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Thin (111) oriented $CoFe_2O_4$ and Co_3O_4 films prepared by decomposition of layered cobaltates

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ABSTRACT

The formation and structural characterization of highly (111)-oriented Co_3O_4 and $CoFe_2O_4$ films prepared by a novel procedure from 00l-oriented $NaCoO_2$ and $Na(CoFe)O_2$ is reported. The $Na(CoFe)O_2$ films were deposited on MgO, $SrTiO_3$, $LaAlO_3$, and $Zr(Y)O_2$ single crystals with (100) and (111) orientations by chemical solution deposition method and crystallized at 700 °C. Subsequently they were transformed into (111)-oriented spinel phase during post-growth annealing at 800–1000 °C. Morphology and structure of the films was investigated by means of scanning electron microscopy and X-ray diffraction. While all spinel films exhibit pronounced out-of-plane orientation irrespective of substrate, the rate of in-plane orientation strongly depend on lattice misfit values. Different epitaxial phenomena ranging from true one-to-one epitaxy to the existence of many-to-one epitaxy involving two or more orientations were determined by full 3D texture analysis.

1. Introduction

Iron and cobalt oxides form an important class of materials [1]. $CoFe_2O_4$ is a good candidate for applications in magneto-optical technology [2–4] and more recently it has also been used in multiferroic composite materials [5]. Considering the need in today's technologies to downsize the components in electronic and telecommunication devices, the most urgent step is to prepare ferrite materials in a form of thin films. $CoFe_2O_4$ and Co_3O_4 crystallize in cubic spinel structure with a face-centered cubic (fcc) oxide anion sublattice. The crystal structure of spinels along the [111] direction is the hexagonal primitive (oblique) and the O^{2-} sublattice in spinels presents in the [111] direction an fcc stacking sequence ABCA.

Layered transition metal oxides with α-$NaFeO_2$ or γ-$NaCoO_2$ type structures have been thoroughly investigated due to their possible use as materials in rechargeable ion batteries and thermoelectric energy conversion devices [6]. Due to their structural complexity, these compounds are systematized according to the anion environment around the alkali metal and the size of the repeat unit perpendicular to the alkali metal layer [7]. For example, O3 refers to a structure with octahedrally coordinated alkali ions and a stacking of three CoO_2^- layers. Similarly, P2 refers to a structure with trigonal prismatic coordinated alkali ions and a stacking of two CoO_2^- layers.

$Na(CoFe)O_2$ compound crystallizes in rhombohedral structure, space group $R\bar{3}m$ (a = 0.2975 nm, c = 1.595 nm [8]). The crystal structure consists of two-dimensional triangular lattice of $(CoFe)O_2^-$ layers of edge sharing $(CoFe)O_6$ octahedra separated by sodium ions. Adjacent $(CoFe)O_2^-$ layers are offset laterally to create a three-layer O3 structure. The sodium atoms occupy the octahedral holes between these layers. Four different phases have been reported in the thermodynamic $NaCoO_2$ chemical system. Among the known three $NaCoO_2$ phases forming the O3 structures the so called α-$NaCoO_2$ phase crystallizes in rhombohedral structure, space group $R\bar{3}m$. The coordination of sodium ions in these structures is octahedral. Only one thermodynamic phase delineated as γ-phase phase exhibits a two-layer P2 structure. Its crystal structure consists of layers of edge-sharing rhombohedrally distorted CoO_6^{3-} octahedra separated by an insulating layer of Na^+ ions forming trigonal NaO_6 prisms. Along the [001] direction, the O^{2-} sublattice in $Na(CoFe)O_2$ and α-$NaCoO_2$ form ABCA sequence with ccp symmetry, while the

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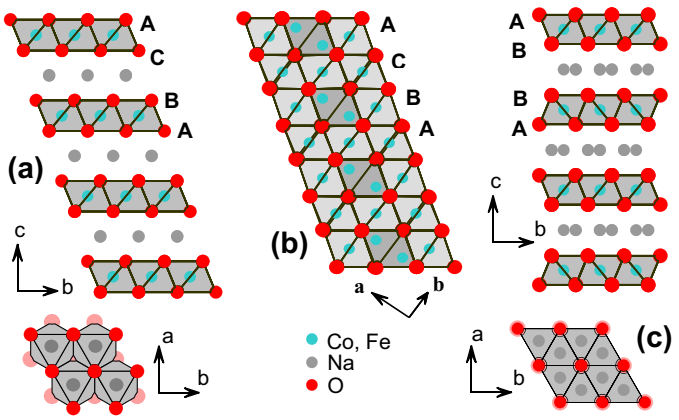

Fig. 1. Schematic diagram of the crystal structures of (a) rhombohedral O_3-type $NaCoO_2$, (b) cubic $CoFe_2O_4$, and (c) hexagonal P2-type $NaCoO_2$.

O^{2-} sublattice in γ-$NaCoO_2$ forms ABBA sequence with hexagonal symmetry. The crystal structures of all related compounds are depicted in Fig. 1.

A variety of methods has been applied for the deposition of ferrite thin films, namely, atomic layer deposition (ALD, [9]), molecular beam epitaxy (MBE, [10,11]), pulse laser deposition (PLD, [12–15]). Using these relatively sophisticated and cost expensive methods epitaxially grown thin films can be prepared. Taking into account drawbacks of these methods such as small area of deposition, wastage of depositing material, necessity to clean the working chamber after each deposition, and high investment and working costs, chemical solution deposition (CSD) method can be used as a convenient alternative [16]. In spite of considerable effort to obtain oriented spinel films by means of CSD methods, the literature on their successful preparation remains very scarce. In vast majority spinel films exhibiting random orientation growth are obtained [17–20].

