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SYNTHESIS AND ELECTRON MICROSCOPIC STUDIES OF NANOSTRUCTURED $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.3, 0.5) SYSTEMS

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ABSTRACT

Synthesis of $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.3, 0.5) systems using sol-gel method involving lanthanum acetylacetonate, strontium acetylacetonate and cobalt acetylacetonate as starting materials have been reported. The $LaCoO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ have nanocrystalline particles at 600°C. Proszki computer programme reveals that the structures of $LaCoO_3$ is hexagonal, $La_{0.5}Sr_{0.5}CoO_3$ is cubic and $La_{0.7}Sr_{0.3}CoO_3$ is rhombohedral.

Keywords: Nanostructure, hexagonal, cubic, rhombohedral, acetylacetonate.

INTRODUCTION

The $LaMO_3$ perovskite-structured oxides that display high oxygen ion mobility have been extensively studied (Islam et al, 1996). These materials are useful in solid oxide fuel cells and effective as heterogeneous catalysts. Also, $La_{1-x}Sr_xCoO_3$ systems have recently attracted the interest of many workers because they exhibit metal-insulator (M-I) transition by Sr-doping or temperature rise (Mineshige et al, 1996). In most of the work available in the literature, $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.3, 0.5) systems have been prepared by the conventional solid phase reaction normally involving La_2O_3, $CoCO_3$ and $SrCO_3$ powders in the desired ratios ($0.0 < x < 0.7$). However, it is interesting to note that a particular material may have different electrical, magnetic and structural properties depending upon the method of preparation, starting materials and temperature (Li et al, 1994, Murugavel et al, 1998). This paper report on the preparation of nanostructured $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.3, 0.5) systems using lanthanum, strontium and cobalt acetylacetonates as starting materials via a novel sol-gel route.

EXPERIMENTAL PROCEDURE

Lanthanum acetylacetonate $La(acac)_3$), strontium acetylacetonate ($Sr(acac)_2$) and cobalt acetylacetonate ($Co(acac)_2$) have been used as precursors for this study carried out via a novel sol-gel route. The synthesis details of the various compounds are given below.

PREPARATION OF $LaCoO_3$

The mixture containing 20ml 0.7M $La(acac)_3$ and 20ml 0.7M $Co(acac)_2$ solutions was magnetically stirred for 10min. 20ml ethyleneglycol and 10ml of distilled water were added while under continuous stirring. After 60min, the sol obtained was dried at 80°C for another 60min to get a gel which was decomposed at 500°C for 20h. The powder obtained was calcined at 600°C for 24h to get the desired oxide.

PREPARATION OF $La_{0.5}Sr_{0.5}CoO_3$

To a solution of $La(acac)_3$ prepared by dissolving 0.3051g in 20ml methanol was added solution of $Sr(acac)_2$ 0.1999g in 20ml methanol. 20ml methanolic solution of 0.07M $Co(acac)_2$ was then added. The mixture was magnetically stirred for 60min and then 20ml ethyleneglycol was added. The resultant mixture was then stirred for another 60min to ensure effective mixing. A few drops of distilled water were then added under continuous stirring. The sol obtained was kept at 40°C for 15h. The gel formed was dried at 60°C for 5h. The xerogel obtained was decomposed at 400°C for 24h to give the powder sample. This was then calcined at 600°C for 24h to obtain the desired oxide.

PREPARATION OF $La_{0.7}Sr_{0.3}CoO_3$

1.527g of $La(acac)_3$ was dissolved in 50ml methanol. To this solution was added 0.4298g of $Sr(acac)_2$ dissolved in 21.5ml

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methanol. 71.5ml of 0.07M $Co(acac)_2$ solution was added to the mixture and magnetically stirred for 10min. Thereafter, 40ml ethyleneglycol was added. After min, 20ml distilled water was added dropwisely and the mixture stirred for 60min. The sol obtained was dried at 60°C for 70min to give a gel which was decomposed at 400°C for 24h. The powder obtained was calcined at 600°C for 24h to get the desired oxide.

