



ELNES study of chemical solution deposited $\text{SrO}(\text{SrTiO}_3)_n$ Ruddlesden–Popper films: Experiment and simulation

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ARTICLE INFO

Article history:

Received 18 May 2009

Received in revised form

27 August 2009

Accepted 9 September 2009

PACS:

79.20.Uv

71.15. – m

Keywords:

Ruddlesden–Popper

ELNES

DFT

Chemical solution deposition

ABSTRACT

This article analyzes electron energy-loss near-edge fine structures of the $\text{SrO}(\text{SrTiO}_3)_n$ Ruddlesden–Popper system and of the parent compounds SrTiO_3 and SrO by comparison with first principles calculations. For that, the fine structures of chemical solution deposited Ruddlesden–Popper films have been experimentally recorded by means of transmission electron microscopy. Moreover, density of states computations using an all-electron density-functional code have been performed. It is shown that the appearance and shape of the experimental O–K and Ti– $L_{2,3}$ fine structure features result from the crystallography-dependent electronic structure of the investigated oxides, which display technologically interesting dielectric as well as lattice–structural properties.

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1. Introduction

Layered ternary oxides with the composition $\text{AO}(\text{ABO}_3)_n$ exhibit a large variety of physical properties, among them thermoelectricity, magnetism, electronic and ionic conductivity [1–4]. The nature and magnitude of these specific properties can be modified by the choice of the cations A and B and of the ABO_3 : AO ratio n , which depends on the synthesis conditions. For the standard Ruddlesden–Popper phases with $A = \text{Sr}$ and $B = \text{Ti}$ [5] and for related compounds with two- and four-fold positive cations recent experiments have revealed excellent thermoelectric properties upon doping with transition-metal and rare-earth elements [1,2,6–8]. Magnetism can be introduced by choosing a magnetic B ion [3,4,9,10]. Charge ordering phenomena with strong consequences for the electronic conductivity result if the A site is partially occupied by cations with two different charges, and the B cation is multivalent [11–13], or if oxygen vacancies are formed in

an oxygen-deficient environment [4]. If B is simultaneously magnetic and multivalent, one may even arrive at multifunctional materials, in which the different functions are coupled and external fields acting on one functionality simultaneously also affect the other one [14,15].

In the present study we focus on the spectroscopic properties of the original Ruddlesden–Popper (RP) system $\text{SrO}(\text{SrTiO}_3)_n$. RP phases have been suggested as materials for a tunable X-ray monochromator [16], because earlier X-ray investigations indicated that RP phases reversibly form in an external electric field. Earlier theoretical studies focused on the stability, electronic and dielectric properties of the lower members of the series [17,18] as well as on layered compounds with the parent oxides SrO and SrTiO_3 [19–21]. For the lower members of the series density-functional-based effective mass calculations exhibit a thermoelectricity superior to the one of the parent compounds [22]. Depending on the chemical environment very thin layers of Ruddlesden–Popper phases can form on the surface of SrTiO_3 [23], yet, such scales are prone to island formation such as TiO_2 on SrTiO_3 [24]. Due to the technological complexity of accurate layer-by-layer growth using molecular beam epitaxy [25] or pulsed laser deposition [26], chemical solution [27,28] and mechanical activation synthesis routes [29] have recently attracted attention.

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The chemical solution procedure promises a low-cost route to the large-scale fabrication of thin films. Imaging in the transmission electron microscope (TEM) has shown the high regularity of the crystal structure of the lower members of the series [29].

For an application in an optical device both this regularity of the layered structure and the concomitant electronic properties of the film are of key importance. Thus, the present study aims at evaluating the electronic and spectroscopic properties of such chemical solution deposited films by a combination of near edge fine structures in electron energy-loss edges in the TEM and all-electron density-functional analyses of the corresponding densities of electronic states. Special focus is on the short- to medium-range local atomic structure and its influence on the electronic properties, as recent investigations [30,31] suggest such more long-range correlations beyond the established fingerprinting of the first coordination shell [32]. The present study is organized as follows: after the introduction Section 2 describes briefly the structure of $(\text{SrTiO}_3)_n\text{SrO}$ crystallographic shear phases. The experimental and computational details are given in Section 3. Section 4 reports on TEM as well as on computational results, which are then discussed comparatively. Finally, Section 5 draws conclusions regarding the consequences for fingerprinting RP phases.

