

SYNTHESIS OF $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ NANO POWDER BY GLYCINE NITRATE PROCESS

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Abstract: $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ nano powder was synthesized by the glycine nitrate process from an aqueous solution of lanthanum, strontium, chromium nitrates and glycine. Heating the precursor solution induced a combustion reaction and a black-colored ash was obtained. The density, size and morphology of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ powder depended strongly on the nitrate to glycine ratio. However, the pH value of the precursor solution had no significant effect. It was found that the secondary minor phase, LaCrO_4 , was observed in the powder heat treated at temperatures lower than 1100°C . A single phase perovskite, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$, was successfully fabricated when the ash was heat treated at 1200°C for 5 h.

Keywords: solid oxide fuel cells, LaCrO_3 , Perovskite, glycine nitrate process (GNP)

INTRODUCTION

LaCrO_3 -based perovskite materials have been widely used as the ceramic interconnect of solid oxide fuel cells (SOFCs), because of their high electrical conductivity, high thermal conductivity and good phase stability under a reducing atmosphere as well as air [1, 2]. Recently, A and B site co-doped LaCrO_3 has received a great deal of attention as a potential candidate to replace the Ni-YSZ currently used as the anode material of SOFCs. In order to create an anode with sufficient porosity and small enough particles to achieve a high surface area and allow fuel to pass through to the electrode, nano-sized particles are needed.

There are various methods of synthesizing ceramic powders, for example, the solid state reaction, the sol-gel, Pechini and glycine nitrate processes, and so on. Of these processes, the glycine nitrate process (GNP) is one of the most attractive methods, as it allows homogeneous nano-sized particles to be obtained via a self-ignited combustion process using metal nitrates and glycine. It has the advantage of being an easy and speedy process. The amine ($-\text{NH}_2$) and carboxyl ($-\text{COO}$) groups can make complexes with metal ions, which prevent the metal nitrates from segregating before the combustion reaction occurs [3-5].

In this study, Sr doped LaCrO_3 nano powder was synthesized by the GNP from lanthanum, strontium and chromium nitrates and glycine. The phase evolution behavior and microstructure of the LaCrO_3 were investigated in terms of the metal ion/glycine ratio and the pH of the precursor solution.

EXPERIMENTAL PROCEDURE

Lanthanum, strontium and chromium nitrates and glycine were used as the starting materials. The nitrates and glycine were dissolved in distilled water. The pH value of the solution was approximately 3. The molar ratio of lanthanum to strontium was fixed at 0.8:0.2, while various nitrates to glycine molar ratios of 1:1, 1:1.5 and 1:2 were used. The pH of the precursor solution was also varied using nitric acid. After stirring the precursor solution at 80°C for 2 h, it was then heated up to enable the water to evaporate, causing the solution to become dry. Once the combustion reaction started, it was completed in less than 5 min., with the exact time depending on the amount of starting materials used. The obtained ash was calcined in a tube furnace at 500, 1000, 1100 and 1200°C for 5 h. The experimental details are shown in Fig. 1.

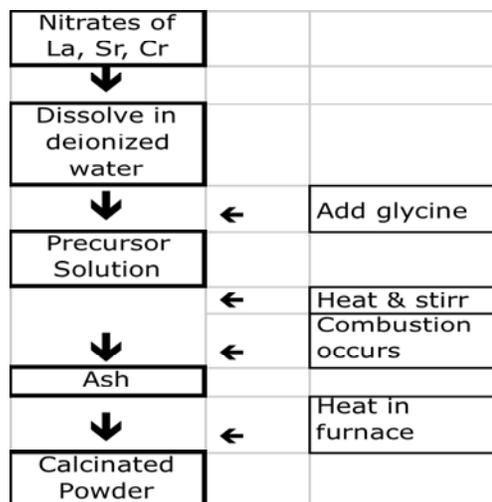


Fig. 1: Flow chart of glycine nitrate Process (GNP)

The phase identification of the calcined powder was performed by powder X-ray diffraction. The powder morphology and microstructure were observed by field emission scanning electron microscopy (SEM)

RESULTS AND DISCUSSION

In this study, the effects of two processing variables were examined: 1) the nitrate/glycine molar concentration and 2) the pH value of the precursor solution. Glycine is known to act as a chelating agent for various metal ions. It contains a carboxylic acid group at one end and an amino group at the other end. While in solution, glycine turns into a zwitterion and complexes metal ions, which can be of any ionic size.

