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Nano-sized $LaMnO_3$ powders prepared by spray pyrolysis from spray solution containing citric acid

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Nano-sized lanthanum manganites ($LaMnO_3$) were prepared by spray pyrolysis process from the spray solution with citric acid as organic additive. The $LaMnO_3$ precursor powders obtained from the spray solution with citric acid had thin wall and hollow structures. The thickness of the wall of the precursor powders was below 50 nm. The post-treated $LaMnO_3$ powders had slightly aggregated morphology of the primary powders with nanometer size. The post-treated $LaMnO_3$ turned to nano-sized powders after simple milling by hand using agate mortar. The mean sizes of the $LaMnO_3$ powders obtained from the spray solutions with concentrations of citric acid as 0.4 and 0.8 M at a post-treatment temperature of 800°C were 80 and 200 nm, respectively. The mean size of the $LaMnO_3$ powders changed from several tens nanometer to submicron size according to the post-treatment temperatures. The mean crystallite sizes of the $LaMnO_3$ powders obtained from the spray solution with citric acid at post-treatment temperatures between 700 and 1000°C changed from 26 to 36 nm.

Key-words : Nano powders, Spray pyrolysis, Lantanium manganite

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1. Introduction

Perovskite type lanthanum manganites ($LaMnO_3$) and the related compounds has been recently the subject of interest of researchers due to their unique physical and chemical properties such as giant magneto-resistance and catalysis.[1)-2)] This type of materials have great potential for use in a wide range of applications such as electrode materials in solid oxide fuel cells, exhaust gas sensors in automobiles, membranes for separation processes and as catalysts.[3)-7)]

A traditional synthesis route for $LaMnO_3$ is solid state reaction of the constituent oxide powders at 1300°C.[8)] This thermal activation leads to large powder size, limited degree of chemical homogeneity and low specific surface areas (generally below 10 m^2/g). To overcome the disadvantages of the solid-state reaction method, recently, several synthesis techniques of $LaMnO_3$, such as physical technique, chemical vapor deposition, microemulsion, mechanosynthesis, and other chemical solution methods such as sol–gel, polymeric gel, amorphous citrate or co-precipitation have been reported.[9)-16)] However, post-treatment process performed to improve the characteristics of the powders obtained by chemical solution methods causes the size growth and aggregation between the powders.

Spray pyrolysis as an aerosol process has been successfully applied to prepare ceramic powders, because it is a simple, inexpensive, and continuous process, and the prepared powders have spherical shape, narrow size distributions, and high phase purity.[17)-18)] Kumar et al. prepared Sr-doped $LaMnO_3$ powders by a novel spray pyrolysis named as "auto-ignition process."[19)] Spray solution was prepared by polymerization process of metal components and citric acid at high temperature. The citrate precursor solution produced the nanocrystalline $La_{0.84}Sr_{0.16}MnO_3$ powders by a novel spray pyrolysis. However, the effects of citric acid on the properties of the precursor and post-treated Sr-doped $LaMnO_3$ powders were not well studied.

In this work, nano-sized $LaMnO_3$ powders were prepared by spray pyrolysis. Citric acid was added to the spray solution to produce the precursor powders with hollow and porous structure. The powders post-treated at temperatures between 700 and 1000°C turned to nano-sized $LaMnO_3$ powders after simple milling process.

2. Experimental procedure

The spray pyrolysis equipment used consisted of droplet generator, quartz reactor, and a teflon bag filter. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which are carried into the high temperature tubular reactor by a carrier gas. The flow rate of air used as a carrier gas was 45 L/min. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. Lanthanum nitrate hexahydrate and manganese (II) chloride tetrahydrate were used as starting materials to prepare $LaMnO_3$ powders. The overall solution concentration of lantanum and manganese components was fixed at 0.2 M. The concentration of citric acid monohydrate used as an organic additive was changed from 0.2 to 1.5 M. The precursor powders obtained by spray pyrolysis were post-treated at temperatures between 700 and 1100°C for 2 h in air atmosphere. The crystal structures of the precursor and post-treated $LaMnO_3$ powders were investigated by using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The mean crystallite sizes of the $LaMnO_3$ powders were calculated using Scherrer's equation. Measurement of the thermal properties of the precursor powders was performed on a thermo-analyzer (TG–DSC, Netzsch, STA409C, Germany) in the temperature range from 40 to 700°C (10°C/min). The morphological characteristics of the powders were investigated by using scanning electron microscopy (SEM, JEOL, JSM-6060) and transmission electron microscope (TEM,

