

Synthesis of an oxygen nonstoichiometric $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase

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Received 19 May 2005; received in revised form 6 October 2005; accepted 10 October 2005

Available online 8 November 2005

Abstract

$\text{Sr}_6\text{Co}_5\text{O}_{15}$, a member of the $(\text{A}_3\text{Co}_2\text{O}_6)_m(\text{A}_3\text{Co}_3\text{O}_9)_n$ [$\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$] series, showed oxygen nonstoichiometry. $\text{Sr}_6\text{Co}_5\text{O}_{15.12}$, $\text{Sr}_6\text{Co}_5\text{O}_{14.98}$, $\text{Sr}_6\text{Co}_5\text{O}_{14.45}$ and $\text{Sr}_6\text{Co}_5\text{O}_{14.26}$ were prepared by a solid state reaction in air. The $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase is stable in the temperature range of 873–973 K in air, there are structure transitions at 773 K and above 1023 K. With the loss of oxygen, the a -axis parameter of the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase decreased from 9.4988(3) Å ($\text{Sr}_6\text{Co}_5\text{O}_{15.12}$) to 9.4390(4) Å ($\text{Sr}_6\text{Co}_5\text{O}_{14.26}$) and the c -axis parameter increased from 12.3772(3) Å ($\text{Sr}_6\text{Co}_5\text{O}_{15.12}$) to 12.5066(4) Å ($\text{Sr}_6\text{Co}_5\text{O}_{14.26}$) with decreasing oxygen content. The Rietveld analysis of the powder X-ray diffraction data suggested that the increase in the c -axis was mainly due to the increase in the Co–Co distance between the CoO_6 trigonal prism and CoO_6 octahedron.

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Keywords: A. Ceramics; A. Oxides; C. Thermogravimetric analysis; C. X-ray diffraction; D. Crystal structure

1. Introduction

The oxygen content in the SrCoO_{3-x} system is one of the factors determining the phase stability and crystal structure; the orthorhombic (brownmillerite-type), cubic (perovskite-type) and rhombohedral phases are the main phases that have been studied [1–12]. The rhombohedral phase, which is thought to have a hexagonal BaNiO_3 -type structure, is currently known as $\text{Sr}_6\text{Co}_5\text{O}_{15}$. The crystal structure of $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was analyzed by Harrison et al. using powder neutron diffraction data [13].

Members of the $(\text{A}_3\text{Co}_2\text{O}_6)_m(\text{A}_3\text{Co}_3\text{O}_9)_n$ (or $\text{A}_{3m+3n}\text{Co}_{2m+3n}\text{O}_{6m+9n}$) and $(\text{A}_8\text{Co}_6\text{O}_{18})_\alpha(\text{A}_8\text{Co}_8\text{O}_{24})_\beta$ (or $\text{A}_{4\alpha+4\beta}\text{Co}_{3\alpha+4\beta}\text{O}_{9\alpha+12\beta}$) [$\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$] series have pseudo-one-dimensional structures consisting of Co–O chains and alkaline earth atoms, in which CoO_6 octahedra and CoO_6 trigonal prisms are connected sharing their faces and alkaline earth atoms isolate the Co–O chains [13–27]. $\text{Sr}_6\text{Co}_5\text{O}_{15}$ ($m = 1, n = 1$) is a member of the $(\text{A}_3\text{Co}_2\text{O}_6)_m(\text{A}_3\text{Co}_3\text{O}_9)_n$ series, and four consecutive CoO_6 octahedra and one CoO_6 trigonal prism are connected in the unit cell (space group $R\bar{3}2$, $a = 9.5035(2)$ Å and $c = 12.3966(4)$ Å [13]), as shown in Fig. 1.

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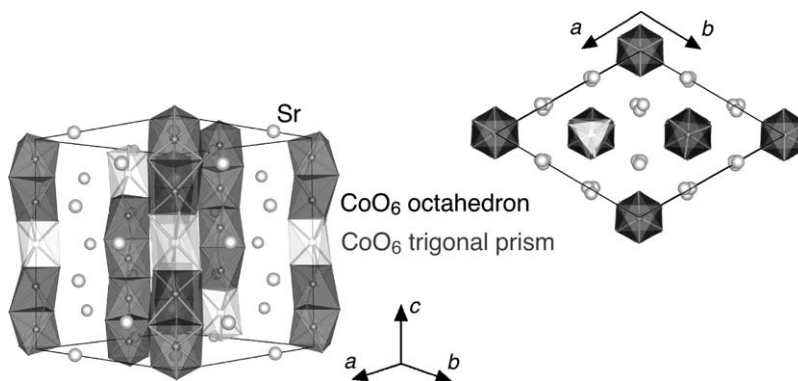


Fig. 1. Crystal structure of $\text{Sr}_6\text{Co}_5\text{O}_{15}$.

