Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 3149–3155

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Oxygen nonstoichiometry and cobalt valence in misfit-layered cobalt oxides

Y. Morita,[a] J. Poulsen,[a] K. Sakai,[a] T. Motohashi,[a] T. Fujii,[b] I. Terasaki,[b] H. Yamauchi,[a] and M. Karppinen[a],*

[a] *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama-shi, Kanagawa-ken 226-8503, Japan*
[b] *Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan*

Received 25 March 2004; received in revised form 10 May 2004; accepted 14 May 2004

Abstract

The hexagonal CoO_2 layer is the main building unit of the newly established category of misfit-layered and related oxides showing—as a general feature—excellent thermoelectric characteristics. Here we use high-quality samples of the three prototype phases, $Na_{0.77}CoO_{2+\delta}$, $Ca_3Co_{3.95}O_{9+\delta}$ and $(Bi,Pb)_2Sr_2Co_2O_{8+\delta}$, and apply both precise wet-chemical redox analysis techniques and thermogravimetric annealing experiments to approach the not-yet-addressed questions concerning oxygen nonstoichiometry and the valence of Co in these phases. In terms of the oxygen-stoichiometry tunability, substantial variation in the overall oxygen content upon reducing/oxidizing annealing is observed only for $Ca_3Co_{3.95}O_{9+\delta}$. The valence of Co in all the samples is found to lie in a range of 3.0–3.3, being significantly lower than the commonly believed values of 3.3–3.5.

Keywords: Misfit-layered cobalt oxides; Oxygen content; Cobalt valence; Wet-chemical analysis; Thermogravimetry

1. Introduction

Misfit-layered (ML) cobalt oxides [1,2] are potential hosts for unexpected or multiple (seemingly contradictory) functions. The first manifestation of such function is the excellent thermoelectric figure of merit recently revealed for several ML cobalt oxides [3–9]. In Fig. 1, we show a multi-layered crystal structure that schematically describes the structures of the known ML cobalt oxides. The structure consists of two subsystems, i.e., (1) a CoO_2 layer of edge-sharing CoO_6 octahedra of hexagonal symmetry, and (2) a rock-salt-type block of $MO_{1\pm\omega}$ (M = Co, Bi, etc.) and $AO_{1\pm\varepsilon}$ (A = Ca, Sr, etc.) layers; these are alternatively piled along the c-axis with a layer sequence of CoO_2–$AO_{1\pm\varepsilon}$–$(MO_{1\pm\omega})_m$–$AO_{1\pm\varepsilon}$. The two subsystems are incommensurate along the b-axis direction, but have the lattice parameters, a, c and β, in common. Ignoring the possibilities of additional incommensurate modulation among the AO and MO layers and nonstoichiometry within the individual layers, an ML cobalt-oxide phase is typically approximated with a chemical formula, $[M_mA_2O_{2+m}]_qCoO_2$, where q is the ratio between the b-axis lattice parameters of the two subsystems, i.e., $q = b_1/b_2$. However, to be precise each ML cobalt-oxide phase should be referred to using a formula that allows at least internal modulation and oxygen nonstoichiometry within the rock-salt-type subsystem, i.e., $[(MO_{1\pm\omega})_x]_m\ [(AO_{1\pm\varepsilon})_y]_rCoO_2$.

For an $[(MO_{1\pm\omega})_x]_m\ [(AO_{1\pm\varepsilon})_y]_rCoO_2$ phase with $m > 0$, the number of $AO_{1\pm\varepsilon}$ layers that sandwich the $MO_{1\pm\omega}$ layer(s) is fixed at $r = 2$. However, in order to include the first "high-figure-of-merit" thermoelectric oxide, Na_yCoO_2 [3], in the general classification scheme, r should be considered as a variable having two possible values, i.e., $r = 1$ or 2. Accordingly, Na_yCoO_2 in which each two adjacent CoO_2 layers are separated by a single, nonstoichiometric Na layer[1] only may be regarded as

---

*Corresponding author. Fax: +81-45-924-5365.
E-mail address: karppinen@msl.titech.ac.jp (M. Karppinen).

[1] Though to discuss the Na_yCoO_2 phase within the general categorization scheme of ML cobalt oxides is highly useful in many senses, one should also keep in mind that Na occupies not a "rock-salt position" but a hexagonal lattice site in Na_yCoO_2.