Glycine also acts as a fuel during the combustion reaction, where it is oxidized by the nitrate ions giving off nitrogen, water and carbon dioxide gases. The characteristics of the resulting nano powder such as the particle size, surface area and density strongly depend on the temperature during the combustion. This can be controlled by adjusting the glycine to nitrate ratio.

Secondly, the dissociation state of the carboxyl and amino groups of glycine may change, depending on the pH value of the precursor solution, which can affect its molecular structure. For example, at pH=2.34, approximately half of the $-\text{COOH}$ groups were ionized, while the $-\text{NO}_2$ groups were completely ionized. As the pH value was decreased, the dissociation of the $-\text{COOH}$ groups decreased.

Dark green colored powders were obtained after heating the precursor solution at 500°C and dark brown colored powders were obtained after heating it at either 1000°C or 1100°C . This coloring could be caused by the glycine concentration in the precursor solution. The powder samples synthesized from the solution with a high glycine concentration have a large amount of carbon residue. This is because glycine evaporates along with water during the combustion reaction, forming a hydrocarbon compound, which is left behind in the ash, causing the dark coloring.

Another reason might be the oxidation of chromium. The nitrates of lanthanum and strontium have a white color, unlike that of chromium, which has a dark blue/black color. Hence, the change in the oxidation state of chromium from Cr^{3+} to Cr^{4+} during the combustion reaction is another possible cause of the powder coloration.

An $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ perovskite was formed after heat treating the ash at 500°C , whose quantity increased with increasing heat treatment temperature.

Fig. 1 shows the XRD patterns of the powders heat treated at 1100°C for 5 h, which were prepared from the precursor solutions having various nitrate/glycine ratios and pH=1.

Increasing the molar concentration of glycine reduces the amount of minor phases of SrCrO_4 present, as seen in the XRD results. However, the heat treatment of the powder at high temperatures over 1100°C is essential to achieve a single phase and control the particle size and size distribution of the sample.

A SrCrO_4 phase still remained in all of the powders heat-treated at 1100°C . The EDS analysis (Fig. 2) shows that the lumps present are made up of approximately 48% Sr, 26% Cr and 13% O. From the XRD examination of these samples, we know that this minor phase is SrCrO_4 . A single phase perovskite can be obtained using heat treatment at 1200°C for 5 h.

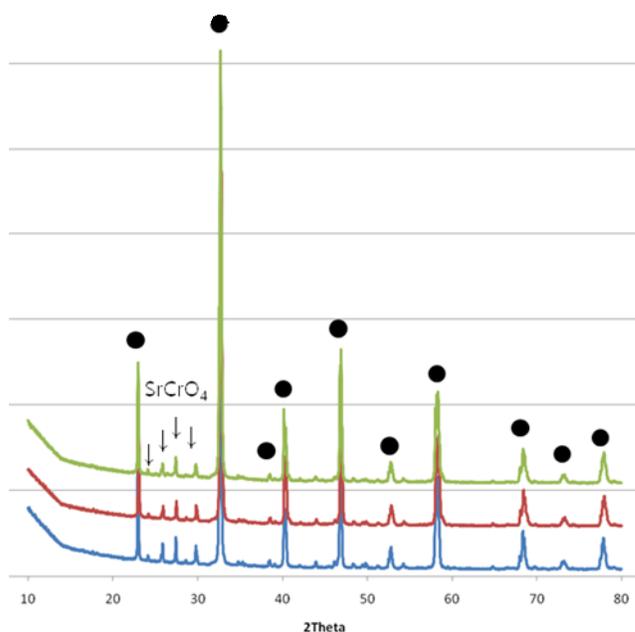
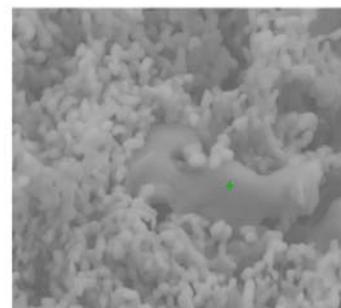


Fig. 2. XRD patterns of the samples heat-treated at 1000°C which were prepared from the precursor solutions of nitrate: glycine=1:2, 1:1.5, and 1:1 (from the top).



