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A study of the crystallization of CSD-prepared $La_{0.5}Sr_{0.5}CoO_3$ thin films using analytical electron microscopy

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Abstract

The crystallisation of chemical solution deposition (CSD) prepared $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin films was studied using analytical electron microscopy (AEM). In the first stages of crystallisation, where the particle size was in the nanometer range, experimental selected area electron diffraction (SAED) patterns were compared to calculated (simulated) patterns in order to determine the phase composition. In samples prepared at 350°C an amorphous phase, nanocrystalline $Sr(NO_3)_2$ and Co_3O_4 were found as well as large crystals (up to 0.5 μm) of $SrCO_3$. Samples annealed at 500°C consisted mainly of the cubic LSCO (perovskite) phase and an amorphous phase. In samples fired at 650°C the pure perovskite phase with a grain size of 50–150 nm was found.

Keywords: Electron microscopy; Films; LSCO oxide electrodes; Perovskites

1. Introduction

$La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin films have been extensively investigated because of their use as oxide electrodes for ferroelectric memory devices.[1,2] LSCO is a very attractive electrode material in all applications involving lead-based perovskite ferroelectric thin films, e.g. Pb(Zr, Ti)O_3 (PZT), because of its perovskite structure with lattice parameters close to those of PZT and a low electrical resistivity of about 90 μΩ cm at room temperature.[2–4] Extensive studies have shown that PZT exhibits better fatigue characteristics when in contact with conducting oxide electrodes than with Pt electrodes.[1–5]

The capacitor structures consisting of PZT and various electrodes are typically prepared in the temperature range 600–700°C. Recently, thin films consisting of the pure perovskite phase of titanium-rich (Pb, La) (Zr, Ti)O_3 (PLZT) and PZT were prepared after heat treatment at 400°C.[6] The usually reported crystallisation temperatures of the LSCO electrodes, prepared by chemical solution deposition (CSD) methods, are between 600 and 800°C.[7,8] In order to reduce the processing temperature of the LSCO electrodes to the crystallisation temperatures of PZT the evolution of the microstructure and the crystallization of CSD-prepared LSCO thin films were studied using analytical electron microscopy (AEM).

2. Experimental

LSCO thin films were prepared from a water solution of lanthanum nitrate $La(NO_3)_3x6H_2O$, strontium nitrate $Sr(NO_3)_2$ and cobalt nitrate $Co(NO_3)_2$ $x6H_2O$ with the addition of 9 wt.% polyvinyl alcohol (PVA) (Moviol 4/88) using CSD.[9] Thin films of 0.5 M solution were deposited on thermally oxidized and platinum-coated silicon substrates using spin-coating at 5000 rpm for 30 s. In order to determine the crystallization temperature, LSCO thin films were dried for 5 min at 150°C and annealed for 30 min in a RTA furnace at different temperatures in the range between 350 and 650°C with a heating rate of 2°C/min from room temperature to 400°C and 10°C/min from 400 to 650°C.

For the transmission electron microscope (TEM) observations samples were thinned from the substrate side by mechanical grinding, dimpling and finally by ion milling. Using a Jeol 2000 FX analytical electron

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microscope, equipped with an EDXS system (Link AN 10000 with UTW Si(Li) detector), the degree of crystallisation and the chemical composition of the phases present were studied as a function of annealing temperature. Experimental selected-area electron diffraction (SAED) patterns were compared to calculated patterns in order to identify the phases. Simulated electron diffraction "powder" patterns were calculated using the EMS program package (Electron Microscopy Simulation program from Dr. P. Stadelmann, EPFL-CIME, Lausanne, Switzerland).[10]

As a result of the calculations, listings of the positions of the powder lines and the intensity of the lines were created. Intensities were calculated from the structure factors and corrected by a shape factor depending on the crystal size. Dynamical effects were not considered in the calculations. To be able to compare experimental and simulated patterns a program package was developed which was able to convert the calculated intensity distributions to SAED images.

3. Results

After annealing at 350°C the microstructure of the samples consisted of a matrix phase, where besides an