0022-4596/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.05.023

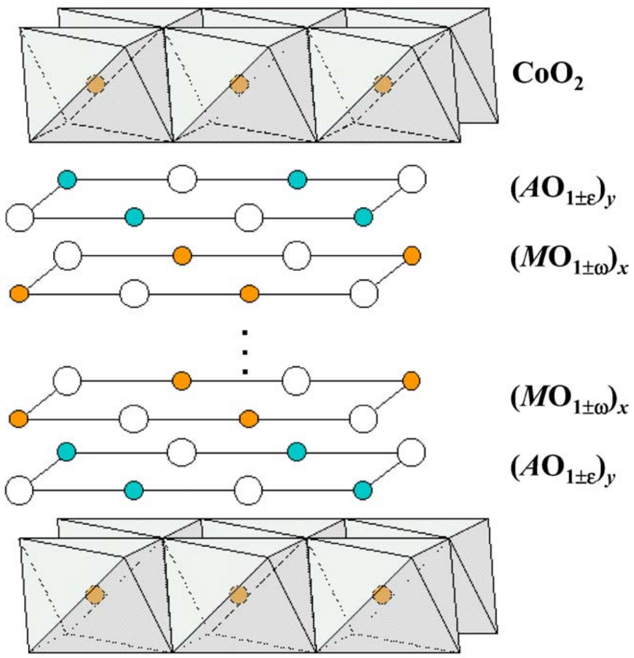

Fig. 1. Schematic illustration of the crystal structure of an ML cobalt-oxide phase, $[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_rCoO_2$, consisting of two subsystems, CoO_2 and $AO_{1\pm\varepsilon}$-$(MO_{1\pm\omega})_m$-$AO_{1\pm\varepsilon}$, that are incommensurate along the b-axis direction, but have the lattice parameters, a, c and β, in common.

the parent ($m = 0$, $r = 1$) phase of the ML cobalt-oxide family.

For a transition-metal oxide with strongly correlated electrons, the room-temperature thermoelectric power approaches the high-temperature limit given by Heikes formula. This was recently discussed by Koshibae et al. [10], the apparent motivation of the discussion being the need to rationalize the unexpectedly high room-temperature thermoelectric power observed for Na_yCoO_2. It was shown that the thermoelectric power of Na_yCoO_2 and related oxides of high-valent cobalt is governed by the (average) valence of the Co species (V(Co)) together with the symmetry and strength of the crystal field upon these species, increasing in general with decreasing V(Co) within $3 \leqslant V(\mathrm{Co}) \leqslant 4$. Assuming $V(\mathrm{Co}) = 3.5$ and a strong-crystal-field situation, i.e., low spin state for both Co^{III} and Co^{IV}, the authors estimated the high-temperature limit of thermopower at 154 μV/K [10]. This value is of the same order of magnitude as those experimentally obtained for the ML cobalt oxides [3,11]. The low spin state has already been experimentally shown for the Co species in the ML cobalt oxides [12,13]. On the other hand, the precise values of V(Co) in Na_yCoO_2 and other $[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_rCoO_2$ oxides have not been satisfactorily addressed yet.

Here we use high-quality samples of three different ML cobalt-oxide phases, and combine precise wet-chemical redox analysis to thermogravimetric (TG) annealing experiments to approach the questions concerning oxygen nonstoichiometry and valence of cobalt in the $[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_rCoO_2$ misfit oxides. A summary of the samples included in the present study is given in Table 1.

2. Experimental

Single-phase samples corresponding to the three prototype ML phases of $(NaO_{1\pm\varepsilon})_yCoO_2$, $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ and $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ were synthesized with stoichiometries of $Na_{0.77}CoO_{2+\delta}$, $Ca_3Co_{3.95}O_{9+\delta}$ and $(Bi_{2.1-z}Pb_z)Sr_{2.15}Co_2O_{8+\delta}$ ($z = 0$ and 0.4), respectively. The precise cation composition of each sample was confirmed (with an accuracy better than 3% for each cation)[2] by means of inductively coupled-plasma atomic-emission spectroscopy (Seiko Instruments: SPS-1500VR) analysis.

The samples of $Na_{0.77}CoO_{2+\delta}$ and $Ca_3Co_{3.95}O_{9+\delta}$ were synthesized in polycrystalline form through solid-state reaction routes from appropriate powder mixtures of Na_2CO_3, $CaCO_3$, and Co_3O_4. For $Na_{0.77}CoO_{2+\delta}$ in order to minimize the evaporation of sodium during the synthesis, a so-called "rapid heat-up" technique [11] was employed: the thoroughly mixed starting materials were directly placed in a furnace preheated at 800°C and fired for 12 h in air [14]. The $Ca_3Co_{3.95}O_{9+\delta}$ sample was fired twice at 900°C (for 20 h each) in air, first in powder form and then as a pellet. After the final heat treatment, all the polycrystalline samples were furnace-cooled to room temperature. The two $(Bi,Pb)_{2.1}Sr_{2.15}Co_2O_{8+\delta}$ samples were single crystals grown by a floating-zone technique in air. Details of the growth procedure were described earlier [6].

The absolute oxygen contents were determined by cerimetric and/or iodometric titrations. Both titration methods are based on dissolution of the sample (10–50 mg) in acidic solution (1 M HCl) and subsequent reduction of Co^{III} and Co^{IV} as well as other high-valent species, i.e., Bi^{V}, Pb^{IV} and O^{-I}, with Fe^{2+} (cerimetric titration) or I^- (iodometric titration) ions [15,16]. The experimental details were as described elsewhere [16].