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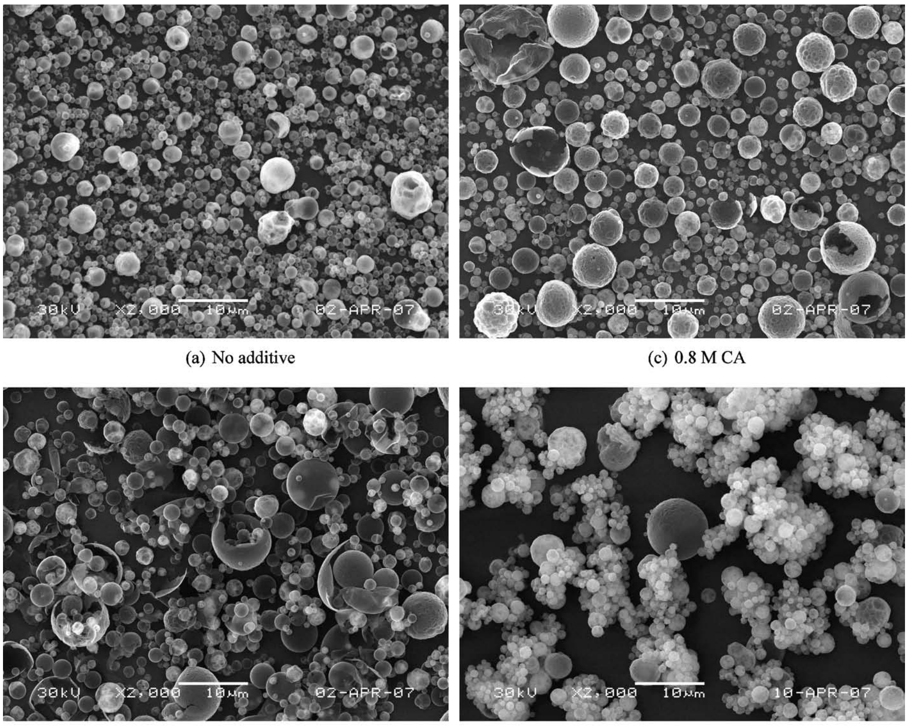


(a) No additive (c) 0.8 M CA

(b) 0.4 M CA (d) 1.5 M CA

Fig. 1. SEM photographs of $LaMnO_3$ precursor powders obtained from the spray solutions with and without citric acid.

FEI, TECHNAI 300K). The post-treated powders were milled by hand using agate mortar for the preparation of TEM sample.

3. Results and discussion

The $LaMnO_3$ precursor powders with filled or hollow structures were prepared by spray pyrolysis from the spray solutions with and without citric acid. The effect of the concentration of citric acid added to the spray solutions on the morphology of the $LaMnO_3$ precursor powders was shown in **Fig. 1**. The precursor powders obtained from the spray solution without citric acid had fine size, spherical shape and filled morphology. On the other hand, the $LaMnO_3$ precursor powders obtained by spray pyrolysis from the spray solutions with citric acid had different morphologies according to the concentration of citric acid. The $LaMnO_3$ precursor powders with large size, hollow and thin wall structures were prepared from the spray solutions with concentrations of citric acid between 0.2 and 0.8 M. The high drying and decomposition rates of particles and the gas evolution from the decomposition of the citric acid generated the $LaMnO_3$ precursor particles with hollow and thin wall structures. The hollow wall of the $LaMnO_3$ precursor powders (Fig. 1b) had low thickness below 50 nm in the high magnification SEM photograph. However, the precursor powders (Fig. 1d) obtained from the spray solution with high concentration of citric acid had fine size, spherical shape and filled morphology. The high concentration of citric acid within the droplet formed a highly viscous gel during the drying and decomposition processes of the droplets. The viscous gel promoted the volume precipitation of precursors within the droplets and resulted in the formation of powders with a spherical shape and a filled morphology.[20]