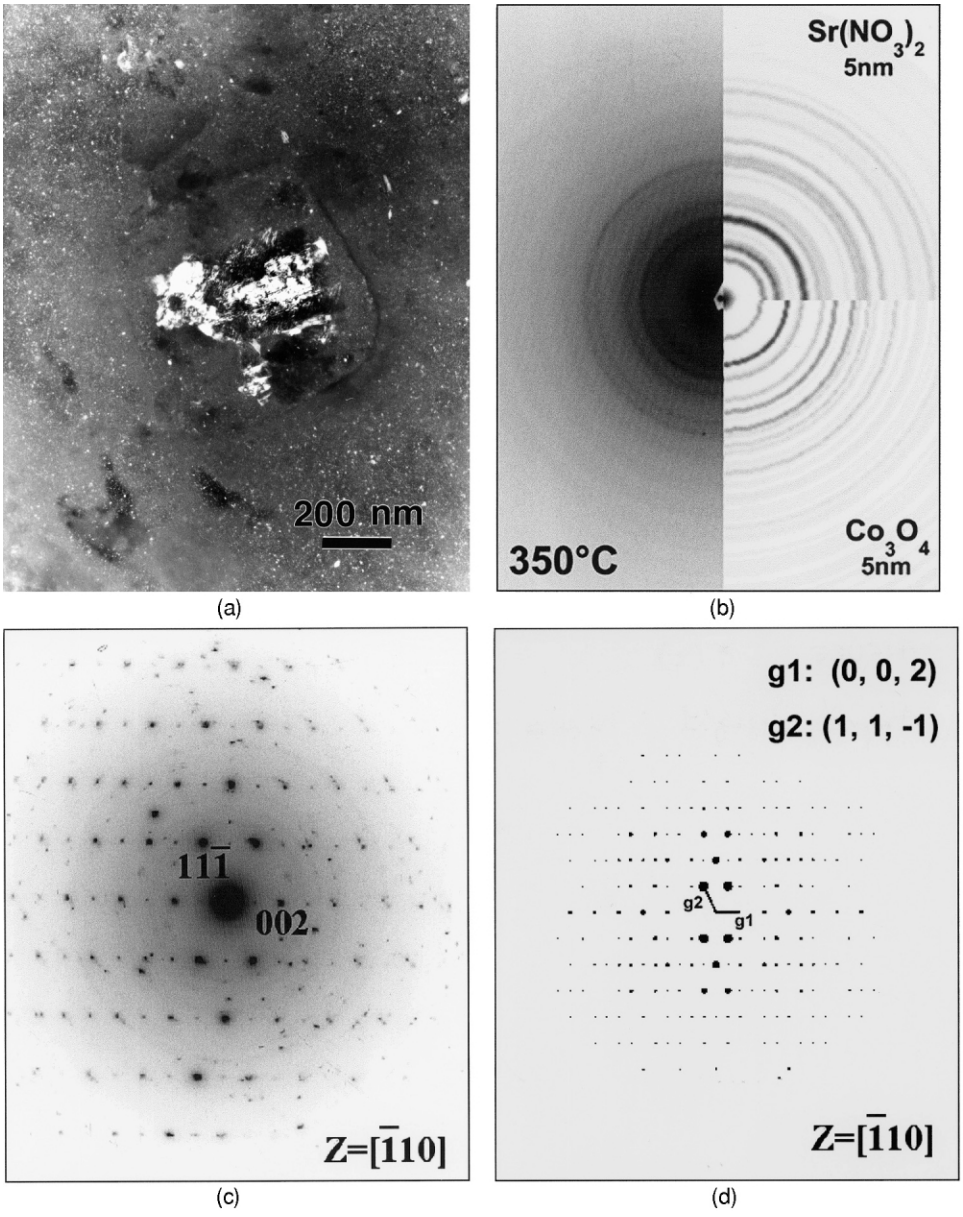

Fig. 1. Microstructure of the sample after annealing at 350°C: (a) TEM micrograph (dark-field image); (b) experimental SAED pattern compared to the calculated (simulated) pattern of $Sr(NO_3)_2$ (top right) and Co_3O_4 (bottom right); (c) experimental SAED pattern of regularly shaped crystal $SrCO_3$; (d) calculated SAED pattern of the cubic $SrCO_3$ phase in [−110] zone axis.