The oxygen-content tunability of the three ML phases was investigated by means of oxygenation and deoxygenation annealings performed in a thermobalance (Perkin Elmer: Pyris 1) for the as-air-synthesized samples in 1 atm O_2 and 1 atm N_2 atmosphere, respectively. In these experiments, a small (10–60 mg) portion of the sample was heated to 750–1000°C. Slow

---

[2] In terms of the numbers revealed for the oxygen stoichiometry and the valence of cobalt from the wet-chemical redox analysis data, small changes in the cation composition used for calculating these numbers would change the absolute value of δ, but not significantly affect the value of V(Co).

Table 1
Presently investigated ML cobalt-oxide samples: (i) commonly used "nick name", (ii) cation composition from reported crystal structure refinement, (iii) systematic name based on the $[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_r\mathrm{CoO_2}$ notation, and (iv) nominal cation composition used in the present study to obtain single-phase samples

Nick name	Refined structure	Systematic name	Present composition
$\mathrm{NaCo_2O_4}$	$\mathrm{Na_{0.74}CoO_2}$ [18]	$(\mathrm{NaO}_{1\pm\varepsilon})_y\mathrm{CoO_2}$	$\mathrm{Na_{0.77}CoO}_{2+\delta}$
$\mathrm{Ca_3Co_4O_9}$	$\mathrm{[CoCa_2O_3]_{0.62}CoO_2}$ [23]	$[(\mathrm{CoO}_{1\pm\omega})_x][(\mathrm{CaO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$	$\mathrm{Ca_3Co_{3.95}O}_{9+\delta}$
$\mathrm{Bi_2Sr_3Co_2O_8}$	$\mathrm{[Bi_{1.74}Sr_2O_4]_{0.55}CoO_2}$ [27,28]	$[(\mathrm{BiO}_{1\pm\omega})_x]_2[(\mathrm{SrO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$	$\mathrm{Bi_{2.1}Sr_{2.15}Co_2O}_{8+\delta}$
$\mathrm{(Bi,Pb)_2Sr_3Co_2O_8}$	—	$[(\mathrm{Bi,Pb})\mathrm{O}_{1\pm\omega})_x]_2[(\mathrm{SrO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$	$\mathrm{(Bi_{1.7}Pb_{0.4})Sr_{2.15}Co_2O}_{8+\delta}$

heating and cooling rates (0.5–1°C/min) were used to guarantee an essentially equilibrium situation during the annealing.

3. Results and discussion

3.1. Oxygen content and valence of cobalt: wet-chemical analysis

The absolute oxygen contents were determined for all the as-air-synthesized samples of $\mathrm{Na_{0.77}CoO}_{2+\delta}$, $\mathrm{Ca_3Co_{3.95}O}_{9+\delta}$ and $\mathrm{(Bi,Pb)_{2.1}Sr_{2.15}Co_2O}_{8+\delta}$ by the two independent redox titration methods, cerimetry and iodometry. For each sample, parallel experiments were made, with a reproducibility of about ± 0.005 for each method and an agreement of better than ± 0.02 between the results of the two methods for the same sample. Table 2 summarizes the average values for the oxygen content and the valence of cobalt as calculated from the parallel titration experiments for the samples. In terms of the given V(Co) value, one should recognize that it represents the actual $\mathrm{CoO_2}$-layer Co valence unambiguously only in the case of $(\mathrm{NaO}_{1\pm\varepsilon})_y\mathrm{CoO_2}$. For $[(\mathrm{CoO}_{1\pm\omega})_x][(\mathrm{CaO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$ the value is an average of the two different Co sites, whereas for $[((\mathrm{Bi,Pb})\mathrm{O}_{1\pm\omega})_x]_2[(\mathrm{SrO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$ it may overestimate the real value of V(Co), since it is calculated assuming a valence state of III for Bi and II for Pb. In the following, we discuss the results in more detail for each phase separately.

$(NaO_{1\pm\varepsilon})_yCoO_2$: The γ-$\mathrm{Na}_y\mathrm{CoO_2}$ phase, first reported in 1970s [17,18] is frequently referred to as $\mathrm{NaCo_2O_4}$ [3,10,12], which has lead to a supposition that the valence of cobalt would be 3.5 [10,12]. Here, both cerimetric and iodometric titrations revealed a value of 3.26 for V(Co) in our $\mathrm{Na_{0.77}CoO}_{2+\delta}$ sample (Table 2). The obtained V(Co) value is compatible with $y = 0.77$ and $\varepsilon = -0.98$ in the systematic formula of $(\mathrm{NaO}_{1+\varepsilon})_y\mathrm{CoO_2}$. These numbers are well comparable to those of $y = 0.74$ and $\varepsilon = -1$ revealed for the phase through Rietveld refinement of neutron powder diffraction data [19]. It thus seems, in agreement with our previous results [14,20] that the Na-rich $(\mathrm{NaO}_{1+\varepsilon})_y\mathrm{CoO_2}$ phase is essentially stoichiometric in terms of oxygen.