2. Crystal structure of $\text{SrO}(\text{SrTiO}_3)_n$ Ruddlesden–Popper phases

The parent structures of the RP [5] compounds in the Sr–Ti–O system are the cubic perovskite SrTiO_3 [33] and the cubic rock-salt type SrO [34]. In a simple model, the crystal structure of the RP phases $\text{SrO}(\text{SrTiO}_3)_n$ [35] is composed of layers of n SrTiO_3 unit cells that are separated by an additional SrO(001) layer. These structures show tetragonal symmetry with the described layers perpendicular to the fourfold axis. For the first two members with $n = 1$ and 2, this is visualized in Fig. 1. In the Sr–Ti–O system, only the RP phases up to $n = 3$ have been found as thermodynamically stable regular compounds. From $n = 4$ on pronounced phase intermixing is obtained [29].

Structure data for the phases used in this paper are presented in Table 1. Since all atoms of the additional SrO(001) layer

experience SrO-type coordination from one side and SrTiO_3 -type coordination from the other, these atoms possess an environment which is unique for the RP phases and which promises potential for fingerprinting. It may as well be seen as a regularly built-in extrinsic stacking fault, created by shifting two adjacent SrTiO_3 units by a lattice vector $(0.5\ 0.5\ 0)$ against each other. Compared with the cubic phases, the atomic site symmetries are lower for all sites in the RP phases, and in particular there exist $n+1$ symmetrically inequivalent O sites. The altered atomic environment leads to distortions of the atomic distances and of the TiO_6 octahedra with respect to the cubic phases. These are strongest for the RP $n = 1$ phase, however, the distortions here act equally from both sides on the SrTiO_3 layer, leading to a perfectly tetragonal distortion of the octahedron. Most significant is a compression of the c axis (perpendicular to the layers) by about

Table 1
Crystal structure data for SrO, SrTiO_3 , and RP $n = 1$.

SrO [34]			
Space group $225\text{Fm}\bar{3}\text{m}$			
$a = 5.140\text{Å}$			
Atom	x	y	z
Sr(4a)	0	0	0
O(4b)	0.5	0.5	0.5
SrTiO_3 [33]			
Space group $221\text{Pm}\bar{3}\text{m}$			
$a = 3.901\text{Å}$			
Atom	x	y	z
Sr(1a)	0	0	0
Ti(1b)	0.5	0.5	0.5
O(3c)	0.5	0.5	0
RP $n = 1$ [35]			
Space group $139\text{I4}/\text{mmm}$			
$a = 3.889\text{Å}$			
$c = 12.600\text{Å}$			
Atom	x	y	z
Sr(4e)	0	0	0.355
Ti(2a)	0	0	0
O1(4c)	0	0.5	0
O2(4e)	0	0	0.152

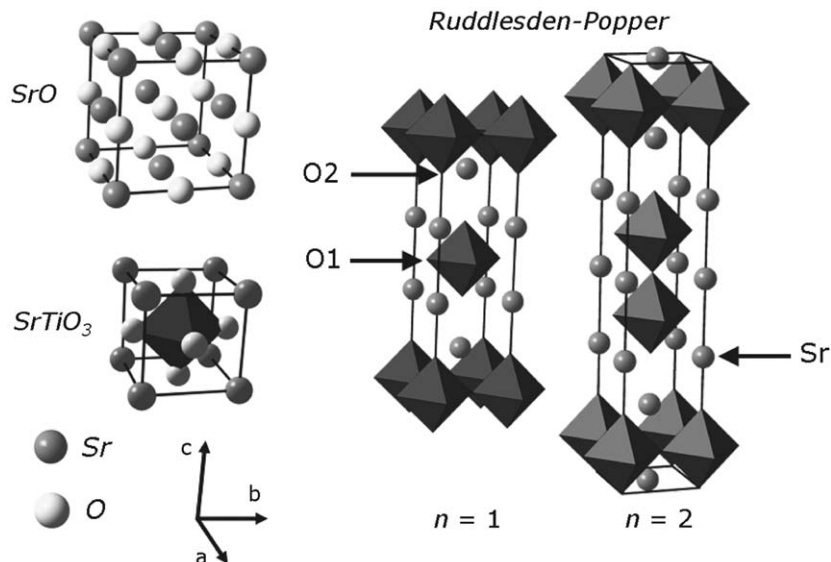


Fig. 1. Drawing of the SrO, SrTiO_3 , and Ruddlesden–Popper $n = 1$ and 2 crystal structures. The TiO_6 octahedra are indicated in black/dark gray. O atoms occupy the corners, and are not drawn in the RP phases. Ti, occupying the center of the octahedra, were omitted for clarity. Unit cells are outlined. Not to scale.

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