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Preparation and identification of nano-perovskite $LaCrO_3$ from the thermal decomposition of an heterobimetallic complex using microwave radiation

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ABSTRACT

In this research, the heterobimetallic complex $La[Cr(C_2O_4)_3].10H_2O$ was prepared by mixing an equimolar aqueous solution of $K_3[Cr(C_2O_4)_3]$ complex and $La(NO_3)_3$ solution and as a precursor for the preparation of nanoperovskite $LaCrO_3$, it was exposed to microwave radiation. The possible changes made in the structure of the decomposition product of this aberrant complex and the formation of new mineral phases was identified using X-ray diffraction (XRD) and FT-IR spectroscopy. The microstructure and morphology of the product were examined by scanning electron microscope (SEM) and determination of chemical composition and purity by EDX analysis.

1. Introduction

Nanoparticles are important materials in the chemistry field [1]. Bimetallic oxide nanoparticles due to the presence of unique physical and chemical properties such as quantum effect, high surface area, small particle size, good reactivity, mobility, mechanical, thermal, optical, catalytic and magnetic properties have been widely studied around the world [2]. Perovskite type oxides $LnMO_3$, where Ln is a lanthanide ion and M is an intermediate metal, are among the most important materials for catalytic applications, electrode materials and solid electrolytes for fuel cells, gas sensors, Solar cells and light emitting diodes [3-5]. One of the reasons why perovskite oxides show good catalytic activity is the existence of structural defects in their crystal structure [6-8] .Perovskites are one of the inorganic compounds whose physical properties change with the application of an external electric field and lead to countless applications in optical regulators, baroelectric storage, non-volatile memory applications and infrared detection [9].

One of the methods of preparing mixed metal oxide $LaCrO_3$ is the precursor method. In this method, a compound is prepared as a precursor whose molecule contains reactive components with the appropriate stoichiometry of the final mineral substance. Then, from the thermal decomposition of the precursor, oxide minerals are obtained as the final product. In this method, because there are metal ions inside a molecule, the penetration and diffusion distance of a cation is very short, and mixing is done on an atomic scale. Using this method, mineral phases with accurate stoichiometry can be obtained. The method of solid state decomposition of molecular precursors has advantages such as excellent stoichiometry, high degree of homogeneity and purity, size and morphology control of nanostructures, product uniformity and stability and no need for complicated devices [10]. In addition, the preparation of these materials through microwave radiation is fast, clean and economical in terms of energy. It also has certain advantages such as excellent control of reaction parameters, no direct contact of the heat source with the reactant and high heating rate.

In the microwave process, matter is heated by energy conversion. If the material is coupled to the microwave field, this energy conversion enables very fast heating rates. In microwave heating, the heat is generated inside the material instead of coming from an

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external source. This type of heating leads to the distribution of temperature throughout the body and with a maximum inside it. If one of the components of the reaction is a microwave absorber, it is sufficient to carry out the reaction and prepare the mineral substance. But if the components of the reaction are not microwave absorbers, a secondary absorber such as carbon powder or graphite should be added to the reaction mixture, because different forms of carbon when exposed to microwave radiation reach a temperature higher than 1000 ^{0}C in a very short time [11-15].

2. Exprimental

All the chemicals used with high purity (≥ 97 %) were obtained from Merck Chemical Company and were used without further purification. Potassium oxalate ($K_2C_2O_4.H_2O$), oxalic acid ($H_2C_2O_4.H_2O$), potassium dichromate ($K_2Cr_2O_7$), lanthanum (III) nitrate $La(NO_3)_3.6H_2O$, ethanol, acetone.

The diffraction pattern (XRD) of the samples was recorded using an X-ray diffraction device owned by Rigaku D-max C-III. The XRD device was α K Cu with a wavelength (λ = 0.154184 nm) and a nickel filter. Infrared spectra were taken using Shimadzu FT-IR 160 device. The study and examination of the morphology and microstructure of the samples was done using a scanning electron microscope (SEM) MIRA3 TESCAN model. Checking the purity of the sample was done using the EDAX spectrum with the help of a SEM device equipped with EDAX analysis. Also, an LG-inteilwave microwave radiation source with a maximum power of 900 watts was used.

