In-Situ High Temperature Characterization of La-Cr-O Thin Films by XRD, Raman, and TEM

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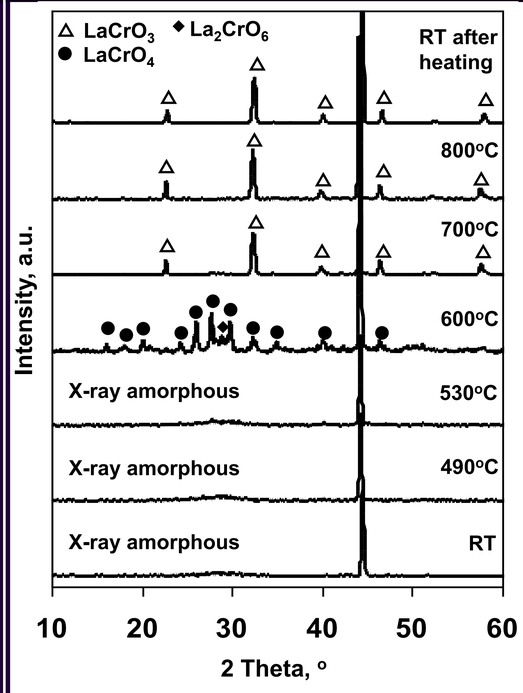
Introduction

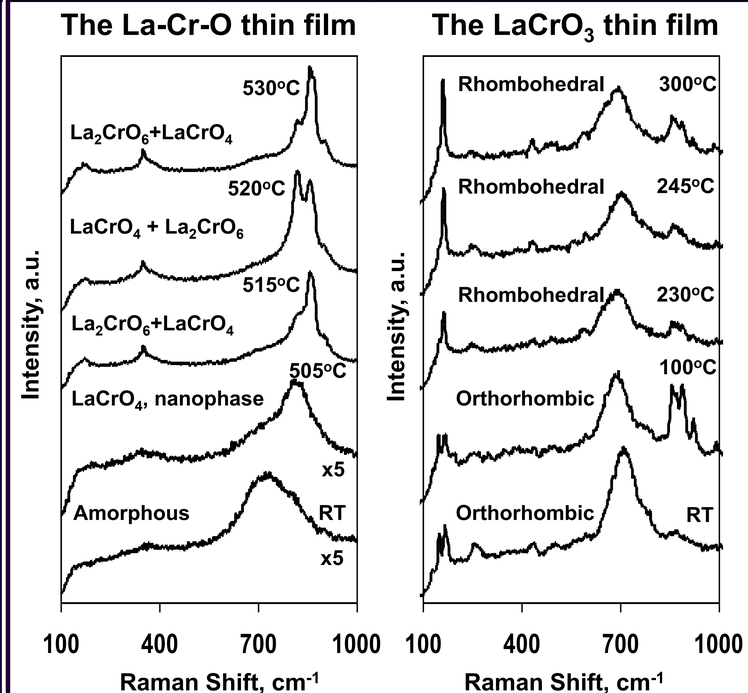
Catalytically active self-organized nano structured $LaCrO_3$ thin film is a prospective material for perovskite related membrane reactors for synthesis of the syngas ($CO+H_2$) and for the high purity oxygen separation by selective diffusion. It also can be used as a protective coating against oxidation and corrosion of metallic interconnect for lower temperature SOFCs. For La-Cr-O based films deposited by magnetron sputtering, the films are typically amorphous because of unheated substrates. The films can be transformed to the required $LaCrO_3$ orthorhombic perovskite structure by additional annealing. In this work results of high temperature XRD, micro-Raman and TEM study of the structural evolution of La-Cr-O → $LaCrO_4$ → $LaCrO_3$ thin films are reported. A structural analysis of the film development as a function of temperature and environment is presented. The unique film structure is detected.