CHARACTERIZATION TECHNIQUES

The morphology and particle size distribution were analyzed by employing a Leica S440i scanning electron microscope and a Quantimet Q500MC image analyser respectively. Energy dispersive X-ray analysis (EDAX) was carried out by employing an Oxford instruments ISIS Si detector. Transmission electron microscope images were recorded with a JEOL 3010 microscope. The phase compositions of the powders obtained by the sol-gel method were determined by employing a Seifert 3000 X-ray powder diffractometer with Cu-Kα radiation (θ–θ geometry). The BET surface area measurement was done by nitrogen adsorption employing a Micromeritics Accusorb 2100E instrument.

RESULTS AND DISCUSSION

$LaCoO_3$

Fig.1 shows the XRD pattern of the prepared $LaCoO_3$ perovskite at 600°C and which also shows single phase (JCPDS file 9-358). Proszki computer program for lattice parameter refinement reveals that the prepared $LaCoO_3$ is hexagonal with unit cell parameters: a = 5.2287A° and c = 12.8996A°. Electron microscopic examination of the prepared $LaCoO_3$ using Scanning Electron Microscope (SEM)(Fig.2) reveals that most of the particles are less than about 100nm. The BET surface area of the prepared $LaCoO_3$ is 225m2/g while the

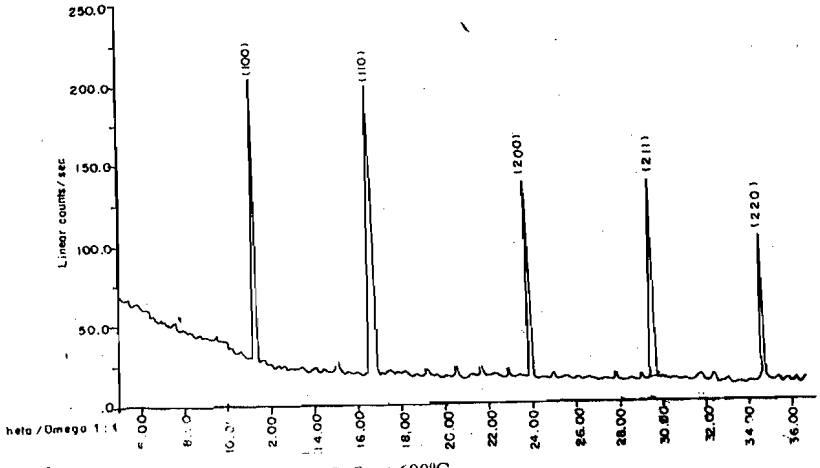

Fig. 1. The XRD pattern of $LaCoO_3$ at 600°C.

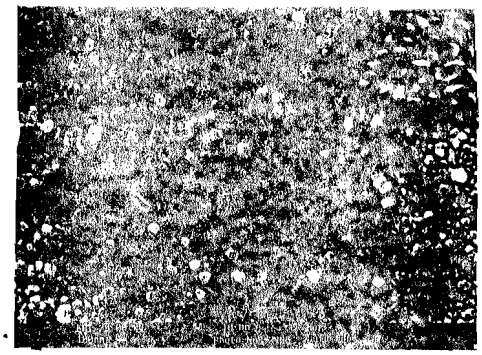

Fig 2. The SEM micrograph of $LaCoO_3$ at 600°C.

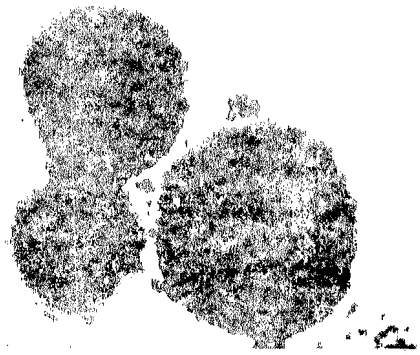

Fig. 3. The TEM micrograph of $LaCoO_3$ at 600°C.