0.01 mol of lanthanum (III) nitrate dissolved in 10 ml of distilled water was added to 10 ml of distilled water containing 0.01 mol of potassium tris oxalatochromate (III). After stirring the mixture for half an hour, a green precipitate was obtained, which was dried in an oven at a temperature of 50°C after washing with water, ethanol and ether. Then, samples of this raw powder were poured into a small porcelain cup and this cup was placed inside a larger porcelain cup containing copper oxide as a secondary microwave absorber. Then it was exposed to microwave radiation at 900 watts for 10 minutes. After this time, it was completely decomposed and a black powder was obtained.[10]

3. Results and Discussion

3-1. Investigating the preparation of nanoperovskite $LaCrO_3$ using XRD

Scheme (1) shows the diffraction pattern of the decomposed complex. In this pattern, numerous peaks with low and high intensity have appeared. Comparison of the major diffraction peaks appearing in this pattern with the JCPDS card of the $LaCrO_3$ phase (JCPDS NO:24-1016) shows that these peaks are related to this phase [16]. Therefore, XRD analysis confirms the preparation of $LaCrO_3$ phase from $La[Cr(C_2O_4)_3]$. $10H_2O$ precursor under microwave irradiation. In the XRD pattern, using the Debye-Scherer equation, the average size of nanoparticles (D) was estimated to be about 16 nm from the line width β=0.413 at the half height of the major peak (100%) appearing at 2Θ =33.

$$D = \frac{0/9\ \lambda}{\beta\ \mathrm{Cos}\Theta}$$

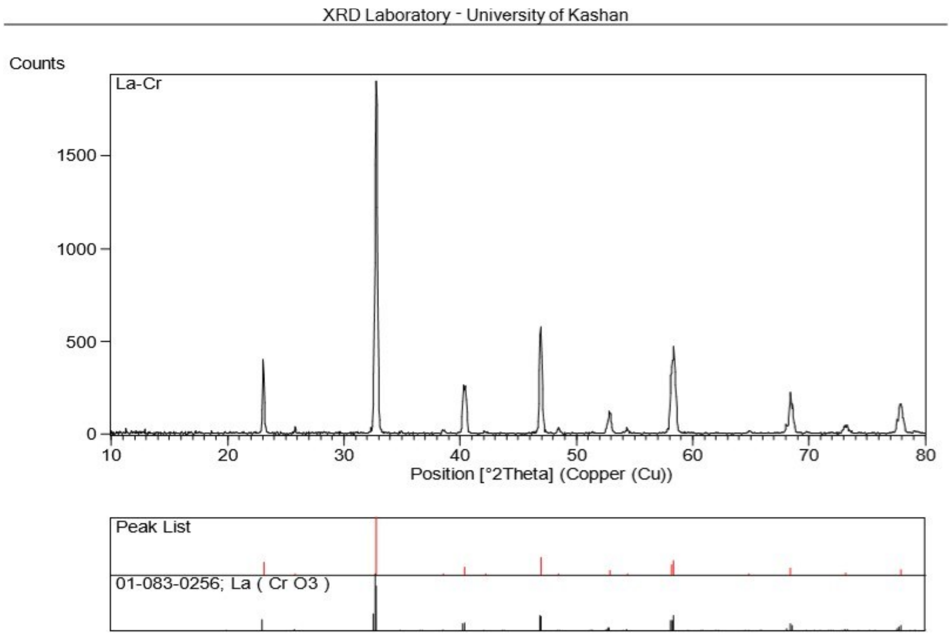
3-2. Investigating the preparation of nanoperovskite $LaCrO_3$ using FT-IR

Scheme (2) shows the FT-IR spectrum of the raw powder of $La[Cr(C_2O_4)_3].10H_2O$ complex. The wide band in the range of 3000-3500 cm^{-1} indicates the presence of water and the bands appearing at around 817, 1290, 1435 and 1653 cm^{-1} are characteristic of oxalato ligand [17].