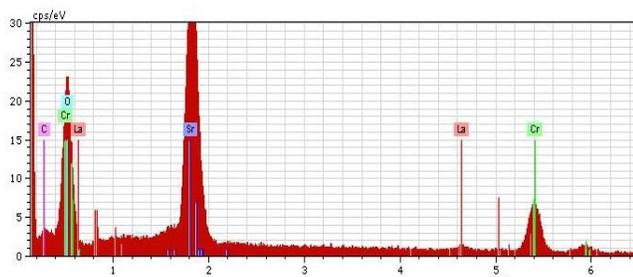


Fig. 3: SEM photograph and EDX analysis of SrCrO₄

The apparent density of the powders showed little variation at the same molar concentration ratio, but different pH values; however, a more significant difference was seen as the molar concentration ratios increased. This is summarized in Table 1.

Table 1: Apparent density of the powder which was prepared from the precursor solution with different nitrate to glycine molar ratios.

Nitrate to glycine ratio	Particle density (g/cm ³)
1:1	0.80
1:1.5	0.75
1:2	0.70

As is evident in Table 1, an increase in the glycine molar concentration results in a decrease in the apparent density. This could be due to the fact that all of the glycine reacts during combustion, creating empty pores or spaces in the heat treated powder, thus making the sample more porous. This phenomenon can be seen in the SEM images.

The particle size, surface area and density of the powder strongly depended on the glycine to nitrate ratio and the heat treating temperature. Figs. 4, 5, and 6 show the SEM images of the powders which were prepared from the precursor solutions with different glycine to nitrate ratios.

From the SEM images, we observed that an increase in the nitrate to glycine ratio led to the production of smaller and more porous particles. Also, a reduction in the pH value resulted in smaller particles. However, the particles prepared from the precursor solution at pH 2 seem to show the most optimal results. The particles with a smaller size were found to have a lower density, as they can agglomerate together creating clumps, allowing more space in between them and thus reducing the density.

Glycine acts as a fuel during the GNP. This process is a rapid self-sustaining process. Thus,

increasing the amount of glycine would lead to an increase in the rate of combustion of the metal nitrates and cause the reaction to combust faster and hotter, drying out the nitrates and producing smaller primary particles. These particles can aggregate quickly, because they are close together and sticky, leading to the formation of the rod like structures shown in Figs.5 and 6.

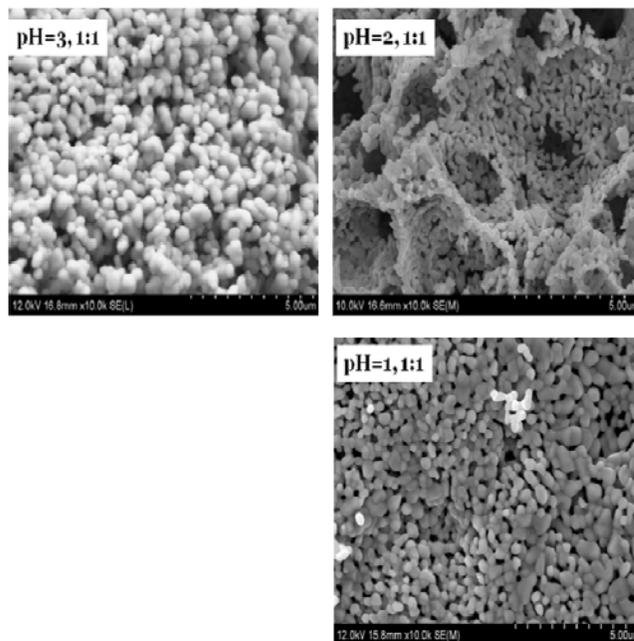


Fig. 4: SEM photographs of La_{0.8}Sr_{0.2}CrO₃ powders. (Nitrate to glycine ratio is 1:1)

