

Thermoelectric Misfit-Layered Cobalt Oxides (I): Oxygen Nonstoichiometry and Cobalt Valence

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We have developed chemical approaches to accurately determine and control the oxygen content and the valence of cobalt in the newly established misfit-layered and related cobalt oxides. These are materials that show - as a general feature - excellent thermoelectric characteristics. Employing two independent wet-chemical redox methods, *i.e.* cerimetric and iodometric titration, it is revealed that the valence of cobalt in the prototype thermoelectric oxides, $\text{Na}_y\text{CoO}_{2+\delta}$, $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ and $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8+\delta}$, lies in a range of 3.1~3.3 for samples synthesized in air. These valence values are significantly lower than those assigned to the phases on the basis of “nominal” or structural considerations. For the Pb-based misfit-layered cobalt oxide, $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$, a thermogravimetric H_2 reduction technique is introduced that allows us to simultaneously estimate lead and oxygen contents of the sample. With thermogravimetric oxygenation/deoxygenation annealing experiments carried out for all the systems in both O_2 and N_2 atmospheres it is shown that only for $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ wide-range oxygen-content tuning is possible: by annealing an as-air-synthesized $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ sample in N_2 at 750 °C the oxygen content, $9+\delta$, is reduced from 9.24 to ~8.96, and then again increased back to ~9.24 by recycling in O_2 .

Key words: Misfit-layered oxides, Oxygen stoichiometry, Cobalt Valence, Thermogravimetry, Redox analysis

1. INTRODUCTION

The recently discovered misfit-layered cobalt oxides,¹ $[\text{M}_m\text{A}_2\text{O}_{m+2}]_q\text{CoO}_2$, are promising candidates for high-efficiency thermoelectric materials.²⁻⁵ The structure of these oxides consists of two subsystems: (i) a CoO_2 layer of edge-sharing CoO_6 octahedra of hexagonal symmetry, and (ii) a rock-salt-type $\text{AO}-(\text{MO})_m\text{-AO}$ block ($M = e.g.$ Co, Bi, Pb; $A = e.g.$ Ca, Sr). The two subsystems are incommensurate along an in-layer direction. Besides rather characteristically exhibiting non-stoichiometry in terms of cation composition, misfit-layered oxides are also likely to show oxygen nonstoichiometry within one or more of the three types of layers, MO , AO and CoO_2 .⁶

The valence state of cobalt has been suggested to play a key role in realizing the characteristic high thermoelectric power of the misfit-layered oxides.⁷ Therefore in order to gain deeper understanding of these exciting materials it is dispensable to accurately determine the oxygen content and thereby the value of cobalt valence, $V(\text{Co})$, for each misfit-layered oxide. Also desired is to find proper conditions for controlling $V(\text{Co})$ by means of oxygen-content tuning, in cases when such tuning is first found possible.

In the present study we have employed precise chemical analysis methods to determine the value of $V(\text{Co})$ and to establish the degree of oxygen nonstoichiometry in various representative misfit-

layered cobalt-oxide phases. Note that among the studied systems included are the most important “[$\text{M}_m\text{A}_2\text{O}_{m+2}$] $_q\text{CoO}_2$ -type” phases of $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$, $\text{Bi}_2\text{Sr}_{2.15}\text{Co}_2\text{O}_{8+\delta}$ and $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$, and also the first “high-figure-of-merit” thermoelectric oxide,² $\text{Na}_y\text{CoO}_{2+\delta}$, that is not strictly speaking a misfit-layered compound but may be regarded as the parent phase for the misfit-layered cobalt oxides. Whereas an $[\text{M}_m\text{A}_2\text{O}_{m+2}]_q\text{CoO}_2$ phase repeats the layer sequence of $\text{AO}-(\text{MO})_m\text{-AO-CoO}_2$ ($m = 1$ or 2), in $\text{Na}_y\text{CoO}_{2+\delta}$ adjacent CoO_2 layers are separated by a single, non-stoichiometric (but hexagonal) Na layer only (see Fig. 1 for the structures).

2. SAMPLE SYNTHESIS

The samples of $\text{Na}_y\text{CoO}_{2+\delta}$ ($y = 0.72$ and 0.77), $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ and $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ ($z \approx 0.35$) were synthesized in polycrystalline form through solid-state-reaction routes from appropriate powder mixtures of Na_2CO_3 , CaCO_3 , SrO_2 , PbO_2 and Co_3O_4 . The high quality of the SrO_2 powder was guaranteed by synthesizing it immediately prior to use by a solution method.⁸ For the $\text{Na}_y\text{CoO}_{2+\delta}$ samples a “rapid heat-up” technique⁹ was employed in order to minimize the evaporation of sodium during the synthesis. In this technique, the starting material mixture in an alumina crucible is directly placed in a box furnace preheated at 800 °C and then fired at that

temperature for 12 hours. The $\text{Ca}_3\text{Co}_3.95\text{O}_{9+\delta}$ sample was fired twice at 900 °C (for 20 hours each) in air, first in powder form and then as a pellet, whereas the $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ sample was fired only once at 900 °C as encapsulated in a fused-quartz tube together with a pellet of extra SrO_2 . The function of this separately added SrO_2 was to work as a getter for carbon.¹⁰ The $\text{Bi}_{2.1}\text{Sr}_{2.15}\text{Co}_2\text{O}_{8+\delta}$ sample was a piece of a single crystal grown by a floating-zone technique in air.⁴