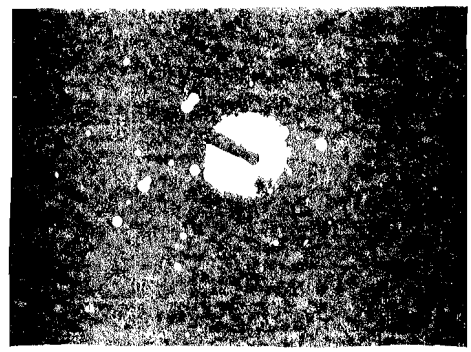

Fig. 4 The Ed micrograph of $LaCoO_3$ at 600°C

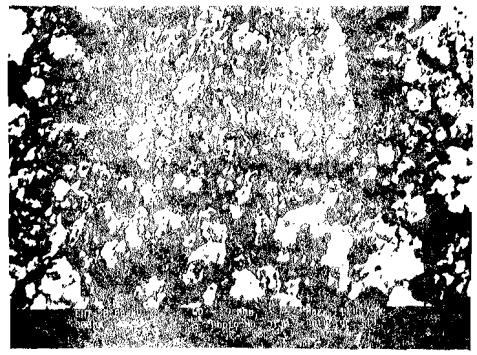

Fig. 5 The SEM micrograph of $La_{0.5}Sr_{0.5}CoO_3$ at 600°C.

Fig. 6. The TEM micrograph of $La_{0.5}Sr_{0.5}CoO_3$ at 600°C.

Fig. 7. The ED pattern of $La_{0.5}Sr_{0.5}CoO_3$ at 600°C.

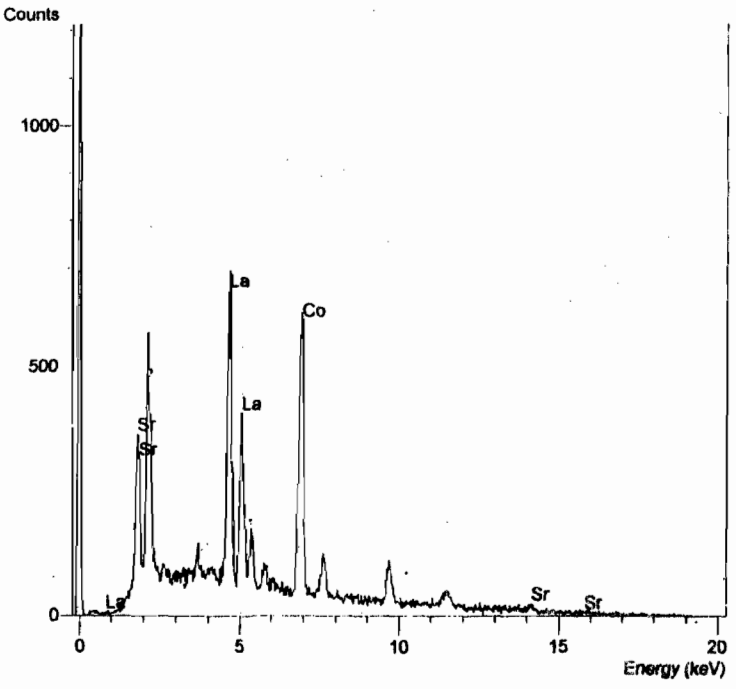

Fig. 9. The EDAX pattern of $La_{0.5}Sr_{0.5}CoO_3$ at 600°C.

TEM image recorded in Fig.3 establishes the spherical nature of the particles. It also shows that the large spherical particles are agglomerates and are actually composed of tinier particles (about 60nm). Fig.4 exhibits the electron diffraction pattern which consists of white spotty patterns confirming the crystallization of $LaCoO_3$ particles on heating to 600°C.