The thermal properties of the $LaMnO_3$ precursor powders prepared by spray pyrolysis from the spray solution with and without citric acid were shown in **Fig. 2**. The concentration of citric acid was 0.4 M. The TG curves of the precursor powders show two weight losses at temperatures below 700°C. The first pronounced weight loss region from 40 to 200°C resulted from the loss of adsorbed water. However, the precursor powders obtained from the spray solution with citric acid had large weight loss compared to those obtained from the spray solution without citric acid. The precursor powders obtained from the spray solution with citric acid included the residual carbon components, which made it easy to adsorb water molecules. The second weight losses were different in the precursor powders obtained from the spray solutions with and without citric acid. The large weight loss region from 250 to 500°C of the precursor powders obtained from the spray solution with citric acid is related to the decomposition of residual carbon components. Exothermic peak at 379.9°C in the DSC curve approves the decomposition of residual carbon component. On the other hand, the exothermic peaks in the DSC curve were not observed form the precursor powders obtained from the spray solution without citric acid. The slight weight loss at temperatures below 500°C of the precursor powders obtained from the spray solution without citric acid was caused by incomplete decompositions of precursors.

The effect of the concentration of citric acid added to the spray solution on the morphology and mean size of $LaMnO_3$ powders post-treated at a temperature of 800°C were investigated by SEM and TEM after simple milling by hand using agate mortar. **Figure 3** shows the SEM photographs of the post-treated $LaMnO_3$ powders. The $LaMnO_3$ powders

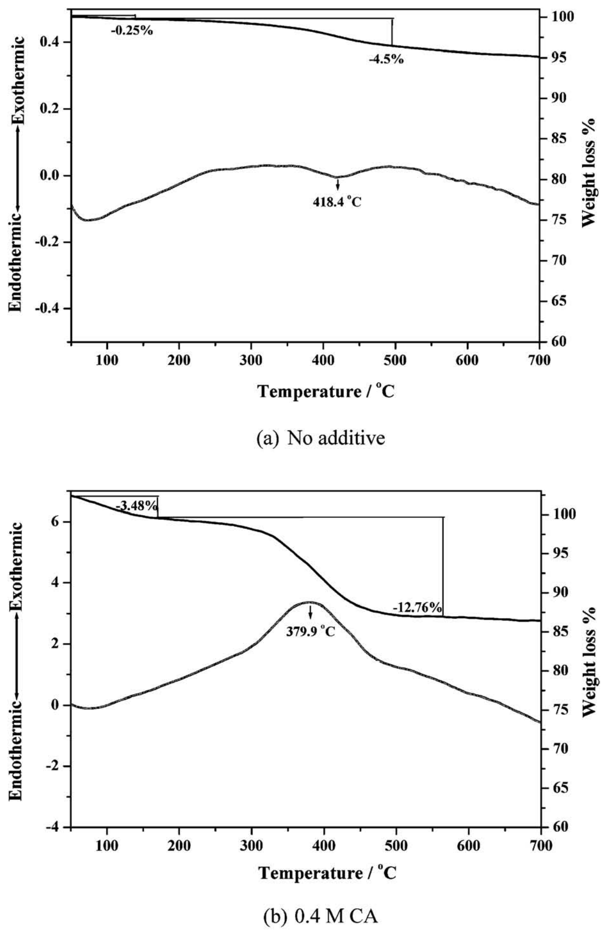


Fig. 2. TG/DSC curves of $LaMnO_3$ precursor powders obtained from the spray solutions with and without citric acid.

obtained from the spray solution without citric acid had several micron sizes, spherical shape and aggregated morphology of the submicronic primary powders. Conversely, the $LaMnO_3$ powders obtained from the spray solutions with adequate concentrations of citric acid had slightly aggregated morphology of primary powders with a nanometer size. The precursor powders with hollow and thin wall structures formed slightly aggregated $LaMnO_3$ powders with nanometer size after post-treatment. The neck strength between the nano-sized primary powders was so weak that the aggregated $LaMnO_3$ powders disintegrated into non-aggregated powders with nanometer size via a simple milling process. On the other hand, the $LaMnO_3$ powders (Fig. 3d) obtained from the precursor powders (Fig. 1d) with fine size and filled structure had aggregated structure of the primary powders with a nanometer size. The morphology and mean size of the post-treated $LaMnO_3$ powders were investigated from the TEM micrographs as shown in **Fig. 4**. The $LaMnO_3$ powders obtained from the spray solution without citric acid had aggregated and hollow morphology. On the other hand, the $LaMnO_3$ powders obtained from the spray solution with citric acid had nanometer size and slightly aggregated morphology. The concentrations of citric acid added to the spray solutions affected the mean size of the $LaMnO_3$ powders. The mean sizes of the $LaMnO_3$ powders obtained from the spray solutions with concentrations of citric acid as 0.4 and 0.8 M were 80 and 200 nm, respectively.