Table 2
Cerimetric and iodometric titration results for the overall oxygen content (δ) and the (actual/average/maximum: see the text) valence of cobalt (V(Co)) in the as-air-synthesized samples

Sample	δ	V(Co)
$\mathrm{Na_{0.77}CoO}_{2+\delta}$	0.02 (cer)/0.02 (iodo)	3.26/3.26
$\mathrm{Ca_3Co_{3.95}O}_{9+\delta}$	0.23 (cer)/0.25 (iodo)	3.15/3.17
$\mathrm{Bi_{2.1}Sr_{2.15}Co_2O}_{8+\delta}$	0.49 (cer)/0.51 (iodo)	3.19/3.21
$\mathrm{(Bi_{1.7}Pb_{0.4})Sr_{2.15}Co_2O}_{8+\delta}$	0.22 (cer)/0.26 (iodo)	3.12/3.16

$[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$: The "$\mathrm{Ca_3Co_4O_9}$" phase that later turned out to be the ML phase, $[(\mathrm{CoO}_{1\pm\omega})_x][(\mathrm{CaO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$ [21,22], was synthesized for the first time in 1968 [23]. A little later a layered structure was suggested for the compound [24]. The average valence of cobalt as calculated from the nominal formula, $\mathrm{Ca_3Co_4O_9}$, equals 3.00, though the phase has also been referred to as "$\mathrm{Ca_9Co_{12}O_{28}}$" with the nominal Co valence at 3.17 [4]. After realizing the ML character of the structure, a stoichiometry of $\mathrm{[Ca_2CoO_3]_{0.62}CoO_2}$ was revealed for it on the basis of precise crystal structure analysis [25]. From this stoichiometry, assuming that the different metal oxide layers, CoO, CaO and $\mathrm{CoO_2}$, are individually stoichiometric in terms of oxygen content, the average valence of cobalt atoms occupying the two different lattice sites in the CoO and $\mathrm{CoO_2}$ layers is obtained at 3.23. Here, for our as-air-synthesized $[(\mathrm{CoO}_{1\pm\omega})_x][(\mathrm{CaO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$ sample at the stoichiometry of $\mathrm{Ca_3Co_{3.95}O}_{9+\delta}$, the overall oxygen content was determined at $\delta = 0.23/0.25$ by cerimetric/iodometric titrations (Table 2). This corresponds to an average Co valence of 3.15/3.17, i.e., a value somewhat lower than the one expected on the basis of individually oxygen-stoichiometric layers. Thus, our result suggests presence of oxygen vacancies in $[(\mathrm{CoO}_{1\pm\omega})_x]$ $[(\mathrm{CaO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$. Unfortunately, the presently employed analysis techniques neither allow us to locate the oxygen vacancies nor reveal us the distribution of the excess positive charge between the two types of Co atoms.

$[(BiO_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$: The Bi-based ML oxide, $[(\mathrm{BiO}_{1\pm\omega})_x]_2[(\mathrm{SrO}_{1\pm\varepsilon})_y]_2\mathrm{CoO_2}$, was apparently first synthesized already in 1989 at the nominal stoichiometry of $\mathrm{Bi_2Sr_3Co_2O}_y$ [26]. At that time,

however, it was believed that its basic structure is similar to that of the Bi-based superconductive cuprate, $Bi_2Sr_2CaCu_2O_{8+\delta}$, though in comparison to that the Co-based compound was reported to exhibit a more complex incommensurate structural modulation. Ten years later, it was revealed that the phase is strongly Sr deficient, i.e., closer to the cation stoichiometry of $Bi_2Sr_2Co_2O_y$ [27,28], and has an ML structure with triangular rather than square-planar arrangement for the Co atoms within the CoO_2 layer [28–30]. From precise crystal structure analysis, a stoichiometry of $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ or $[Bi_{1.74}Sr_2O_4]_{0.55}CoO_2$ was concluded for the phase [29,30]. From the given stoichiometry, one may calculate an estimate for the valence of cobalt at 3.33. At the same time, one should be aware of two assumptions thereby made, i.e.: (i) both subsystems are individually oxygen stoichiometric, and (ii) the valence of bismuth is 3.00. However, taking an analogy to the case of the high-T_c superconductor, $Bi_2Sr_2CaCu_2O_{8+\delta}$, not only the first assumption but also the second one requiring an integer valence value for bismuth is not necessarily valid. (Note that for an air-synthesized sample of the $Bi_2Sr_2CaCu_2O_{8.26}$ cuprate, the valence of bismuth was determined at 3.13 [31].) For the present as-air-synthesized single-crystal sample of $Bi_{2.1}Sr_{2.15}Co_2O_{8+\delta}$, the oxygen content was determined at $\delta = 0.49/0.51$ by cerimetry/iodometry (Table 2). Therefore, if the Bi valence is assumed to be 3.00, the valence of cobalt in the CoO_2 layer is estimated at 3.19/3.21. As the assumed value for Bi valence is the lowest possible, the estimate for the Co valence accordingly corresponds to the maximum limit for the actual value of V(Co). Note that a reported result of Hall coefficient measurement suggests that the hole number *per* Co site is even less than 0.1 [32]. Since this maximum possible value of V(Co) is much lower than that calculated from the $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ stoichiometry, i.e., 3.33, our result suggests that parallel to the case of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase, the $[(BiO_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ phase too might possess oxygen vacancies.