$La_{0.5}Sr_{0.5}CoO_3$

Fig. 5 exhibits the SEM micrograph of the $La_{0.5}Sr_{0.5}CoO_3$ powder obtained by sol-gel method at 600°C. The particles are nearly spherical and are less than 300nm. The TEM micrograph in Fig. 6 also confirms the spherical nature of these particles. The powder is

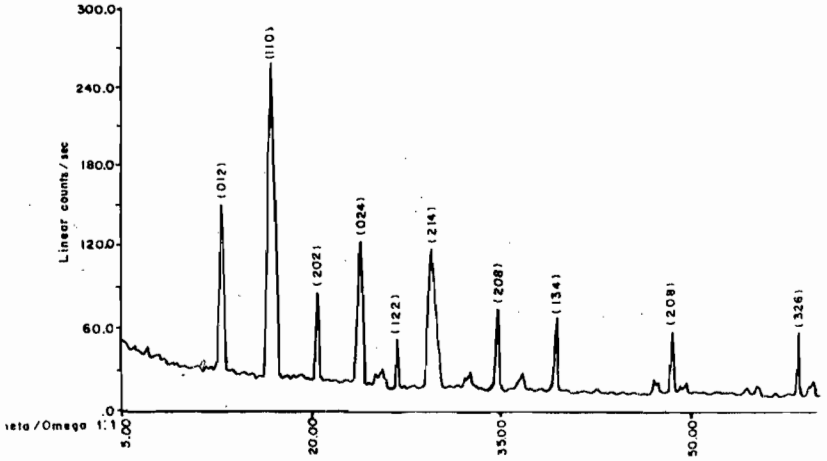

Fig. 8. The XRD pattern of $La_{0.5}Sr_{0.5}CoO_3$ at 600°C.

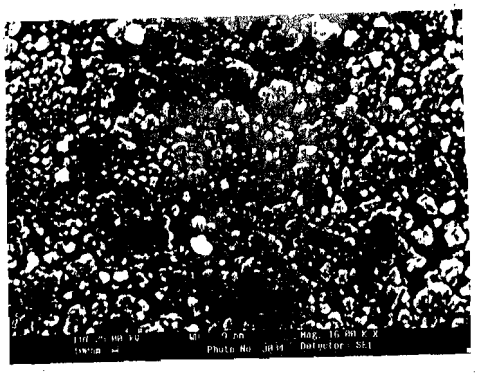

Fig. 10. The SEM micrograph of $La_{0.7}Sr_{0.3}CoO_3$ at 600°C

Fig. 11. The TEM micrograph of $La_{0.7}Sr_{0.3}CoO_3$ at 600°C.

crystalline by the electron diffraction pattern (Fig. 7) and X-ray diffraction pattern (Fig.8). The X-ray diffraction pattern reveals that heating the powder at 600°C for 24hrs gives a cubic phase (JCPDS No. 39-1346) with a = b = c = 3.9951A°. Elemental analysis was done using Energy Dispersive Analysis of X-rays (EDAX). The EDAX result is shown in Fig.9 and reveals that the ratio of La: Sr: Co is 0.5:0.5:1. EDAX result therefore confirms the purity of the phase for $La_{0.5}Sr_{0.5}CoO_3$ powder at 600°C.

The SEM and TEM images of the powder heated to 600°C are presented in Figs. 5 and 6 respectively. These images show that the particles maintain the spherical after heat treatment and also that the spherical particles are in turn composed of tinier particles (~ 200nm). The surface area of the powder was $40m^2/g$.

$La_{0.7}Sr_{0.3}CoO_3$

The SEM and TEM images of the powder of $La_{0.7}Sr_{0.3}CoO_3$ obtained by sol-gel method at 600°C are shown in Figs 10 and 11 respectively. These micrographs show the powder to be spherical. The large particles are composed of tinier particles (80-100nm). EDAX (Fig 12) of $La_{0.7}Sr_{0.3}CoO_3$ was analyzed for quantitative elemental composition by employing the SEM Quant software with ZAF correction procedure. This gave the La:Sr:Co ratio to be 0.7:0.3:1, confirming the composition to be $La_{0.7}Sr_{0.3}CoO_3$.