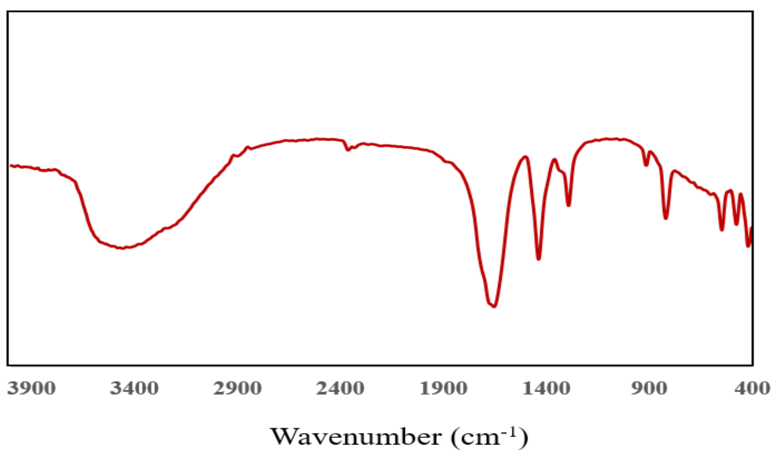
Scheme (3) shows the FT-IR spectrum of the powder obtained from the decomposition of the complex under microwave irradiation. Comparing this spectrum with the precursor complex spectrum in Figure (2) shows that after the decomposition of oxalato and water characteristic bands that were present in the raw powder, they have been completely removed, which indicates the decomposition of the oxalato ligand. Two major bands around the region of 500 cm^{-1} are characteristic of the $LaCrO_3$ oxide network, which is consistent with the reported results [18,19]. Therefore, FT-IR analysis confirms the preparation of $LaCrO_3$ phase under microwave irradiation completely and single phase.

3-3. Investigating the morphology of nanoperovskite $LaCrO_3$ using SEM

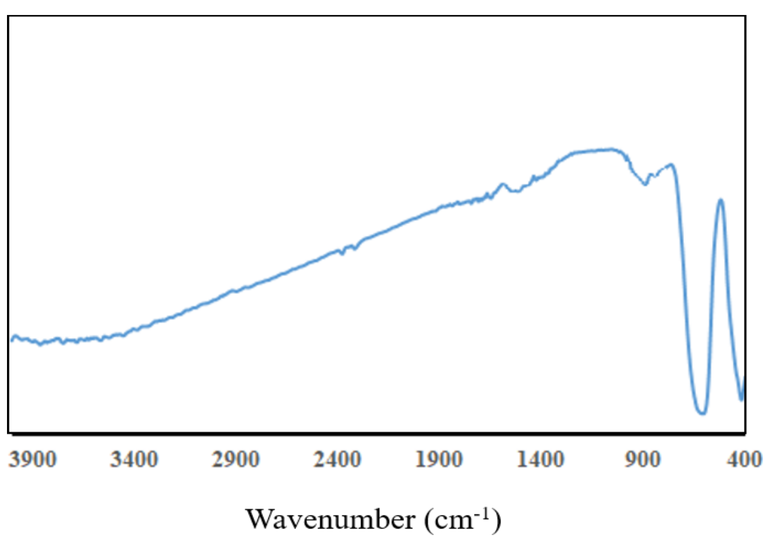
SEM images were taken to understand the morphology and microstructure of the prepared $LaCrO_3$ powder. The SEM micrograph with 1 and 2 micron magnification is given in Scheme (4). SEM images show that the particles are mostly separate, granular and sub-micron. The shape of the particles is almost semi-spherical and they are mostly close in size. The size of the particles is estimated to be between 6 and 14 nm.