The mean size and crystal structure of the $LaMnO_3$ powders prepared by spray pyrolysis can be controlled by changing the post-treatment temperature. The $LaMnO_3$ precursor powders prepared by spray pyrolysis from the spray solution with and without citric acid were post-treated at temperatures between 800 and 1100°C. The concentration of citric acid was 0.4 M. **Figures 5** and **6** show the SEM photographs of the $LaMnO_3$ powders post-treated at various temperatures without milling process. The $LaMnO_3$ powders obtained from the spray solutions without citric acid had spherical-like shape, porous and hollow morphologies after post-treatment at temperatures below 1000°C. Aggregation between the powders occurred at a post-treatment temperature of 1100°C. On the other hand, the $LaMnO_3$ powders obtained from the spray solutions with citric acid had slightly aggregated morphologies of the primary powders at post-treatment temperatures between 800 and 1100°C. The mean size of the primary powders consisting of the several micron sizes changed from several tens nanometer to submicron size according to the post-treatment temperatures.

Figures 7 and **8** show the XRD patterns of the precursor and post-treated $LaMnO_3$ powders obtained from the spray solutions with and without citric acid. The precursor powders had amorphous phases irrespective of the types of spray solution because of the short residence time of the powders inside the hot wall reactor as 0.6 sec. The $LaMnO_3$ powders obtained from the spray solution without citric acid had the orthorhombic phase at post-treatment temperature of 700°C. On the other hand, the $LaMnO_3$ powder obtained from the spray solution with citric acid had the rhombohedral structure at post-treatment temperature of 700°C, in which the separation of $(10\bar{1})/(211)$ peaks in the XRD spectrum occurred. However, the $LaMnO_3$ powders post-treated at temperatures above 800°C had rhombohedral phases irrespective of the types of spray solution. In this work, the $LaMnO_3$ powders prepared by spray pyrolysis had the rhombohedral phase at low post-treatment temperatures, which is preferable since it has higher catalytic activity due to higher degree of cation vacancies.[21)-22)] The mean crystallite sizes of the $LaMnO_3$ powders obtained from the spray solution with citric acid at post-treatment temperatures between 700 and 1000°C changed from 26 to 36 nm, which were calculated by the Scherrer's equation from the width of the XRD peaks located at $2\theta = 46.9$ (orthorhombic crystal structure) and $2\theta = 46.7$ (rhombohedral crystal structure).

4. Conclusion

The effects of citric acid added to the spray solutions on the characteristics of the precursor and post-treated $LaMnO_3$ powders were investigated. The $LaMnO_3$ precursor powders with large size, hollow and thin wall structures were prepared from the spray solutions with concentrations of citric acid between 0.2 and 0.8 M. However, the precursor powders obtained from the spray solution with high concentration of citric acid as 1.5 M had fine size, spherical shape and filled morphology. The characteristics of the post-treated $LaMnO_3$ powders were also affected by the concentrations of citric acid. The mean size of the $LaMnO_3$ powders could be controlled from several tens to several hundreds nanometer by changing the concentration of citric acid added to the spray solution and the post-treatment temperature.