The X-ray diffraction pattern of the powder heated to 600°C is given in Fig. 13 and

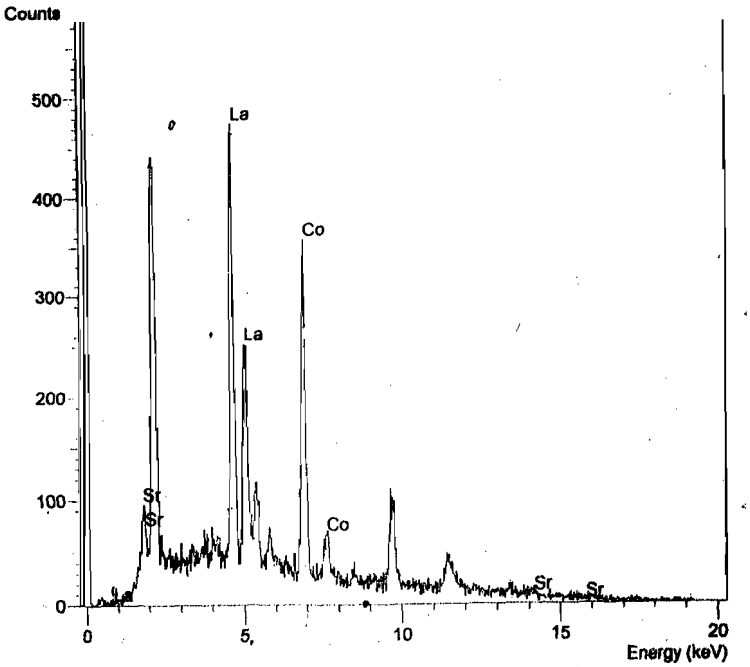

Fig. 12. The EDAX pattern of $La_{0.7}Sr_{0.3}CoO_3$ at 600°C

this shows the formation of pure crystalline phase of $La_{0.7}Sr_{0.3}CoO_3$ when compared with the pattern shown by Mineshige et al (1996). Lattice parameters refinement using the popular proszki computer program reveals that the prepared $La_{0.7}Sr_{0.3}CoO_3$ is rhombohedral having unit-cell parameters: a = 5.4246A°; c = 13.1925A°. The BET surface area of this powder was $126m^2/g$.

CONCLUSION

The present study shows the efficacy of complexes of acetylacetone particularly lanthanum, cobalt and strontium acetylacetonates as precursors for the synthesis of $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.3, 0.5) system via the sol-gel method. The structures of $LaCoO_3$ is

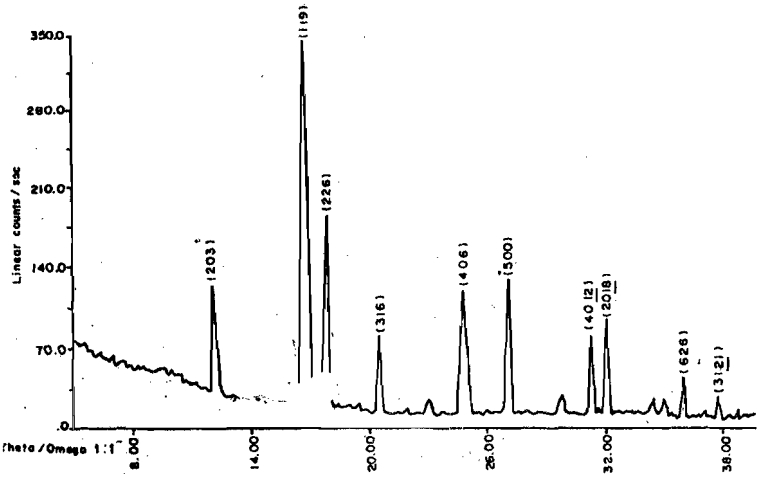

Fig. 13. The XRD pattern of $La_{0.7}Sr_{0.3}CoO_3$ at 600°C.

hexagonal. $La_{0.5}$ $Sr_{0.5}$ CoO_3 is cubic and $La_{0.7}$ $Sr_{0.3}$ CoO_3 is rhombohedral. The structures are influenced by doping levels of strontium.

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