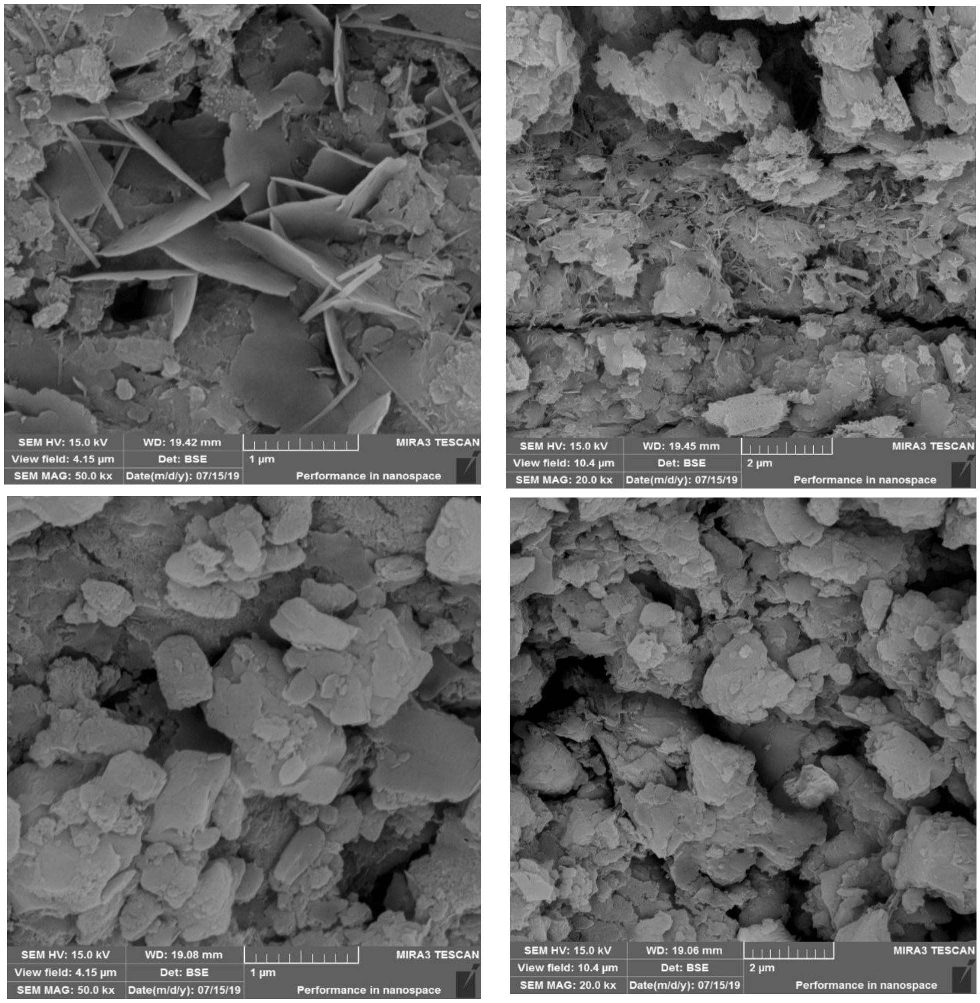
Scheme 1. XRD pattern of nanoperovskite $LaCrO_3$ synthesized by microwave and the second graph of the XRD reference pattern phase $LaCrO_3$ (JCPDS No: 24-1016)



