace for two hours on the degree of 100 °C - 105 °C in order to get rid of moisture water, and then continue the process of heating by increasing temperature 50 °C gradually until reaching the degree of 700 °C.

The mixture is compacted (in pill form), to favor contact between reagents, therefore, nucleation of the product and the diffusion of ions during synthesis. Then we continue the heating process by installing the temperature at 700 degrees Celsius for two hours and increasing the temperature gradually to reach 1000 °C. Finally, we set the temperature to 1000° C for 32 hours.

### Sol-gel flash Method

Among these methods we find the wet synthesis. It allows us to obtain precursors of homogeneous composition at the atomic level and works at very high temperatures. Which are low compared to those used by the ceramic method.

This method is characterized by the fact that in some stages, the precursors are found in gel state. Which is the starting point for many material processing polycrystalline ceramics. For the preparation of the samples, starting materials Sr(NO<sub>3</sub>)<sub>2</sub> have been used Gd<sub>2</sub>O<sub>3</sub> (99%), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%), Cu(NO<sub>3</sub>)<sub>2</sub>·2/1/2H<sub>2</sub>O (99%) and Citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (99.5%) in addition to the concentrated NH<sub>3</sub> to adjust the pH to the appropriate values. Stoichiometric amounts of nitrates are weighed and taken to 250 mL beaker, and dissolved in 100 mL of distilled water to obtain a homogeneous solution of the desired cations (sol), given a pink hue in most cases. The solution is heated at medium temperatures on a heating plate (90 °C), and a tablespoon of citric acid (~ 1g) (organic gel base) is added. When reaching boiling degree, it dissolves by stirring, keeping the temperature at 90 °C. As the solvent evaporates, the solution becomes more viscous until it forms a gel that is taken to the oven at 100 °C to completely evaporate the solvent. The Mass obtained is ground in a mortar to obtain a fine powder. The fine powder that is pre-calcined at 250 °C in a muffle type oven to dissolve nitrates and reach the stage of complete drought. Then a flash appears, as this flash is the flash point of Citric Acid, so that we can eliminate matter organic completely, and form metallic precursors. This precursor is then calcined at high temperatures up to 930 °C in order to obtain a black powder in most cases.

## Results and Discussion

### 1. Ceramic method

#### 1.1. Preparing the studied samples

The following compounds were prepared: Sr<sub>2</sub>CoO<sub>4</sub>, Sr<sub>1</sub>Gd<sub>1</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub>O<sub>4</sub>, Sr<sub>2</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub>O<sub>4</sub>

using ceramic method. The following table shows the processing time of the previous samples thermally, and the temperatures for each of the stages obtained.



**Table1:** Conditions for preparing compounds  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ 

Temperature (°C)	Time
100/105	2 hours
700	2 hours
1000	32hours

1.2: The results of the study show, through X-ray diffraction schemes (Figure 3) for each compound that these compounds crystallize according to the quaternary structure (I4 / mmm Tetragonal) compared to the prepared compounds  $\text{NdSrCo}_{1-x}\text{Cu}_x\text{O}_{4-y}$  [16],  $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$  [17], (Hg, Cr)  $\text{Sr}_2\text{CuO}_4$  [18] that crystallize according to the same structure but with different dimensions.