The precise cation composition as assigned to the samples above was confirmed for all the samples except for $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ by inductively-coupled-plasma atomic-emission spectroscopy (ICP-AES; Seiko Instruments: SPS-1500VR) analysis. In the case of $\text{Pb}_2\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ poor solubility made the ICP-AES analysis impossible. Instead, as described in section 3.2, we developed a thermogravimetric (TG) reduction technique that facilitates estimation of not only the oxygen content but simultaneously also the lead content of the Pb-based misfit-layered cobalt-oxide samples.

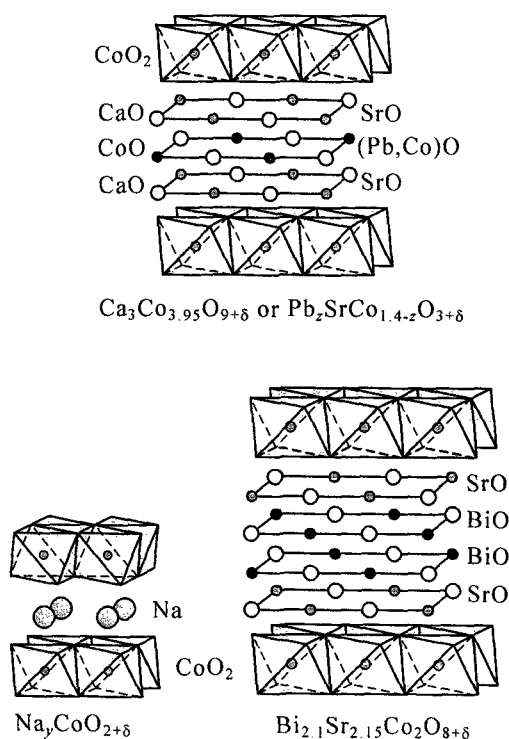


Fig. 1. Schematic illustration of crystal structures of the presently studied misfit-layered and related cobalt oxides.

3. COBALT VALENCE AND OXYGEN CONTENT

3.1 Wet-Chemical Redox Analyses

The overall oxygen content was determined by both cerimetric and iodometric titrations for all the samples that could be dissolved in acidic solution, *i.e.* $\text{Na}_y\text{CoO}_{2+\delta}$, $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ and $\text{Bi}_{2.1}\text{Sr}_{2.15}\text{Co}_2\text{O}_{8+\delta}$. Both titration methods are based on dissolution of the sample (10~50 mg) in 1~3 M HCl solution containing an excess of Fe^{2+} (cerimetric titration) or I^-

(iodometric titration) ions as a reductant to completely reduce Co^{III} and Co^{IV} as well as other possible high-valent cation species (here Bi^{V}). The experimental details were as described elsewhere.¹¹⁻¹³ The values for δ and $V(\text{Co})$ as summarized in Table 1 are all average values from several parallel experiments that revealed the value of δ with a reproducibility better than ± 0.01 . Each $V(\text{Co})$ value was calculated from the corresponding δ value assuming the following valence states for the other elements: Na^{I} , Ca^{II} , Sr^{II} , Bi^{III} , O^{II} . From Table 1, it is seen that the two independent wet-chemical redox analysis methods gave highly agreeable results.

Table 1. Values of $\delta / V(\text{Co})$ as determined for the as-air-synthesized samples by iodometric and cerimetric titrations.

Sample	Iodometry	Cerimetry
$\text{Na}_{0.77}\text{CoO}_{2+\delta}$	0.02 / 3.26	0.02 / 3.26
$\text{Na}_{0.72}\text{CoO}_{2+\delta}$	-0.01 / 3.25	-0.01 / 3.26
$\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$	0.25 / 3.17	0.23 / 3.15
$\text{Bi}_{2.1}\text{Sr}_{2.15}\text{Co}_2\text{O}_{8+\delta}$	0.51 / 3.21	0.49 / 3.19

In the case of $\text{Na}_y\text{CoO}_{2+\delta}$, the $V(\text{Co})$ value revealed from the titration analyses unambiguously represents the actual value of Co valence in the CoO_2 layer. For both of our samples of $y = 0.77$ and 0.72 , $V(\text{Co})$ was determined at 3.26. That the value of $V(\text{Co})$ did not increase with the decrease in y , is compatible with the fact that δ decreased from 0.02 for $y = 0.77$ to -0.01 for 0.72.¹³ In other words, the decrease in the overall positive charge in the Na^+ layer was counterbalanced by the concomitant decrease in the oxygen content. It is also important to recognize that the value obtained here for $V(\text{Co})$, *i.e.* 3.26, is significantly lower than 3.5 that is sometimes wrongly taken for the $\text{Na}_y\text{CoO}_{2+\delta}$ phase based on its "nominal nickname" of NaCo_2O_4 .

