Journal of Alloys and Compounds 657 (2016) 631–638

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Properties of rare-earth orthoferrites perovskite driven by steric hindrance

Emile Haye [a, *], Fabien Capon [a], Silvère Barrat [a], Pascal Boulet [a], Erwan Andre [b], Cédric Carteret [b], Stéphanie Bruyere [a]

[a] Institut Jean Lamour, UMR 7198, CNRS-Université de Lorraine, Parc de Saurupt, 54011 Nancy Cedex, France
[b] Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR7564, 405 Rue de Vandoeuvre, 54601 Villers-lès-Nancy, France

ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form
19 September 2015
Accepted 16 October 2015
Available online 20 October 2015

Keywords:
Thin films
Perovskite
Crystallization kinetic
Goldschmidt factor

ABSTRACT

$REFeO_3$ (RE = La, Pr, Nd, Sm) perovskites present interesting properties and are studied for their potential applications as smart devices and the requirement of miniaturization and low power consumption in such electronic components has led to the development of thin films. The understanding of crystallization mechanisms and the characterization of such perovskites are thus important to understand their properties. In this study, we purpose a systematic comparison of structural, optical and electrical properties of $REFeO_3$ thin films, and we investigate the direct link between properties and crystallographic distortion. The as-deposited films are annealed in air under XRD measurements in order to investigate their complete crystallization kinetic, using Johnson Mehl Avrami Kolmogorov model. TEM observations of films are in agreement with this model. Then, optical and electrical characterization of films were performed by using UV–visible spectroscopy, Fourier Transform Infrared spectroscopy (FTIR), and 4-probes measurements. We found that the activation energy of crystallization, the infrared vibration mode position and the activation energy of conduction mechanism are driven by distortion of the perovskite, which can be described by the Goldschmidt tolerance factor. All the studied properties are shifted due to decrease of RE ionic radius and the direct relationship between structural distortion and physical properties shifting is discussed.

1. Introduction

Lanthanum orthoferrite $LaFeO_3$ has received considerable attention last decades due to its singular properties, with potential application as smart devices (gas sensors, magnetic devices or photocatalytic system [1–3]). The Rare Earth orthoferrites have the formula $REFeO_3$ (RE = rare earth). They crystallize in the distorted perovskite structure (orthorhombic space group: Pnma). The structure can be described as a three dimensional network of FeO_6 octahedra surrounding RE atoms, where Fe–O–Fe angle deviates from 180°. This angle directly depends on RE size: the larger the RE is, the more the chains of octahedra stretch, and the Fe–O–Fe bond angle approaches 180°, and the lattice tends to be cubic. This angle directly drives distance between oxygen 2p orbitals and iron 3d orbitals, which are mainly responsible of electrical and optical properties. The distortion makes thus the system interesting in order to understand the relationship between structure and properties.

In this work, $REFeO_3$ (RE = La, Nd, and Sm) thin films were prepared using reactive magnetron co-sputtering. The effects of the RE composition on the structural, electrical and optical properties were investigated. The kinetics of the crystallization was examined with a goal of understanding mechanisms and the optimal conditions of the post-annealing. The resistivity was precisely determined in addition to spectrophotometry measurements including UV–Vis–NIR and FTIR in far infrared range. We purpose to link properties shifting and distortion of the structure.

2. Materials and methods

Thin films were synthesized by reactive magnetron co-sputtering from two RE (RE = La, Pr, Nd, Sm) and Fe metallic targets at 0.5 Pa. Films have been deposited with a Ar/O_2 flow rate ratio of 21/7 sccm (standard cubic centimeter per minutes), on (100) undoped silicon and amorphous silica (500 μm thick)

* Corresponding author.
E-mail address: emile.haye@univ-lorraine.fr (E. Haye).

http://dx.doi.org/10.1016/j.jallcom.2015.10.135
0925-8388/

Table 1
Deposition conditions.

$D_{target-substrate}$ RE	55 mm	Ar flow rate	21 sccm
$D_{target-substrate}$ Fe	70 mm	O_2 flow rate	7 sccm
Substrate temperature	673 K	Working pressure	0.5 Pa

Discharge characteristic	Fe target	RE target	Duration	Thickness
LaFeO3	0.2 A	110 W	120 min	430 nm
PrFeO3	0.2 A	70 W	120 min	410 nm
NdFeO3	0.2 A	70 W	120 min	370 nm
SmFeO3	0.2 A	70 W	120 min	415 nm