$[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$: For the Pb-for-Bi substituted $[((Bi_{1.7}Pb_{0.4})O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ sample a significant decrease in the oxygen content as compared to that of the pristine $[(BiO_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ phase was observed. This situation is parallel to that known for a related cuprate system, $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$, for which 15% Pb-for-Bi substitution was found to decrease the oxygen content from $\delta = 0.28$ to 0.19 [33]. Here, for our $(Bi_{1.7}Pb_{0.4})Sr_{2.15}Co_2O_{8+\delta}$ sample the oxygen content was determined at $\delta = 0.22$ (cerimetry)/0.26 (iodometry) (Table 2). In other words, the δ value of $\sim$0.50 of the pristine phase had been decreased to a value as low as $\sim$0.24 for the $\sim$20% Pb-for-Bi substituted phase. Moreover, from the analyzed oxygen content value of $\delta \approx 0.24$ in $(Bi_{1.7}Pb_{0.4})Sr_{2.15}Co_2O_{8+\delta}$ we calculate the (maximum) value of V(Co) at $\sim$3.14 based on the assumption that the valence of Bi/Pb is 3.00/2.00. Comparison to the V(Co) value for the pristine $Bi_{2.1}Sr_{2.15}Co_2O_{8+\delta}$ sample (Table 2), reveals that the Pb-for-Bi substitution has not increased but rather somewhat decreased the V(Co) value. This is again a parallel situation to that known for $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ [33], but not straightforwardly expected from the Hall coefficient and resistivity data previously reported for the $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ system [28,32]. That is, in this system the Pb-for-Bi substitution slightly decreases the magnitude of the Hall coefficient and enhances metallic behaviour (though the enhancement was found more pronounced for the out-of-plane than the in-plane resistivity). Based on these facts, one might assume that the carrier concentration had increased. On the other hand, the enhancement in the thermoelectric power seen as a consequence of the Pb substitution in $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ [34,35], might be interpreted to point out to an opposite direction, i.e., decrease in the carrier concentration. Here it should however be recognized that the increase in thermopower with Pb substitution may also be attributed to the change in the misfit or the interfacial strain [35]: thermopower is a function of both the effective mass and the carrier number, and Pb substitution not only changes the Co valence, but also affects the degree of misfit. Finally, it is worthwhile to note that the photoemission and X-ray absorption spectra for the $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$ system were not strongly affected by the Pb substitution [12].

In summary, we may conclude from Table 2 that among the three systems, the valence of cobalt is the highest in $(NaO_{1\pm\varepsilon})_yCoO_2$. Then for the other two systems, $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ and $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$, the value of V(Co) is approximately at the same level. At the same time it is known that among the three phases $(NaO_{1\pm\varepsilon})_yCoO_2$ shows the lowest room-temperature thermoelectric power characteristics [36]. Thus, the present conclusion qualitatively validates the discussion by Koshibae et al. [10] suggesting that the thermoelectric power in the ML cobalt oxides should increase with decreasing magnitude of V(Co).

3.2. Oxygen-content tunability: thermogravimetric analysis

The possibility to tune the oxygen content of the as-air-synthesized samples was investigated for all the three phases by means of oxygenation and deoxygenation annealings performed in a thermobalance in a 1-atm gas flow of O_2 and N_2, respectively. Substantial variation in the oxygen content upon such annealings was observed only for the $Ca_3Co_{3.95}O_{9.24}$ sample of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase, in agreement with a previous report [37] showing a variation range of approximately 0.2 oxygen atoms *per* "$Ca_3Co_{3.95}O_{9+\delta}$ formula unit" for the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase. For the other two phases of $(NaO_{1\pm\varepsilon})_yCoO_2$ and $[((Bi,Pb)O_{1\pm\omega})_x]_2[(SrO_{1\pm\varepsilon})_y]_2CoO_2$, the observed changes in weight/oxygen content were negligible.