Scheme 2. FT-IR spectrum of raw powder of $La[Cr(C_2O_4)_3].10H_2O$ complex



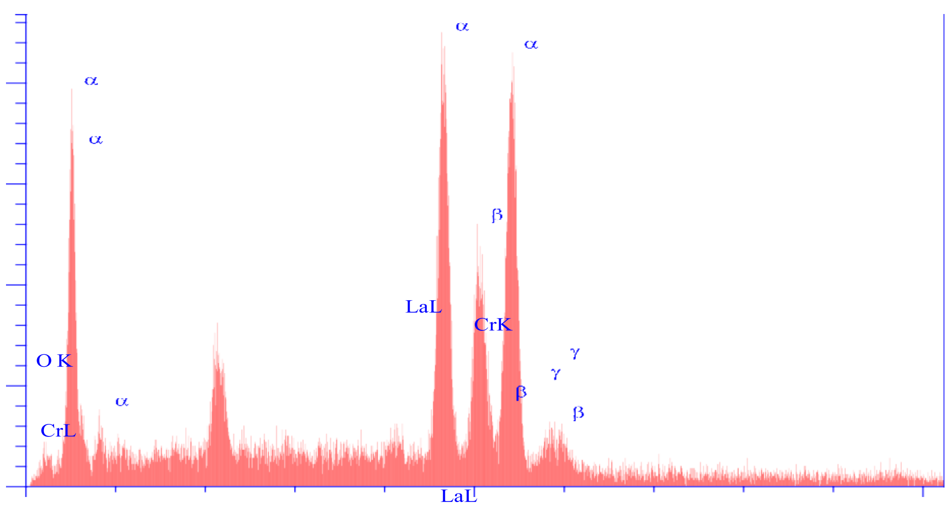
Scheme 3. FT-IR spectrum of $LaCrO_3$ nanoperovskite under microwave irradiation



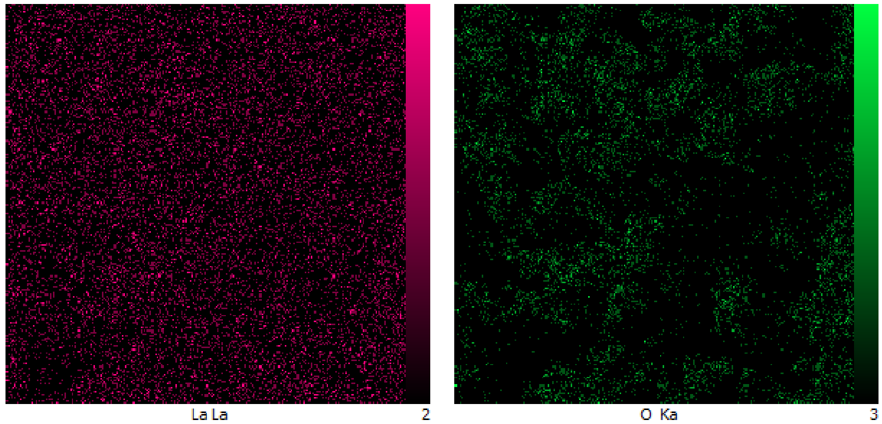
Scheme 4. SEM images of nanoperovskite $LaCrO_3$ synthesized by microwave

3-4. Investigating of nanoperovskite $LaCrO_3$ using EDX

EDX analysis was used to determine the composition and chemical purity of nanoperovskite. Scheme (5) This analysis confirmed the presence of La, Cr and O elements. According to Scheme (6), which shows the EDX map images of nanoperovskite, the mentioned elements have the same distribution in nanoperovskite



Scheme 5. Elemental analysis and EDX of nanoperovskite $LaCrO_3$ synthesized by microwave



Scheme 6. EDX map images of $LaCrO_3$ nanoperovskite synthesized by microwave

4. Conclusion

In this research, nanoperovskite $LaCrO_3$ was formed from the decomposition of the heterobimetallic precursor complex $La[Cr(C_2O_4)_3].10H_2O$ with high purity and very fine and homogeneous grains under microwave irradiation for 10 minutes. Also, perovskite oxide $LaCrO_3$ has an orthorhombic system. This result comes from the fact that the major peak around 2Ɵ=33 is single for $LaCrO_3$. One of the advantages of this type of compound is its catalytic application, semiconducting properties, and its use as chemical sensors to detect gases.

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