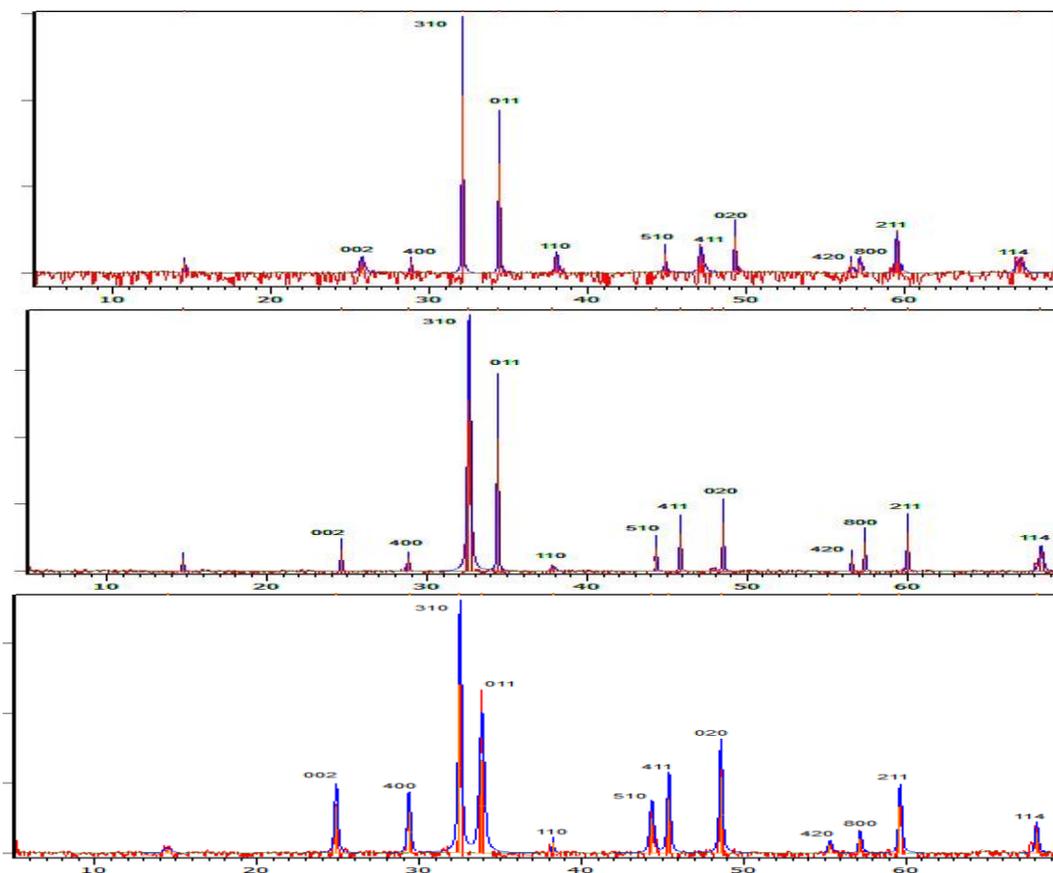


Figure 3: XRD spectrum for compounds  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$

## 2- Sol-gel Flash method

### 2.1. Preparing the studied samples

The following compounds were prepared:  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$  in Sol-gel method. The following table shows the processing time of the previous samples thermally, and the temperatures for each of the stages obtained.

**Table 2:** Conditions for preparing compounds  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ 

Temperature (°C)	Time
90	2 hours
100	8 hours
250	2 hours
930	32 hours



2.2. The results of the study show, through X-ray diffraction schemes (Figure 4) for each compound that these compounds crystallize according to the quaternary structure (I4 / mmm Tetragonal).