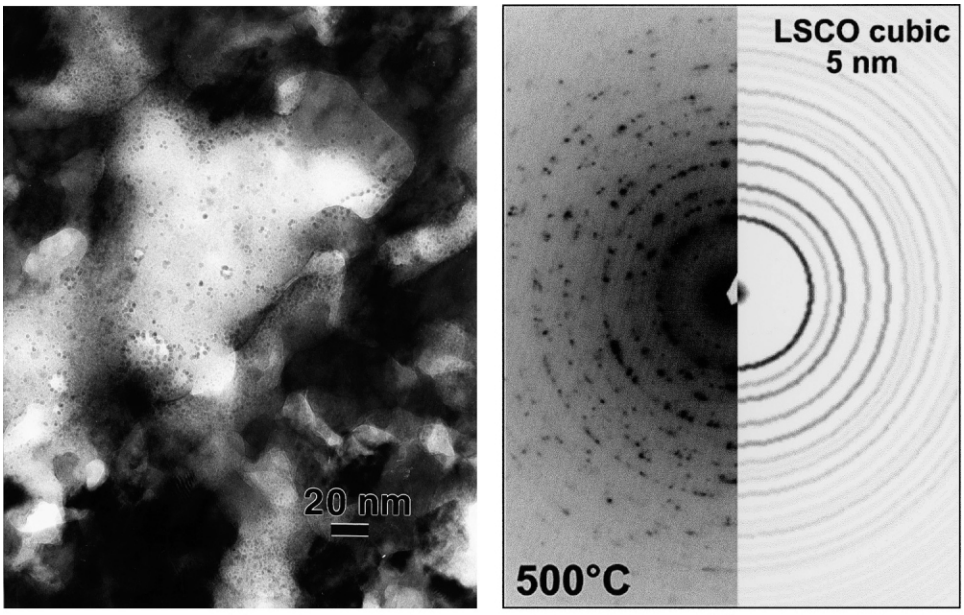

Fig. 2. Microstructure of the sample after annealing at 500°C: (a) TEM micrograph (bright-field image); (b) experimental SAED pattern (left) compared to the calculated (simulated) pattern (right) of cubic LSCO phase.

amorphous phase, fine crystallites with particle sizes of several nm were found using dark-field experiments. Next to the nanocrystals, a few regularly shaped crystals with sizes around 0.5 μm were observed [Fig. 1(a)]. In the SAED pattern of the matrix phase, uniform, slightly diffuse, circles were present indicating a very small particle size [Fig. 1(b)]. In order to identify the nanocrystalline phase the experimental SAED pattern was compared to simulated ones for various phases. No match was found for the cubic or the orthorhombic $La_{0.5}Sr_{0.5}CoO_3$ phase. The best fit was observed for the cubic $Sr(NO_3)_2$ and the cubic Co_3O_4 phase with a particle size around 5 nm [Fig. 1(b)].

From these results we assumed that the matrix phase is composed of an amorphous phase with uniformly distributed nanocrystals of cubic $Sr(NO_3)_2$ and Co_3O_4. The EDXS spectrum of the matrix phase was in accordance with this assumption showing strong peaks of Co and La and small peaks of Sr. From an EDXS spectrum of regularly shaped crystals it was found that this second phase is enriched in Sr. The SAED pattern of a regularly shaped crystal is shown in Fig. 1(c). The pattern could be indexed as $SrCO_3$. For comparison, a simulated SAED pattern of strontium carbonate in the [−110] zone axis is shown in Fig. 1(d).

In samples prepared at 500°C, besides the well-crystallised LSCO phase with a grain size of around 50 nm the presence of a secondary phase in the form of "islets" was found during the TEM analysis [Fig. 2(a)]. Using dark-field imaging it was determined that this phase is most probably amorphous. The experimental SAED pattern of the crystalline phase matches well with the calculated pattern of the cubic LSCO phase [Fig. 2(b)]. An EDXS spectrum of the secondary phase exhibits a lower La content compared to the LSCO phase.

TEM analysis of the samples after annealing at 650°C revealed a homogeneous and well-crystallised cubic LSCO phase with a grain size between 50 and 150 nm[9] [Fig. 3(a)]. The experimental SAED pattern matches well with the simulated pattern of the cubic $La_{0.5}Sr_{0.5}CoO_3$ phase [Fig. 3(b)].

4. Discussion

During annealing at low temperature (350°C), nanometer-sized crystals of Co_3O_4 and strontium nitrate appeared from the amorphous matrix. Due to the presence of larger $SrCO_3$ crystals the amorphous phase is La-rich, which is confirmed by EDX-spectra (according to Section 3). The origin of the large, regularly shaped crystals of strontium carbonate could be an Sr-containing compound (nitrate, oxide) which crystallise during the first stages of the samples preparation prior to annealing (spin-coating and drying). On annealing in air enriched with CO_2, which originated from the decomposition of PVA, this compound converts to strontium carbonate, retaining the starting morphology. Annealing the samples at 500°C produced mainly the perovskite