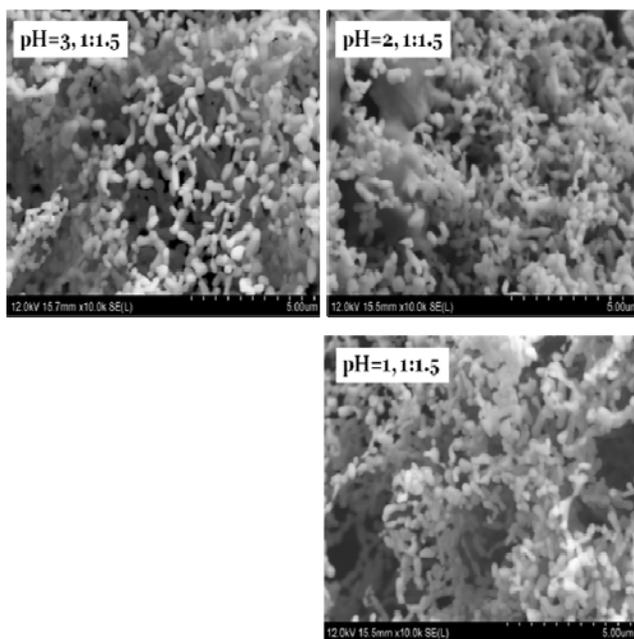


Fig. 5: SEM photographs of La_{0.8}Sr_{0.2}CrO₃ powders. (Nitrate to glycine ratio is 1:1.5)

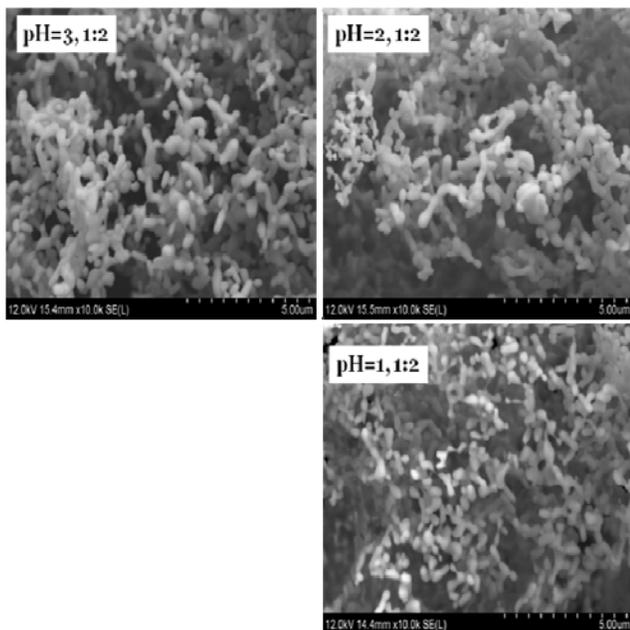


Fig. 6: SEM photographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ powders. (Nitrate to glycine ratio is 1:2)

CONCLUSION

$\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ nano powder was synthesized using the glycine nitrate process (GNP) and the resultant combustion ash powder was heated at 500°C , 1000°C and 1100°C . The X-ray diffraction results indicated the presence of a minor phase, i.e. SrCrO_4 , in the samples heat treated at temperatures below 1100°C . Also, the amount of minor phases present decreases as the glycine concentration is increased.

The glycine affected the morphology of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ particles. The addition of glycine likely led to more porous and loosely packed $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ aggregates, because of the resulting increase in the combustion rate and the rod like aggregation of the particles.

The pH value of the precursor solution influences the morphology and microstructure of the resultant powder. Reducing the pH value of the samples led to the production of smaller particles and their aggregation.

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