One of the problems in the $(\text{A}_3\text{Co}_2\text{O}_6)_m(\text{A}_3\text{Co}_3\text{O}_9)_n$ and $(\text{A}_8\text{Co}_6\text{O}_{18})_\alpha(\text{A}_8\text{Co}_8\text{O}_{24})_\beta$ series is that other members are synthesized as byproducts in addition to the target member because of the similarity of the sample compositions. $\text{Sr}_6\text{Co}_5\text{O}_{15}$ can be obtained by annealing at 1148 K in air [13]. Our previous study on $\text{Sr}_6\text{Co}_5\text{O}_{15}$ showed that $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was not always stable below 1148 K. For example, an unidentified Sr–Co–O phase was obtained below 773 K from $\text{Sr}_6\text{Co}_5\text{O}_{15}$, and $\text{Sr}_6\text{Co}_5\text{O}_{15}$ exhibited weight loss at high temperatures [28]. Understanding the stability and nonstoichiometry of $\text{Sr}_6\text{Co}_5\text{O}_{15}$ is important since contamination by an impurity phase and the variation of sample composition often affect the physical properties.

In this study, we investigated the relation between the synthesis conditions and formation of the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase. Four samples of the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase with different oxygen contents were prepared by a solid state reaction, and the crystal structures were refined. Throughout this paper, we will refer to the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase obtained by heating at 1173 K in air simply as $\text{Sr}_6\text{Co}_5\text{O}_{15}$.

2. Experimental

SrCO_3 (99.99+%, Rare Metallic Co.) and Co_3O_4 (99.95%, Kanto Chemical Co.) powders were used as starting materials. The powders were mixed in the appropriate proportion (molar ratio of Sr:Co was 6:5) in an agate mortar with ethanol, and pressed into a pellet form. The pellet was put on a Pt sheet and heated (Yamato, muffle furnace FO310) at 1173 K for 210 h in air with intermediate grindings every 70 h to obtain single phase $\text{Sr}_6\text{Co}_5\text{O}_{15}$. In this study, four samples of the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase with different oxygen contents were prepared as follows: (a) $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was heated at 1123 K for 70 h in air and then cooled in the furnace (it took about 0.6 h to decrease the temperature inside the furnace from 1123 K to 773 K and 2.5 h from 773 K to 373 K); (b) $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was heated at 1123 K for 15 h in air and cooled outside the furnace at room temperature in air; (c) $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was heated at 873 K for 15 h in air and quenched in liquid nitrogen; (d) $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was heated at 973 K for 15 h in air and quenched in liquid nitrogen.

The X-ray powder diffraction (XRD) patterns were recorded by a diffractometer (Rigaku, RINT2200) using $\text{Cu K}\alpha$ radiation with a pyrolytic graphite monochromator. The crystal structures were refined by the Rietveld method using the program RIETAN-2000 [29] with XRD data in the range $10^\circ \leq 2\theta \leq 120^\circ$ (scan step 0.03°). Thermogravimetry and differential thermal analysis (TG-DTA) were carried out in air at a heating and cooling rate of 10 K/min (Rigaku, TG8120). Quantitative analysis of oxygen was performed by the He carrier melting–infrared absorption method (LECO, TC-436).

3. Results and discussion

Upon heating at 1173 K in air, an unidentified impurity phase formed on the surface of the pellet in contacted with the Pt sheet. Single phase $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was obtained by scraping away the surface of the pellet. In the energy dispersion X-ray spectroscopy analysis (EDS, JEOL JSM-6460LA), no Pt contamination was detected in $\text{Sr}_6\text{Co}_5\text{O}_{15}$.

Fig. 2 shows the TG-DTA curves for $\text{Sr}_6\text{Co}_5\text{O}_{15}$ measured over the temperature range 300–1173 K in air at a heating and cooling rate of 10 K/min. $\text{Sr}_6\text{Co}_5\text{O}_{15}$ showed weight loss above 650 K; the sample weight decreased with increasing temperature. The weight loss was about 1.2% at 1000 K. No endothermic and exothermic peaks were

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