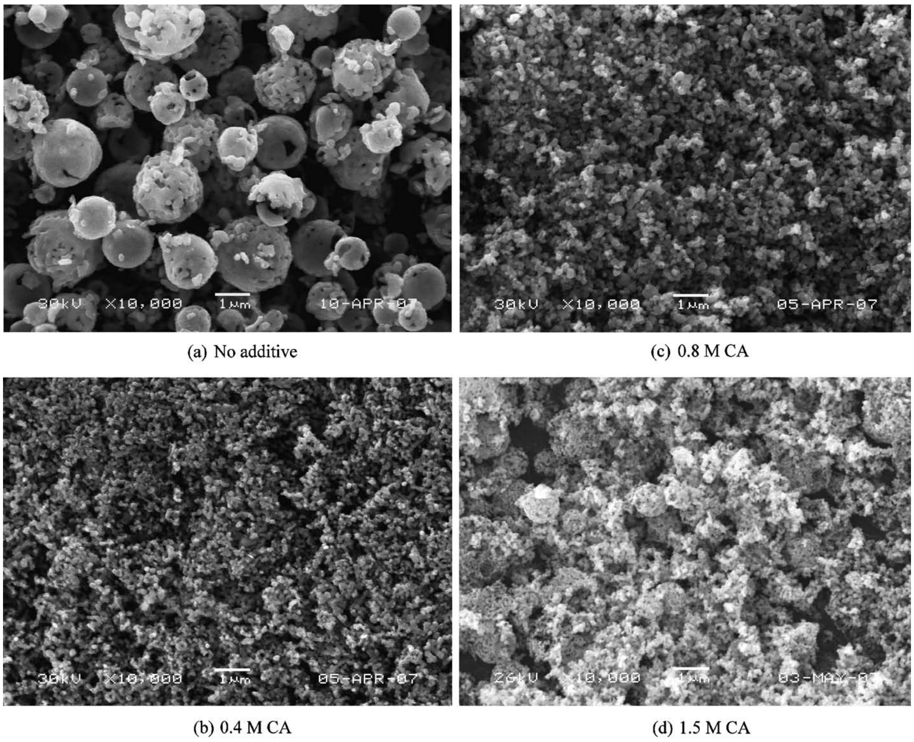


Fig. 3. SEM photographs of post-treated $LaMnO_3$ particles obtained from the spray solutions with and without citric acid.

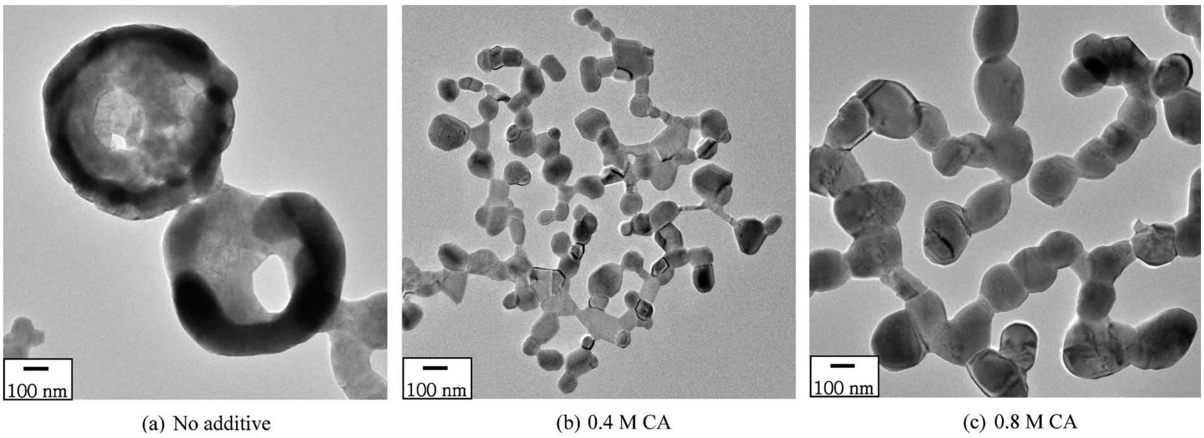


Fig. 4. TEM micrographs of $LaMnO_3$ powders post-treated at temperature of 800°C.