In order to elucidate the oxygen depletion/incorporation behaviour of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase in more detail, we performed the following TG run for the as-air-synthesized $Ca_3Co_{3.95}O_{9.24}$ sample (Fig. 2): first the sample was heated in N_2 up to 750°C, then cooled back to room temperature in N_2, and subsequently the same sample was subjected to heating up to 850°C and cooling back to room temperature in O_2. Note that our preliminary TG experiments had revealed that the ML phase starts to decompose in N_2 above 750°C (to a mixture of $Ca_3Co_2O_6$ and CoO) and melts in O_2 above 900°C. From Fig. 2, upon heating in N_2 oxygen depletion starts in $Ca_3Co_{3.95}O_{9.24}$ around 350°C and continues up to 750°C. At 750°C, the weight loss detected corresponds to an oxygen content of $\delta \approx -0.04$. This value should be close to the minimum oxygen content tolerated by the $Ca_3Co_{3.95}O_{9+\delta}$ phase. From Fig. 2, we also note that at about 530°C there is a small but visible change in the slope of the TG curve for the N_2 annealing. This suggests that at that temperature/oxygen content the bonding strength of oxygen atoms being removed slightly changes. It might therefore mark a possible phase transition point. Upon cooling down the oxygen-depleted $Ca_3Co_{3.95}O_{9+\delta}$ phase from 750°C in N_2, the oxygen content remains low (Fig. 2). On the other hand, by recycling in O_2 oxygen is incorporated into the $Ca_3Co_{3.95}O_{9+\delta}$ phase again. Upon heating in O_2 oxygen incorporation starts at about 300°C. The maximum in oxygen content is reached by 400°C after which the phase again starts to loose oxygen. In comparison to the behaviour in N_2 atmosphere, in O_2 the oxygen loss occurs more moderately. It is interesting to note that in O_2 the oxygen content is not decreased below the level ($\delta \approx 0.10$) where the (possible) phase transition occurs. The oxygen depletion upon heating and the subsequent incorporation upon cooling are reversible in O_2 when the recycling is carried out slowly enough (here 0.5°C/min). As a result of the slow cooling in O_2, the oxygen content in $Ca_3Co_{3.95}O_{9+\delta}$ is increased back to the original level of $\delta \approx 0.24$ (Fig. 2).

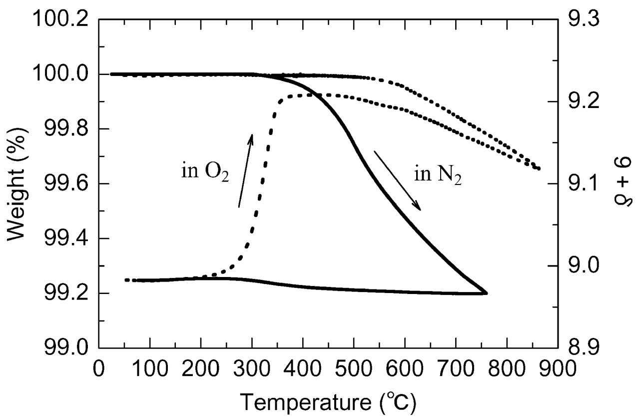

Fig. 2. TG curves for $Ca_3Co_{3.95}O_{9+\delta}$ showing its deoxygenation and oxygenation characteristics. First as-air-synthesized $Ca_3Co_{3.95}O_{9.24}$ is deoxygenated by heating (up to 750°C) and cooling in N_2 (—) and subsequently oxygenated by heating (up to 850°C) and cooling in O_2 (- - -). The mass of the sample was ~60 mg and the heating and cooling rates were 0.5°C/min.

The steady decrease seen in weight within 350–750°C for our $Ca_3Co_{3.95}O_{9+\delta}$ sample of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase indicates that the oxygen content of this phase can be tuned in a continuous manner. Moreover, the TG curve for the N_2 annealing can be conveniently utilized to read the proper annealing temperature (corresponding to the desired oxygen content) when one aims at preparing a sample with a certain intermediate oxygen-content value, i.e., so-called temperature-controlled oxygen depletion (TCOD [15,16]) annealing. To demonstrate the power of such an approach, we prepared a series of oxygen-controlled $Ca_3Co_{3.95}O_{9+\delta}$ samples by the TCOD method by subjecting portions of the as-air-synthesized sample to appropriate post-annealing treatments to decrease the oxygen content. In each TCOD annealing, a small sample (~50 mg) was heated in pure (99.998%) N_2 gas with a rate of 1°C/min to a predetermined temperature. At the final annealing temperature, an isothermal heating period of 12–24 h was applied, after which the sample was cooled down to room temperature with a fast cooling rate of 20°C/min. Since we carried out these annealings in a thermobalance of high sensitivity, a good estimation for the amount of depleted oxygen was obtained from the in situ TG detection of the weight change. Here the TCOD annealings for $Ca_3Co_{3.95}O_{9+\delta}$ were carried out at temperatures of 400°C, 500°C, 600°C and 750°C. To guarantee homogeneity in the oxygen content, each sample was annealed at the target temperature until no further weight losses were detected. The resultant TG curves are shown in Fig. 3. The observed weight losses corresponded to oxygen losses of $\Delta\delta = 0.04(5)$, 0.12(5), 0.17(5) and 0.25(5), respectively. From X-ray diffraction analysis, all the TCOD products were found to be single-phase samples of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase. Moreover, we prepared a fully oxygenated single-phase sample of $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ by annealing a portion of the as-air-synthesized sample in 90 atm O_2 at 400°C for 24 h. We then precisely analyzed the oxygen content of the thus prepared series of oxygen-controlled $Ca_3Co_{3.95}O_{9+\delta}$ samples by means of cerimetric and/or iodometric titrations. The results are given in Table 3.