XRD Analysis of La-Cr-O Thin Film



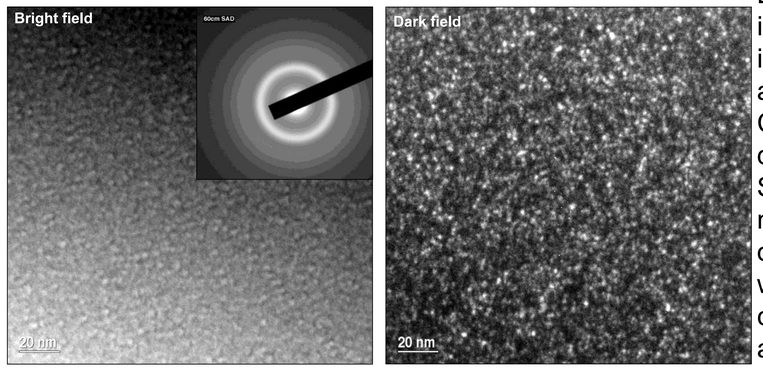
In situ XRD was performed to study the structural evolution of the RF deposited La-Cr-O thin film during the heating in air. First, local ordering of X-ray amorphous film occurs via nucleation and subsequent growth that leads to a formation of medium range and short range ordered clusters. Such locally ordered phase has no characteristics of a crystalline phase such as visible peaks or diffraction spots in XRD or SAED patterns. Further heating initiates long range ordering of the monoclinic monazite type $LaCrO_4$ and La_2CrO_6 phases following by the formation of $LaCrO_3$ orthorhombic perovskite. Therefore, the thin film with a nanoporous self organized microstructure is formed as a result of the two consecutive phase transitions by heat induced processes from the amorphous La-Cr-O state.

Raman Spectra during Heating of La-Cr-O and $LaCrO_3$ Thin Films

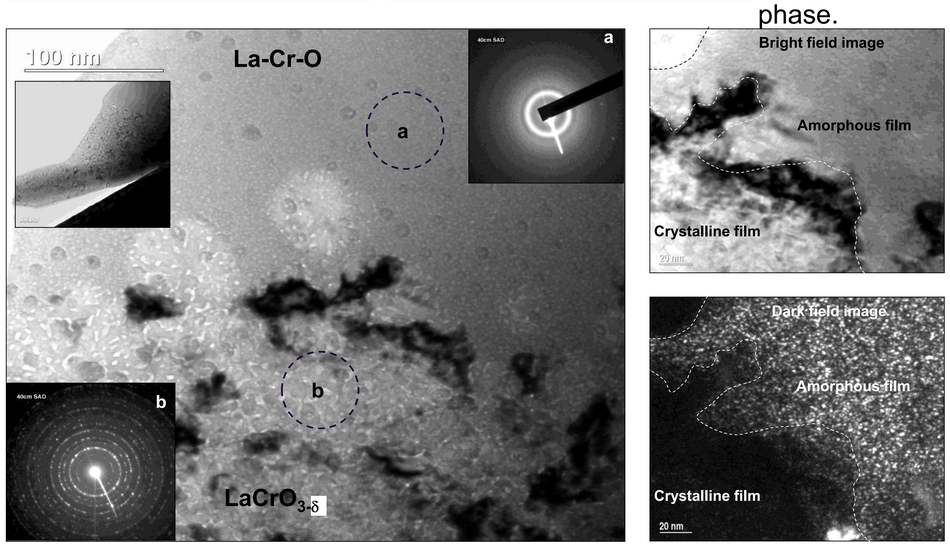


In situ micro-Raman spectroscopy was used to study the vibrational properties of La-Cr-O and $LaCrO_3$ thin films. Both La-Cr-O to $LaCrO_4$ (La_2CrO_6) phase transition at 505-515°C and $LaCrO_3$ thin film orthorhombic to rhombohedral phase transition at 230°C were demonstrated. Bands belonging to $LaCrO_4$ and La_2CrO_6 phases have also been detected during the heating of orthorhombic $LaCrO_3$ at 100°C in air.