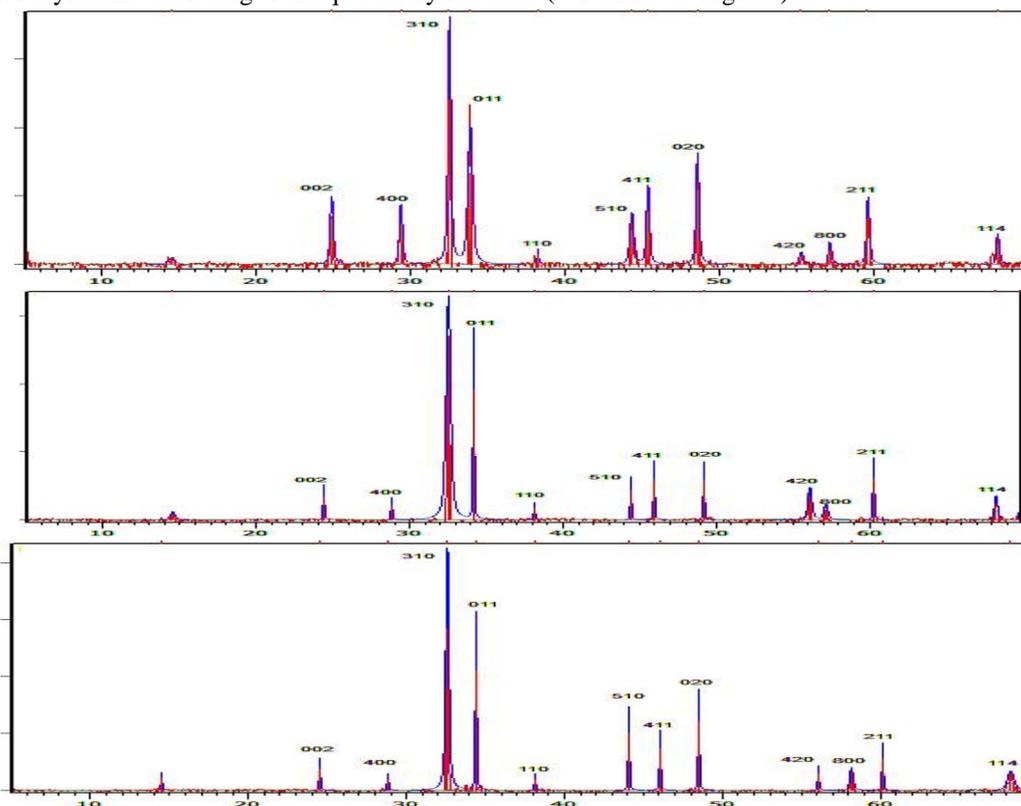


Figure 4: XRD spectrum for compounds  $Sr_2CoO_4$ ,  $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$ ,  $Sr_2Co_{0.75}Cu_{0.25}O_4$

And the table (3) shows the mathematical results of the structural study with both the ceramic and sol-gel methods of compounds:  $Sr_2CoO_4$ ,  $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$ ,  $Sr_2Co_{0.75}Cu_{0.25}O_4$ .

**Table 3:** The mathematical results of the structural study with both the ceramic and sol-gel methods of compounds:

	$Sr_2CoO_4$ , $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$ , $Sr_2Co_{0.75}Cu_{0.25}O_4$		
Samples	$Sr_2CoO_4$	$Sr_2Co_{0.75}Cu_{0.25}O_4$	$Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$
a(Å)	3.8572	3.7907	3.7720
b(Å)	3.8572	3.7907	3.7720
c(Å)	12.1935	12.4112	12.5321
$\alpha$	90	90	90
$\beta$	90	90	90
$\gamma$	90	90	90
V(Å <sup>3</sup> )	175.41	177.94	179.85

The table above shows:

1-When the partial substitution of cobalt with copper is replaced, we notice a decrease in the primary cell parameters (a, b) and an increase in c influence dby Jhan-Teller Effect, and its transformation into deformed octahedral toward c. Therefore, the volume increases. Because the deformation process may cause compression slightly, we notice a decrease (a , b). The structure, in this case, may be considered to have a quadrilateral support of a flat square [19].

2- When partial substitution of the strontium with gadolinium and, at the same time, partial substitution of cobalt with copper, we notice a decrease in the primary cell parameters (a,b), and an increase in c. This is due to Jhan-Teller Effect. In addition, when moving from the oxidation number +2 of the strontium to the +3 of Gadolinium, there will be voids where the oxygen atoms enter. This case is called Interstitial spaces that will increase the volume, compared with reference compounds  $GdSrFeO_4$ [20],  $NdSrCo_{1-x}Cu_xO_{4-y}$  [16].



3- As for granular size: We notice that there is no clear difference between the ceramic and sol-gel methods, because the thermal treatments are the same in both methods.

Also, the physical properties of these compounds  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$  were studied. Resistivity Electric and Conductivity Electric are measured using a device of four probes.