In their previous work [21] the present authors found that (111)-oriented Co_3O_4 thin films can successfully be prepared on α-Al_2O_3(001) substrate by means of CSD method through the transformation of (001)-oriented $NaCoO_2$ thin films. Two factors play crucial role in this procedure: (i) $NaCoO_2$ growths in self-texture mode with c-axis perpendicular to the film plane, and (ii) during crystallization anneal $NaCoO_2$ phase is prone to become deplenished in sodium due to its high volatility. When annealing conditions are properly optimized, the 00l-oriented $NaCoO_2$ transforms into (111)-oriented Co_3O_4 films.

The question arises whether it would be possible to extend its use towards spinel films with technologically more important compositions, or whether another types of substrates can successfully be used. The aim of the present work was to examine the possibility of preparation of oriented Co_3O_4 and $CoFe_2O_4$ thin films on MgO, $SrTiO_3$, yttrium stabilized ZrO_2 ($Zr(Y)O_2$), and $LaAlO_3$ (all with both (100) and (111) orientation) by means of CSD method through the transformation of (001)-oriented layered cobaltates.

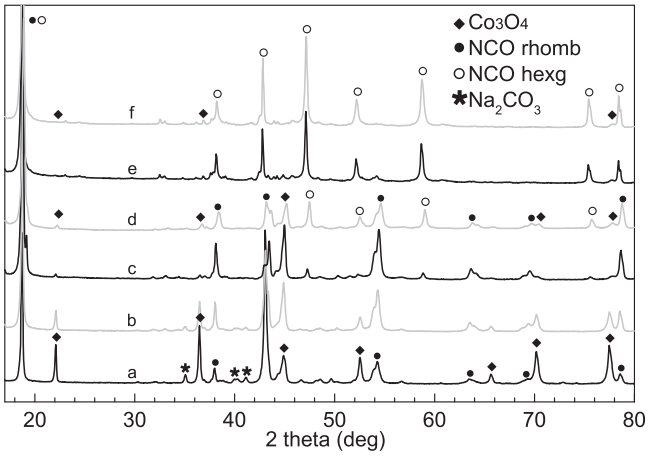

Fig. 2. θ–θ XRD patterns of $NaCoO_2$ powders heat treated under different conditions: (a) 600 °C/60 min; (b) 650 °C/60 min; (c) 700 °C/60 min; (d) 750 °C/15 min; (e) 750 °C/30 min; (f) 800 °C/15 min.

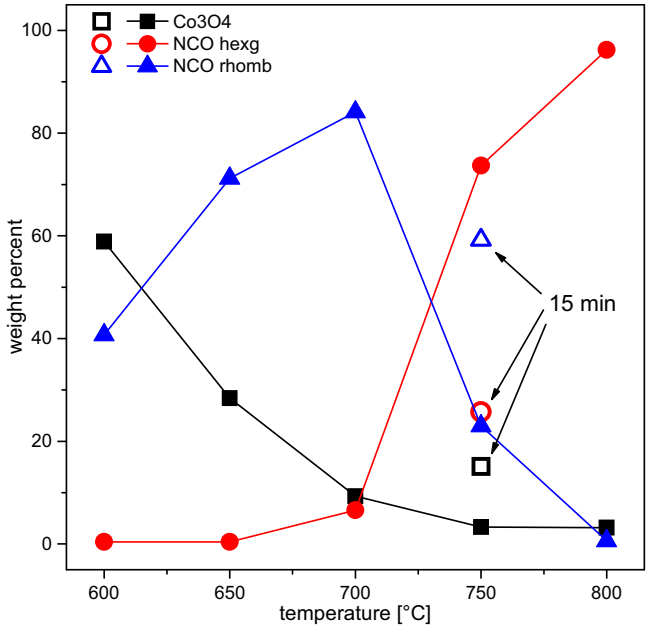

Fig. 3. Development of quantitative phase composition in $NaCoO_2$ powders during annealing under different conditions. Full symbols: samples were annealed for 60 min; empty symbols: samples were annealed for 15 min. Calculations were done using Rietveld analysis of XRD patterns shown in Fig. 2.

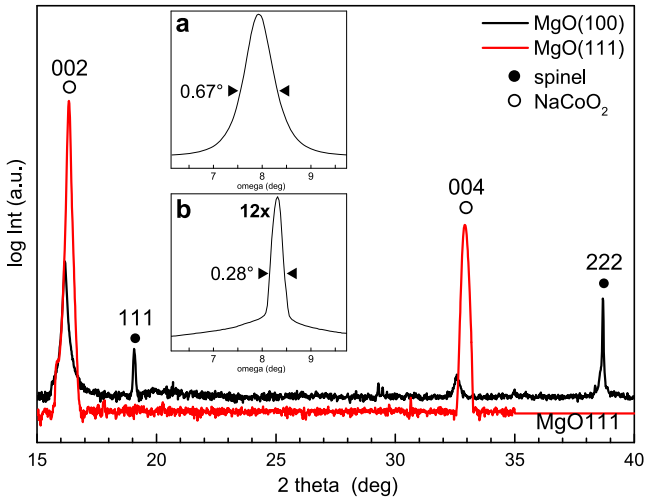

Fig. 4. XRD patterns of $NaCoO_2$ thin films deposited on MgO(100) and MgO(111) substrates and heat treated at 800 °C (intensity in logarithmic scale), together with nested figures of omega scans measured on 002 reflection of $NaCoO_2$ for (a) film on MgO(111), and (b) film on MgO(100). The intensity of omega scan measured on MgO(100) was multiplied by factor 12.