TEM of La-Cr-O Amorphous Thin Films

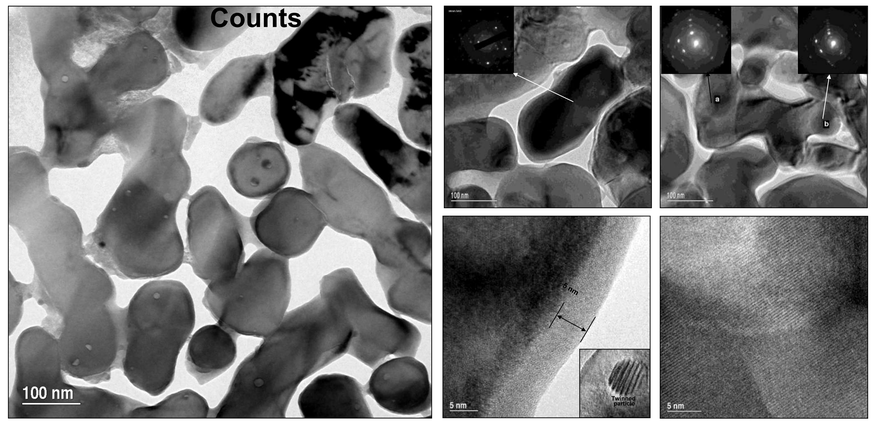


Local structural inhomogeneities in X-ray amorphous La-Cr-O as deposited film; Short-range to medium-range ordered clusters with no characteristics of a crystalline phase.

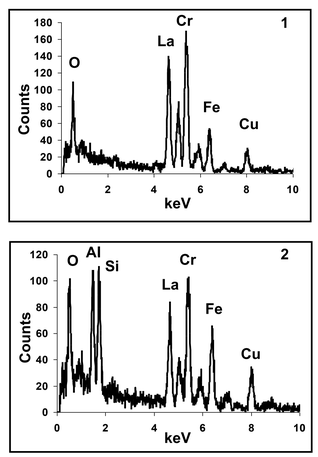


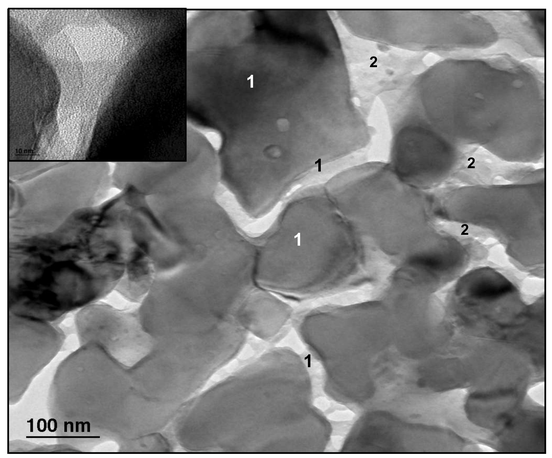
A La-Cr-O sample after heating at 760°C for ~1 hour in the microscope column

TEM of $LaCrO_3$ Perovskite Thin Films, 800°C, 1 h, in air



Bright field TEM micrographs of $LaCrO_3$ perovskite thin film





Chemical composition of $LaCrO_3$ grains and intergranular phases

Summary

- As a result of annealing at different temperatures, different film structures have been formed. The "as-deposited" La-Cr-O thin film was found to be X-ray amorphous with no visible spots in electron diffraction pattern, but after annealing in air, the film transforms first to a mixture of $LaCrO_4$ monazite type monoclinic phase and La_2CrO_6 phase at 600°C and further to the orthorhombic $LaCrO_3$ perovskite phase at 700-800°C
- While no electron diffraction spots can be seen in SAED pattern for La-Cr-O thin film, however its structure consists of short- to medium-range clusters with a size of 1-2nm.
- The $LaCrO_3$ orthorhombic to rhombohedral phase transition at 230°C has been demonstrated by in-situ micro-Raman spectroscopy.
- While annealing of the La-Cr-O thin films in air leads to formation of two consecutive phase transitions with a final orthorhombic $LaCrO_3$ perovskite phase, the annealing of La-Cr-O in vacuum in the TEM column leads to formation of orthorhombic $LaCrO_3$ structure directly at 750-800°C without any intermediate phases.

Acknowledgments

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