**Table 4:** Conductivity values and electrical resistance of compounds  $\text{Sr}_2\text{CoO}_4$ ,  $\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$ ,  $\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$

Samples	Resistivity Electric ( $\Omega/\text{cm}$ )	Conductivity Electric (s/cm)
$\text{Sr}_2\text{CoO}_4$	899	0.0011
$\text{Sr}_2\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$	624	0.0016
$\text{Sr}_1\text{Gd}_1\text{Co}_{0.75}\text{Cu}_{0.25}\text{O}_4$	3497	0.00029

We note from the previous table a decrease in the value of resistance and an increase in the conductivity when the copper element is added. The reason for this is due to the function of new electrons that are resulted from copper, specifically the electron coming from the orbit of  $dx^2-y^2$ . When a fission occurs, it rises from the symmetric orbitals and approaches the transport orbits, so that conductivity increases and the resistance decreases. That is, the movement of inter-oxygen in the NaCl layer is greater than the movement of vacant places in the perovskite layer. This leads to an increase in the electrical conductivity.

As for the adding of  $\text{Gd}^{3+}$  in addition to the copper, which was added previously, we clearly note an increase in resistance, and a decrease in conductivity. The reason is due to the fact that Gd has oxidation number 3+ that will need a larger charge leading to voids being filled with all free electrons. This leads to the absence of free electrons. Consequently, the resistance becomes very high. The conductivity decreases, meaning that the increase in resistance is due to the movement of electrons.

## Conclusions

- When partial replacement of cobalt copper we notice a reduction of the initial cell parameters (a, b) and an increase in c. As a result, the size increases due to Jean Teller effect.
- When performing partial substitution of strontium with gadolinium and, at the same time, partial substitution of cobalt with copper we notice a decrease in the primary cell parameters (a, b) and an increase in c. Consequently, the volume increases due to Jan Tiller Effect.
- The increase in volume, when partial substitution of the strontium with Gadolinium, is due to the entry of oxygen in the vacant sites of the primary level of Octahedral.
- There is no clear difference between the ceramic methods and the sol-gel. This is due to the fact that the heat treatments are the same in both methods.
- When adding the copper element, the resistance decreases, while the conductivity increases, due to the movement of oxygen. In contrast, the resistance increases clearly, and the conductivity decreases when the element Gadolinium is added due to the movement of the electrons.

## Recommendations

- It is possible to conduct a cobalt Mossbauer that determines the oxidation degrees of cobalt at site B in addition to magnetic and electrical properties.
- It is possible to scan by means of a SEM scanning electron microscope to confirm the structure and give information about the sample and its properties such as surface, surface topography and cupin.

## Acknowledgements

I would like express my sincere gratitude to my supervisor Dr. Ahmed Kelzyeh, and Dr. Manar Hassan, Department of Chemistry, Tishreen University, Syria, for stimulating my interest in study the physical properties of perovskite and for the fruitful discussions.