substrates. A radiofrequency (RF) pickling is applied, in order to remove possible contamination of substrate. Direct current (DC) supplier has been used on Fe target, and pulsed DC (4 μs, 50 kHz) was used for the different RE. The argon and oxygen flow rates were controlled by Alphagaz RDM 280 flowmeters, and the total pressure was measured with Baratron gauge, a throttle valve allowing accurate control of the working pressure. Deposition conditions are summarized in Table 1. The targets, with a diameter of 50 mm were positioned at the distance of 70 and 55 mm, for Fe and La respectively, from the rotating substrate holder. A heating element is connected to the substrate holder, which allowed a substrate temperature up to 1073 K. The parameters for the discharge have been fixed at 0.2 A on Fe target, 110 W on La target, and 70 W on Pr, Nd and Sm targets. On RE targets, discharge was controlled by the adjustment of the power which was preferred to a current regulation due to the electrical instabilities. Substrate holder temperature was fixed at 673 K to be under crystallization temperature and in order to minimize the stresses due to the difference of thermal dilatation coefficient between the substrate and the film. At this deposition temperature the films remain amorphous and their morphology is finally equiaxed grain after a post-annealing. The ratio RE/Fe was checked by EDS analysis, in a Philips FEG XL30s scanning electron microscope. Film's thicknesses were measured by SEM cross-section observation, and are given in Table 1. X-ray diffraction (XRD) was performed at room temperature using Bragg-Brentano θ/2θ measurements on a D8 Advance Bruker diffractometer (λ CuKα$_1$ = 1.54056 Å) and the in-situ temperature measurements were performed on a θ/θ D8 Discover diffractometer (λ CoKα = 1.79025 Å), equipped with a domed-hot stage DHS1100. Optical properties of films were measured by different spectroscopic measurements. UV–Vis–NIR spectrometer Varian Cary 5000 (0.2–0.8 μm) reveals the absorption edge of the $REFeO_3$ and bandgap. For infrared measurements, a Nicolet 6700 FTIR was used for the IR absorbance in far infrared from 100 to 200 cm^{-1} (50–100 μm). Measurements were done with nitrogen purge. The baseline was previously obtained on an uncoated substrate. The resistance versus temperature was measured up to 873 K via a heating stage Linkam® associated with a four probes system. At the nanometer scale, films morphology was investigated by Transmission Electron Microscopy (TEM). A JEOL ARM 200 – cold FEG transmission electron microscope operating at 200 kV and equipped with a DRY SD30VG energy-dispersive X-ray spectrometer (EDS) was used. Samples were prepared for TEM by wedge cleavage.

3. Results and discussion

3.1. Structural properties

After deposition, XRD analyses were performed on as-deposited samples, and show amorphous structure. Then, the films were heated up under XRD measurements from room temperature to 698 K at a 8 K/s and then from 700 K to 1000 K, with a step of 25 K. The XRD diagrams are recorded using a step size of 0.02° and 3 s per step (Fig. 1). The crystallization temperature increases when the radii of the RE ions decreases and occurs at around 800, 825, 875, 925 K respectively for $LaFeO_3$, $PrFeO_3$, $NdFeO_3$ and $SmFeO_3$ thin

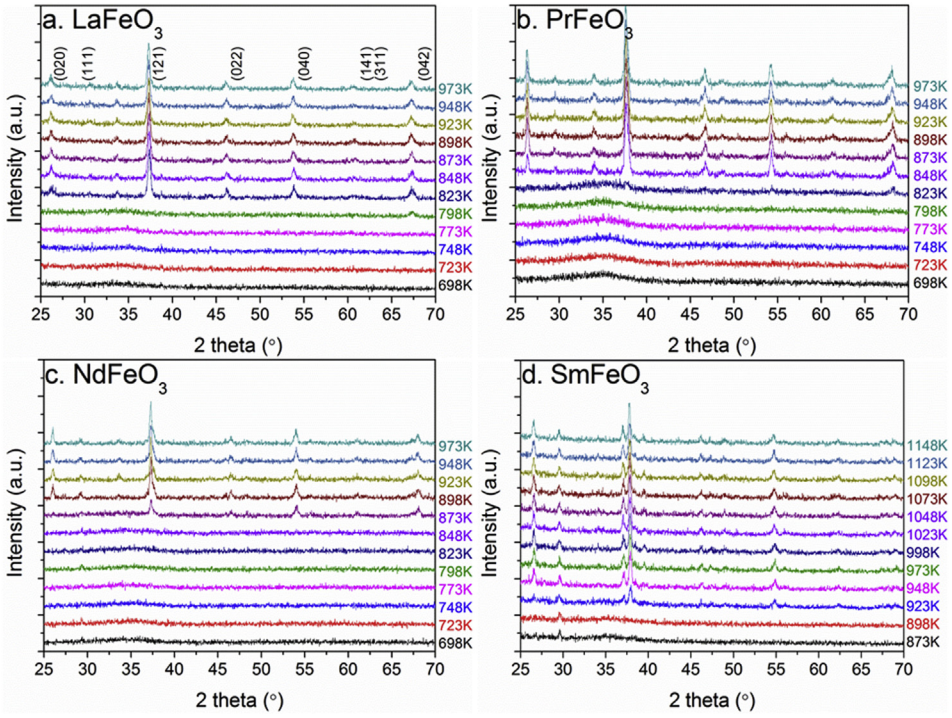

Fig. 1. XRD patterns of REFeO3 film at different temperatures (Co Kα: 1.79025 Å).