Journal of Computer Engineering
ISSN 10003428

Original Research Article
Vol 11, Issue 9, 2022 | ISSN: 1000-3428

Synthesis and Investigation of Physical Properties in Ruddlesden-Popper Perovskite Compounds

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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 ($A_{n+1} B_n O_{3n+1}$) 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 andw hen 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.

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

How to cite: Dr. Yara Almuhanna, Dr. Omar Alkhateeb, Fatima Alsaleh (2022). Synthesis and Investigation of Physical Properties in Ruddlesden-Popper Perovskite Compounds. Journal of Computer Engineering, 11(9), 53–57. DOI: https://doi.org/10.5281/zenodo.19346131

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 $CaTiO_3$ [8]. The perovskite structure takes the general formula 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].

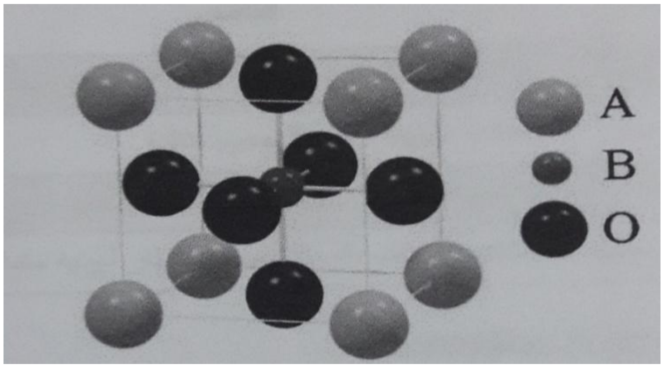

Figure 1: The cell unit of the ABO_3 perovskite system [10]

There are compounds derived from the perovskite structure called the Ruddlesden and Popper series. Their general formula $A_{n+1} B_n O_{3n+1}$ 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].

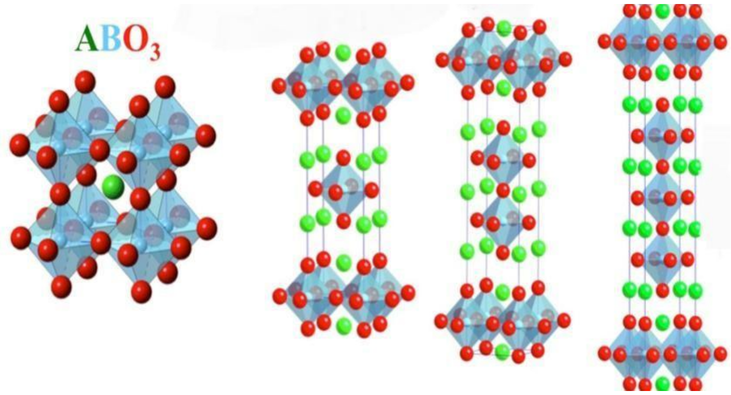

Figure 2: The structure of Ruddelsden and Popper for n = 1,2,3 [12]

The structure of the compounds belonging to the Ruddlesden and Popper series was reached when n = 1 for k_2NiF_4

[13] and n = 2 for $Sr_3Ti_2O_7$ [14] and n = 3 for $Sr_4Ti_3O_{10}$. [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 $Sr(NO_3)_2$ have been used Gd_2O_3 (99%), $Co(NO_3)_2.6H_2O$ (99%), $Cu(NO_3)_2.2/\frac{1}{2}H_2O$ (99%) and Citric acid $C_6H_8O_7$ (99.5%) in addition to the concentrated NH_3toadjust 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_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$ 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 Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$

Temperature (C)	**Time**
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 $NdSrCo_{1-x}\ Cu_x\ O_{4-Y}$ [16], $La_{n+1}Ni_nO_{3n+1}$ [17], (Hg, Cr) Sr_2CuO_4 [18] that crystallize according to the same structure but with different dimensions.