## References

- [1]. Lee, K. T., & Manthiram, A. (2006).  $\text{LaSr}_3\text{Fe}_{3-y}\text{Co}_y\text{O}_{10-\delta}$  ( $0 \leq y \leq 1.5$ ) Intergrowth Oxide Cathodes for Intermediate Temperature Solid Oxide Fuel Cells. *Chemistry of materials*, 18(6), 1621-1626.
- [2]. Lightsey, P. A. (1973). Percolation View of Transport Properties in  $\text{Na}_x\text{WO}_3$ . *Physical Review B*, 8(8), 3586.
- [3]. Mitra, C., Fishman, R. S., Okamoto, S., Lee, H. N., & Reboredo, F. A. (2013). Ground-state and spin-wave dynamics in Brownmillerite  $\text{SrCoO}_2$ . 5—a combined hybrid functional and LSDA+ U study. *Journal of Physics: Condensed Matter*, 26(3), 036004.
- [4]. Demont, A., Hébert, S., Pelloquin, D., & Maignan, A. (2008). The  $\text{Sr}_{2.75}\text{Ce}_{0.5}\text{Co}_2\text{O}_{7-\delta}$  oxide, n= 2 member of the Ruddlesden–Popper series: Structural and magnetic evolution depending on oxygen stoichiometry. *Journal of Solid State Chemistry*, 181(6), 1314-1320.
- [5]. Kulkarni, A., Ciacchi, F. T., Giddey, S., Munnings, C., Badwal, S. P. S., Kimpton, J. A., & Fini, D. (2012). Mixed ionic electronic conducting perovskite anode for direct carbon fuel cells. *International journal of hydrogen energy*, 37(24), 19092-19102.
- [6]. Kraut, E. A., Wolfram, T., & Hall, W. (1972). Electrostatic potentials for semi-infinite and lamellar cubic lattices containing several different kinds of ions per unit cell. *Physical Review B*, 6(4), 1499.
- [7]. Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta crystallographica section A: crystal physics, diffraction, theoretical and general crystallography*, 32(5), 751-767.
- [8]. Parija, B. (2012). Study of Structural, Electrical and Optical Properties of Lead-Free  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  Based Ceramic Systems (Doctoral dissertation).
- [9]. Venkatachalam, V. (2011). Microwave assisted processing of Nanocrystalline Barium Titanate based capacitor devices (Doctoral dissertation, Loughborough University).
- [10]. Borowski, M. (2010). Perovskites: structure, properties, and uses. Nova Science Publishers.
- [11]. Matvejeff, M. (2007). Synthesis and characterization of some Ruddlesden-Popper and spinel type oxides. Helsinki University of Technology.
- [12]. Seppänen, M., & MH, T. (1976). On the Compound  $\text{La}_4\text{CO}_3\text{O}_{10}$ . *Acta Chem. Scand., A; Danem.; DA.* 1976; Vol. 30; No 5; pp. 389-390
- [13]. Plieth, K., & Balz, D. (1954, January). \* Die Struktur Des Kaliumnickel-Fluorids,  $\text{K}_2\text{NiF}_4$ . In *Acta crystallographica* (Vol. 7, No. 10, pp. 637-637). 35 Norre Sogade, PO Box 2148, DK-1016 Copenhagen, Denmark: Munksgaard Int Publ Ltd.
- [14]. Ruddlesden, S. N., & Popper, P. (1958). The compound  $\text{Sr}_3\text{Ti}_2\text{O}_7$  and its structure. *Acta Crystallographica*, 11(1), 54-55.
- [15]. Ruddlesden, S. N., & Popper, P. (1957). New compounds of the  $\text{K}_2\text{NiF}_4$  type. *Acta Crystallographica*, 10(8), 538-539.
- [16]. Grandjean, D., & Weller, M. T. (1993). Structure and oxygen stoichiometry in complex neodymium strontium cobalt copper oxides:  $[\text{NdSrCo}_{1-x}\text{Cu}_x\text{O}_{4-y}]$ . *Materials research bulletin*, 28(7), 685-692.
- [17]. Amow, G., Davidson, I. J., & Skinner, S. J. (2006). A comparative study of the Ruddlesden-Popper series,  $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$  (n= 1, 2 and 3), for solid-oxide fuel-cell cathode applications. *Solid State Ionics*, 177(13-14), 1205-1210.
- [18]. Balamurugan, S., Gopalakrishnan, I. K., Yakhmi, J. V., & Selvam, P. (2001). Magnetization study of (Hg, Cr)  $\text{Sr}_2\text{CuO}_{4+\delta}$  superconductor. *Journal of superconductivity*, 14(4), 519-523.
- [19]. Mitchell, R. H. (2002). Perovskites: modern and ancient (Vol. 7). Thunder Bay: Almaz Press.
- [20]. Singh, S., & Singh, D. (2017). Effect of increasing Sr content on structural and physical properties of  $\text{K}_2\text{NiF}_4$ -type phase  $\text{GdSrFeO}_4$ . *Ceramics International*, 43(3), 3369-3376.