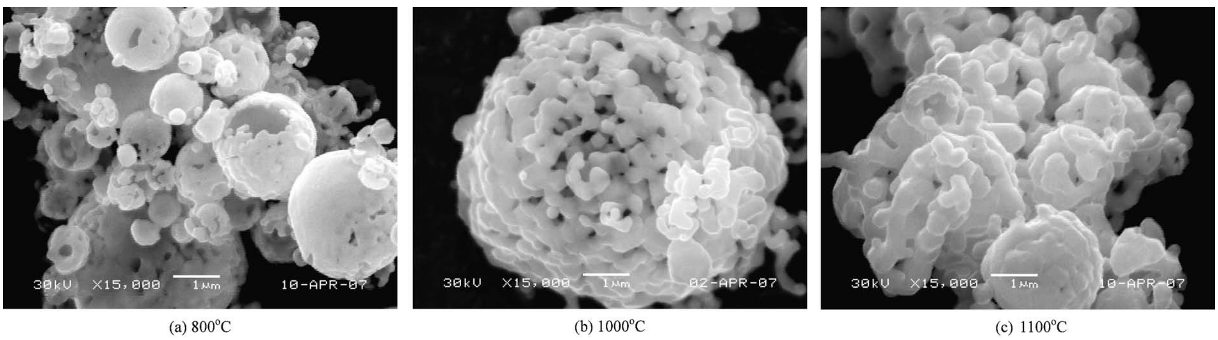
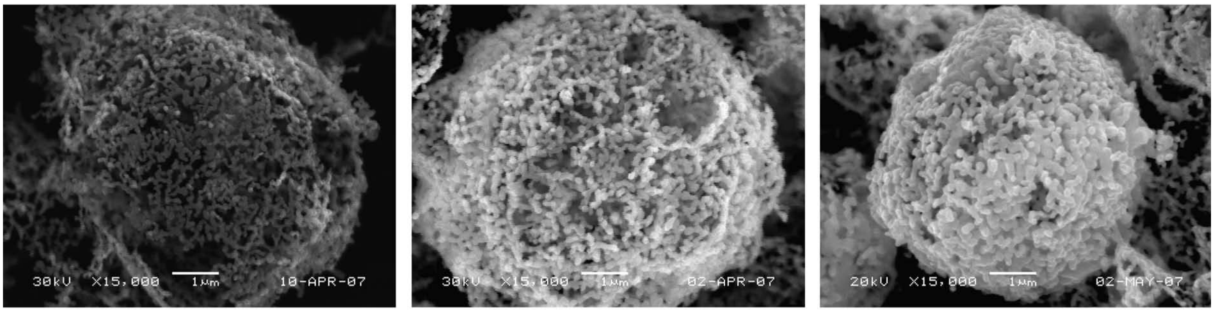


Fig. 5. SEM photographs of $LaMnO_3$ powders obtained from the spray solution without citric acid at different post-treatment temperatures.



(a) 800°C (b) 1000°C (c) 1100°C

Fig. 6. SEM photographs of $LaMnO_3$ powders obtained from the spray solution with citric acid at different post-treatment temperatures.

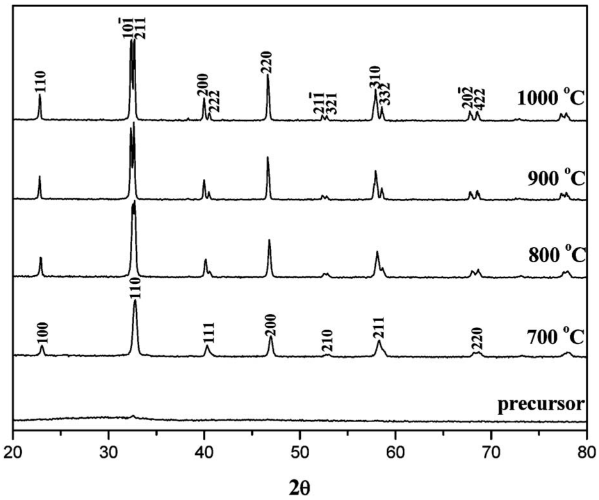


Fig. 7. XRD patterns of $LaMnO_3$ particles obtained from the spray solution without citric acid.

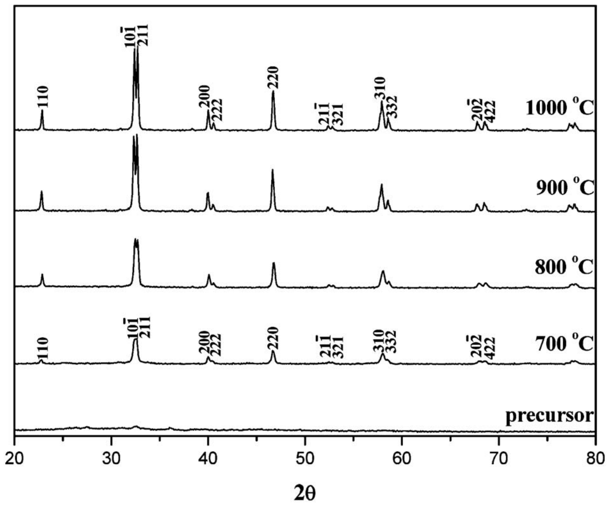


Fig. 8. XRD patterns of $LaMnO_3$ particles obtained from the spray solution with citric acid.

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