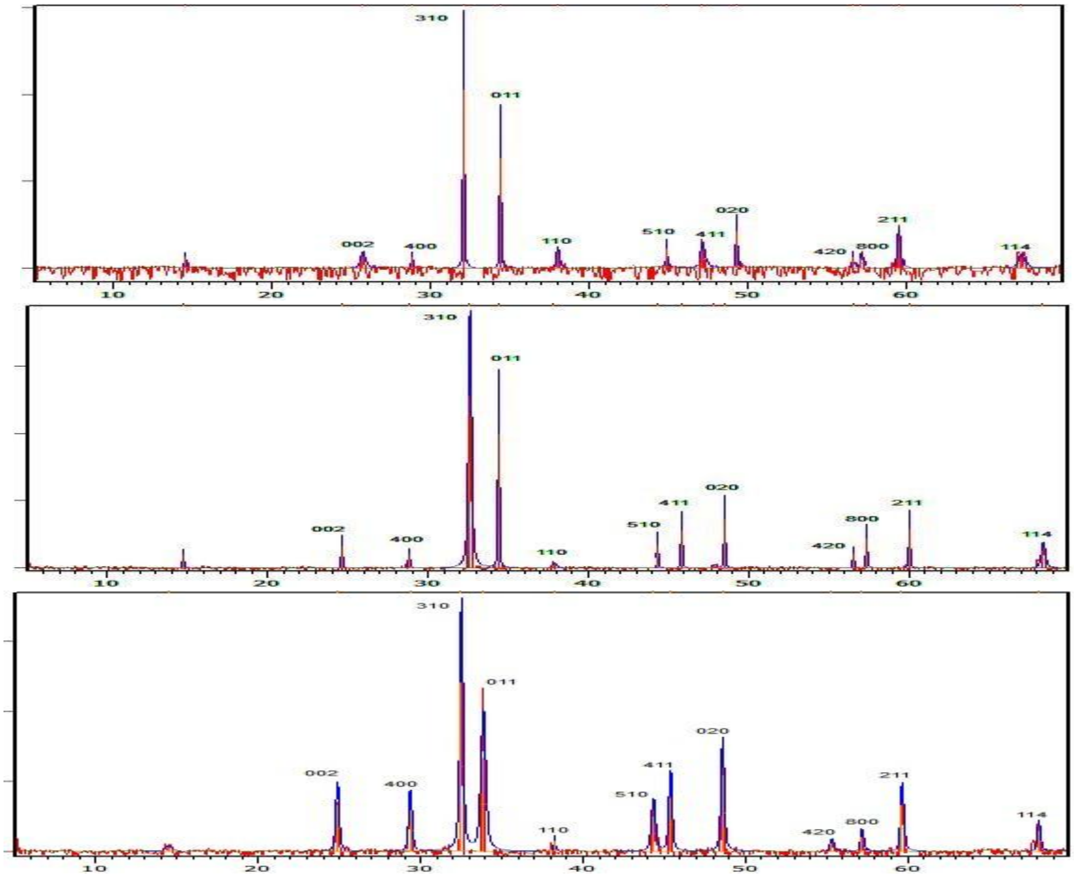

Figure 3: XRD spectrum for compounds Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$

2- Sol-gel Flash method

2.1. Preparing the studied samples

The following compounds were prepared: Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$ 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 Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$

Temperature (C)	**Time**
100	8 hours
250	2 hours
	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).

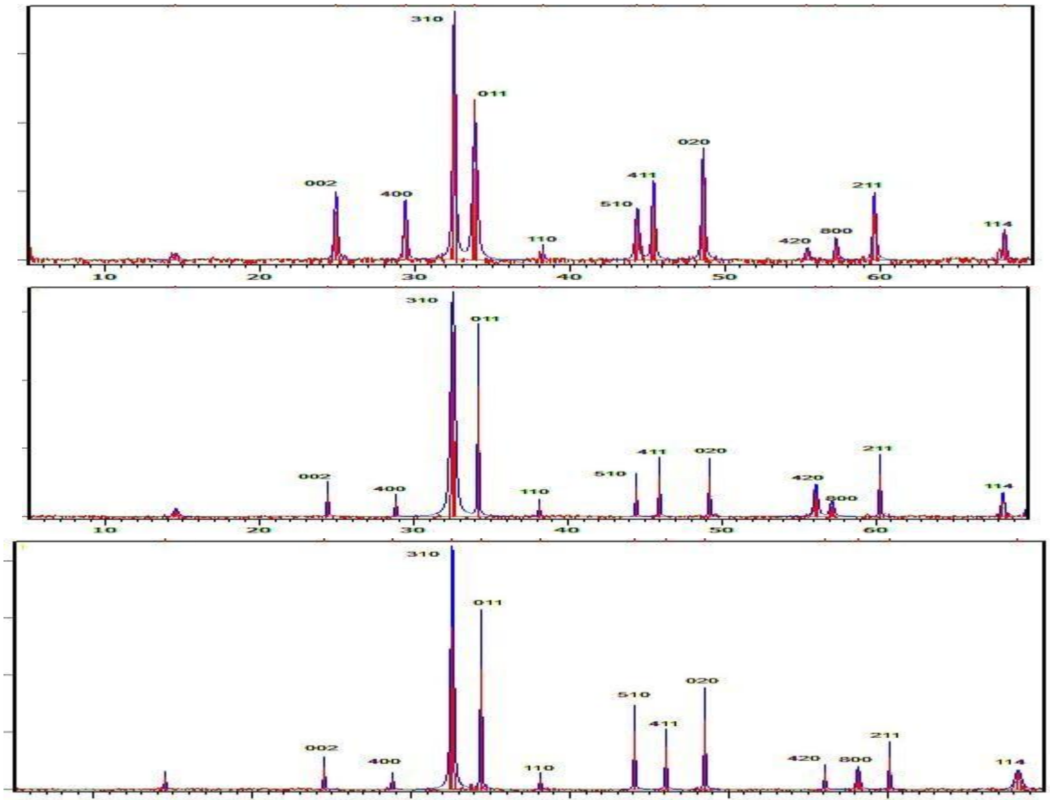

Figure 4: XRD spectrum for compounds Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2\ Co_{0.75}Cu_{0.25}O_4$

And the table (3) shows the mathematical results of the structural study with both the ceramic and sol-gel methods of compounds: Sr2CoO4, Sr1Gd1Co0.75Cu0.25O4, Sr2 Co0.75Cu0.25O4.

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

Sr2CoO4, Sr1Gd1Co0.75Cu0.25O4, Sr2 Co0.75Cu0.25O4

Samples	**Sr_2CoO_4**	**Sr_2**	**$Co_{0.75}Cu_{0.25}$**	**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	12.532 1	
α				
β				

ɣ			
V($Å^3$)	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 JhanTeller 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 compoundsSr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$, $Sr_2Co_{0.75}Cu_{0.25}O_4$were studied. Resistevity Electric and Conductivity Electric are measured using a device of four probes.

Table 4: Conductivity values and electrical resistance of compounds Sr_2CoO_4, $Sr_1Gd_1Co_{0.75}Cu_{0.25}O_4$,

Sr2Co0.75Cu0.25O4

Samples	Resistevity Electric(∩/*cm*)	Conductivity Electric(s/cm)
Sr CoO		0.0011
Sr Co . Cu . O		0.0016
Sr Gd Co . Cu . O	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 increases in the electrical conductivity.

As for the adding of 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.
- 4There 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.

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