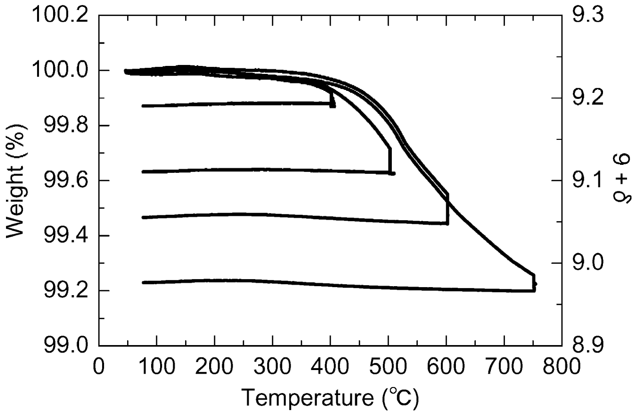

Fig. 3. TG curves for the TCOD annealings carried out for as-air-synthesized $Ca_3Co_{3.95}O_{9.24}$ material at temperatures of 400°C, 500°C, 600°C and 750°C. The mass of the sample was ~ 50 mg, the heating rate was 1°C/min, the cooling rate was 20°C/min, and the length of the isothermal heating period at the final temperature was 12–24 h.

Table 3
Cerimetric and/or iodometric titration results for the overall oxygen content (δ) and the average valence of cobalt (V(Co)) in the variously annealed samples of $Ca_3Co_{3.95}O_{9+\delta}$

Sample	δ	V(Co)
90-atm-O_2-ann	0.29 (iodo)	3.19
As-air-synthesized	0.23 (cer)/0.25 (iodo)	3.15/3.17
N_2-400-ann	0.15 (cer)	3.12
N_2-500-ann	0.05 (cer)/0.08 (iodo)	3.07/3.08
N_2-600-ann	0.00 (cer)/0.00 (iodo)	3.04/3.04
N_2-750-ann	−0.03 (cer)/−0.06 (iodo)	3.02/3.01

For our as-air-synthesized sample, the overall oxygen content was determined at $\delta \approx 0.24$. Upon the 90-atm O_2 annealing the oxygen content increased to $\delta \approx 0.29$, whereas for the TCOD-annealed samples the oxygen content gradually decreased down to $\delta \approx -0.05$. Accordingly as summarized in Table 3, the average valence of cobalt varies from 3.01 to 3.19 for the differently annealed samples of the $[(CoO_{1\pm\omega})_x][(CaO_{1\pm\varepsilon})_y]_2CoO_2$ phase.

4. Conclusions

We systematically investigated the valence state of cobalt in three representative ML cobalt-oxide systems, $Na_{0.77}CoO_{2+\delta}$, $Ca_3Co_{3.95}O_{9+\delta}$ and $(Bi,Pb)_{2.1}Sr_{2.15}Co_2O_{8+\delta}$, by means of two independent wet-chemical redox analysis methods, i.e., cerimetric and iodometric titration. For the air-synthesized samples of these three phases the maximum value of V(Co) was found to lie in the range of 3.1–3.3, i.e., significantly lower than the commonly assumed values of 3.3–3.5. Furthermore, we concluded that among the three systems, the valence of cobalt is the highest in $Na_{0.77}CoO_{2+\delta}$. For $Ca_3Co_{3.95}O_{9+\delta}$, further tuning of oxygen content and thereby the valence state of cobalt was found possible by means of oxygenation/deoxygenation annealings. Through such annealings, it was possible to precisely control the average Co valence within 3.0–3.2 in $Ca_3Co_{3.95}O_{9+\delta}$. Finally, it is emphasized that the three phases, $Na_{0.77}CoO_{2+\delta}$, $Ca_3Co_{3.95}O_{9+\delta}$ and $(Bi,Pb)_{2.1}Sr_{2.15}Co_2O_{8+\delta}$, can be considered as prototypes of the known $[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_rCoO_2$ misfits at $(r,m) = (1,0)$, (2,1) and (2,2), respectively. Therefore, the present conclusion should serve as the basis for understanding this exciting family of ML copper oxides.

Acknowledgments

The present work was supported by a grant from Hayashi Memorial Foundation for Female Natural Scientists, and also through Grants-in-Aid for Scientific Research (Nos. 15206002 and 15206071) from the Japan Society for the Promotion of Science. T. Konno is acknowledged for his contribution in sample preparation.