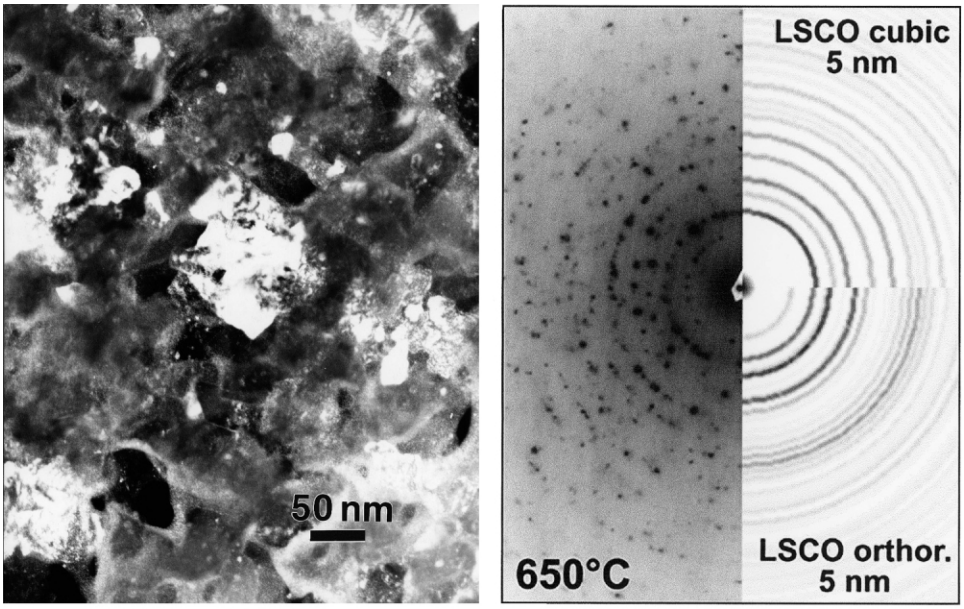

Fig. 3. Microstructure of the sample after annealing at 650°C: (a) TEM micrograph (dark-field image); (b) experimental SAED pattern (left) compared to calculated (simulated) pattern of cubic (top right) and orthorhombic (bottom right) LSCO phase.[9]

LSCO phase with some traces of an amorphous La-depleted phase. The presence of an amorphous phase of different stoichiometry indicates that the stoichiometry of the LSCO phase is not $La_{0.5}Sr_{0.5}CoO_3$. In samples fired at 650°C the pure perovskite LSCO phase was found.

5. Conclusions

Using analytical electron microscopy the evolution of the perovskite $La_{0.5}Sr_{0.5}CoO_3$ phase and the microstructure of thin films were studied. Samples prepared at 350°C were composed of an amorphous phase containing nanocrystals of $Sr(NO_3)_2$ and Co_3O_4. Besides these phases regularly shaped crystals, up to 0.5 μm, of $SrCO_3$ were found. In samples prepared at 500°C, the cubic LSCO phase with a grain size of 50 nm and amorphous "islets" were observed. After annealing at 650°C, TEM analysis revealed a homogeneous and well-crystallized perovskite phase with a grain size between 50 and 150 nm.

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References

1. Warren, W. L., Dimos, D. and Waser, R., Degradation mechanisms in ferroelectric and high-permittivity perovskites. *MRS Bull.*, 1996, **7**, 40–45.
2. Ramesh, R. et al., Scalling of ferroelectric properties in La–Sr–Co–O/Pb–La–Zr–Ti–O/La–Sr–Co–O capacitors. *Appl. Phys. Lett.*, 1994, **64**, 1588–1590.
3. Ramesh, R. et al., Ferroelectric La–Sr–Co–O/Pb–Zr–Ti–O/La–Sr–Co–O heterostructures on silicon via template growth. *Appl. Phys. Lett.*, 1993, **63**, 3592–3594.
4. Aggarwal, S., Yang, B. and Ramesh, R., Low voltage performance in lead based ferroelectric thin film memory elements with (La, Sr) CoO_3 electrodes. In *Thin Film Ferroelectric Materials and Devices*, ed. R. Ramesh. Kluwer Academic Publishers, Boston, 1997, pp. 221–241.
5. Masumoto, H., Hiboux, S. and Muralt, P., Preparation of $La_{1-x}Sr_xCoO_3$ electrodes for ferroelectric thin films by RF magnetron sputtering. *Ferroelectrics*, 1999, **225**, 335–341.
6. Mandeljc, M., Malič, B. and Kosec, M., Synthesis and characterization of lanthanum doped PZT. In *Procedings of the MIDEM Conference '99*, ed. S. Amon, L. Trontelj and I. Šorli. MIDEM, Ljubljana, 1999, pp. 229–234.
7. Wang, F., Uusimaki, A. and Leppavuori, S., Preparation of a $La_{0.5}Sr_{0.5}CoO_3/PbZr_{0.56}Ti_{0.44}O_3/La_{0.5}Sr_{0.5}CoO_3$ multilayer structure on $SrTiO_3(100)$ and $LaAlO_3(100)$ substrates using the sol-gel method. *Appl. Phys. Lett.*, 1995, **67**(12), 1692–1694.
8. Kim, B. J., Lee, J. and Yoo, J. B., Sol-gel derived (La,Sr)CoO_3 thin films on silica glass. *Thin Solid Films*, 1999, **341**, 13–17.
9. Javorič, S., Kosec, M. and Malič, B., Water-based synthesis of $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) electrodes for ferroelectric thin films. *Integrated Ferroelectrics*, in press.
10. Stadelmann, P. A., EMS — a software package for electron-diffraction analysis and HREM image simulation in materials science. *Ultramicroscopy*, 1987, **21**(2), 131–145.