References

[1] P. Boullay, B. Domengès, M. Hervieu, D. Groult, B. Raveau, Chem. Mater. 8 (1996) 1482.
[2] P. Boullay, R. Seshadri, F. Studer, M. Hervieu, D. Groult, B. Raveau, Chem. Mater. 10 (1998) 92.
[3] I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B 56 (1997) R12685.
[4] S. Li, R. Funahashi, I. Matsubara, K. Ueno, H. Yamada, J. Mater. Chem. 9 (1999) 1659.
[5] R. Funahashi, I. Matsubara, S. Sodeoka, Appl. Phys. Lett. 76 (2000) 2385.
[6] T. Itoh, I. Terasaki, Jpn. J. Appl. Phys. 39 (2000) 6658.
[7] S. Hébert, S. Lambert, D. Pelloquin, A. Maignan, Phys. Rev. B 64 (2001) 172101.
[8] D. Pelloquin, A. Maignan, S. Hébert, C. Martin, M. Hervieu, C. Michel, L.B. Wang, B. Raveau, Chem. Mater. 14 (2002) 3100.
[9] D. Pelloquin, A. Maignan, S. Hébert, C. Michel, B. Raveau, J. Solid State Chem. 170 (2003) 374.
[10] W. Koshibae, K. Tsutsui, S. Maekawa, Phys. Rev. B 62 (2000) 6869.
[11] T. Motohashi, E. Naujalis, R. Ueda, K. Isawa, M. Karppinen, H. Yamauchi, Appl. Phys. Lett. 79 (2001) 1480.
[12] R. Ray, A. Ghosray, K. Ghosray, S. Nakamura, Phys. Rev. B 59 (1999) 9454.
[13] T. Mizokawa, L.H. Tjeng, P.G. Steeneken, N.B. Brookes, I. Tsukada, T. Yamamoto, K. Uchinokura, Phys. Rev. B 64 (2001) 115104.
[14] M. Karppinen, I. Asako, T. Motohashi, H. Yamauchi, Chem. Mater., 2004, in press.
[15] M. Karppinen, H. Yamauchi, Oxygen engineering for functional oxide materials, in: A.V. Narlikar (Ed.), International Book Series: Studies of High Temperature Superconductors, Vol. 37, Nova Science Publishers, New York, 2001, pp. 109–143.

[16] M. Karppinen, M. Matvejeff, K. Salomäki, H. Yamauchi, J. Mater. Chem. 12 (2002) 1761.
[17] C. Fouassier, G. Matejka, J.M. Reau, P. Hagenmuller, J. Solid State Chem. 6 (1973) 532.
[18] M. Von Jansen, R. Hoppe, Z. Anorg. Allg. Chem. 408 (1974) 104.
[19] R.J. Balsys, R.L. Davis, Solid State Ionics 93 (1996) 279.
[20] T. Motohashi, M. Karppinen, H. Yamauchi, In: Recent Research Developments in Applied Physics, Oxide Thermoelectrics, Research Signpost, India, 2002, pp. 73–81.
[21] A.C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, J. Hejtmanek, Phys. Rev. B 62 (2000) 166.
[22] Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, T. Kajitani, Jpn. J. Appl. Phys. 39 (2000) L531.
[23] C. Brisi, P. Rolando, Ann. Chim. (Rome) 58 (1968) 676.
[24] E. Woermann, A. Muan, J. Inorg. Nucl. Chem. 32 (1970) 1455.
[25] Y. Miyazaki, M. Onoda, T. Oku, M. Kikuchi, Y. Ishii, Y. Ono, Y. Morii, T. Kajitani, J. Phys. Soc. Japan 71 (2002) 491.
[26] J.M. Tarascon, R. Ramesh, P. Barboux, M.S. Hedge, G.W. Hull, L.H. Greene, M. Giroud, Y. LePage, W.R. McKinnon, J.V. Waszczak, L.F. Schneemeyer, Solid State Commun. 71 (1989) 663.
[27] I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone, K. Uchinokura, Mater. Res. Soc. Symp. Proc. 494 (1998) 119.
[28] T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsubone, M. Ichihara, K. Kobayashi, Jpn. J. Appl. Phys. 39 (2000) 747.
[29] H. Leligny, D. Grebille, O. Perez, A.C. Masset, M. Hervieu, C. Michel, B. Raveau, C. R. Acad. Sci. Ser. IIc; Chim. 2 (1999) 409.
[30] H. Leligny, D. Grebille, O. Perez, A.C. Masset, M. Hervieu, C. Michel, B. Raveau, Acta Crystallogr. B 56 (2000) 173.
[31] M. Karppinen, M. Kotiranta, T. Nakane, S.C. Chang, J.M. Chen, R.S. Liu, H. Yamauchi, Phys. Rev. B 67 (2003) 134522.
[32] T. Yamamoto, K. Uchinokura, I. Tsukada, Phys. Rev. B 65 (2002) 184434.
[33] M. Karppinen, S. Lee, J.M. Lee, J. Poulsen, T. Nomura, S. Tajima, J.M. Chen, R.S. Liu, H. Yamauchi, Phys. Rev. B 68 (2003) 54502.
[34] G. Xu, R. Funahashi, M. Shikano, I. Matsubara, Y. Zhou, J. Appl. Phys. 91 (2002) 4344.
[35] T. Fujii, I. Terasaki, T. Watanabe, A. Matsuda, Jpn. J. Appl. Phys. 41 (2002) L783.
[36] I. Terasaki, Mater. Trans. 42 (2001) b951.
[37] J. Shimoyama, S. Horii, K. Otzschi, M. Sano, K. Kishio, Jpn. J. Appl. Phys. 42 (2003) L194.