For $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$, the overall oxygen content was determined at $\delta = 0.24$ and $V(\text{Co})$ accordingly at 3.16. The structure of $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ with a layer sequence of CaO-CoO-CaO-CoO_2 , however, has two inequivalent Co sites (Fig. 1). Therefore the $V(\text{Co})$ value represents the average of valence values of the two types of Co species. Previously a rough estimation for $V(\text{Co})$ had been obtained at 3.23 from the chemical composition of $[\text{CoCa}_2\text{O}_3]_{0.62}\text{CoO}_2$ as calculated on the basis of crystal structure analysis result for the "degree of misfitness" between the two structure blocks, $[\text{CoCa}_2\text{O}_3]$ and CoO_2 .¹⁴ Thus here again the present value for $V(\text{Co})$ is somewhat lower than that one might have anticipated. The same applies to the $\text{Bi}_{2.1}\text{Sr}_{2.15}\text{Co}_2\text{O}_{8+\delta}$ sample, too. For this phase crystal structure analysis concluded a stoichiometry of $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$ or $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_4]_{0.55}\text{CoO}_2$.¹⁵ Taking the valence of bismuth at III, we get an estimation for $V(\text{Co})$ at 3.33. Against this value, the present wet-chemical redox analysis revealed a value of 3.20 for $V(\text{Co})$. It should be emphasized that even this

number may be overestimated of the real value of $V(\text{Co})$, since it was calculated assuming the lowest possible valence value of III for bismuth.

3.2 Thermogravimetric H_2 Reduction

For the $\text{Pb}_z\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ sample the oxygen content was estimated based on hydrogen reduction experiments carried out in a thermobalance (Perkin Elmer: Pyris 1) in 5 % H_2/Ar atmosphere. In a TG reduction the sample is heated to high temperatures in a reducing atmosphere to decompose it to a known reduction product, typically consisting of metals and/or simple oxides.¹⁶ From the weight loss accompanying the decomposition the amount of oxygen in the starting material may be calculated providing that the reduction residues are well defined in terms of composition. Note that in comparison to the wet-chemical redox analysis methods both the reproducibility and accuracy of the TG reduction method are, however, considerably lower.

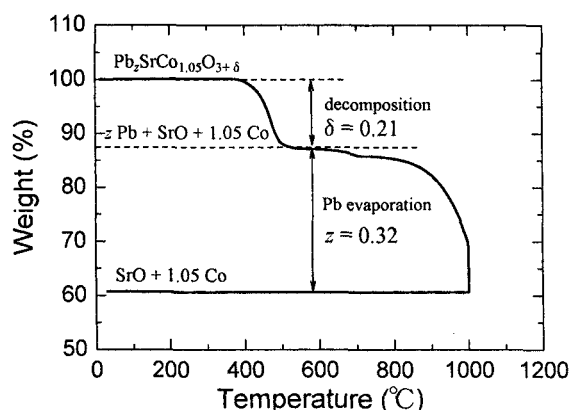


Fig. 2. TG reduction curve of $\text{Pb}_z\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ (with nominal z at 0.35) recorded in 5 % H_2/Ar gas flow for a 20-mg sample with a heating rate 2 °C/min. At 1000 °C the sample is isothermally heated for 4 hours.

In Fig. 2, shown is a typical TG reduction curve for our $\text{Pb}_z\text{SrCo}_{1.4-z}\text{O}_{3+\delta}$ sample with a nominal Pb content, z , of 0.35. Upon heating in 5 % H_2/Ar the misfit-layered phase decomposes in a single step at 400~500 °C into a mixture of Pb, Co and SrO. Further increase in temperature above 900 °C results in fast evaporation of lead. We found that this second weight-loss step may be conveniently utilized in estimating the Pb content in the sample. Therefore in order to guarantee complete evaporation the sample was kept at 1000 °C for 4 hours. During this isothermal heating period the weight of the sample was confirmed to well saturate. After taking into account the thus determined value of Pb content, z , the oxygen content in the original sample was calculated from the weight loss due to the first step. Here z was determined at 0.32 and δ at 0.21. We note that the value determined for z is close to the nominal one. To calculate the precise valence value for cobalt from the values determined for z and δ is somewhat unambiguous, as the valence of Pb is not known. We therefore only give the possible variation range for it: assuming tetravalent/

divalent Pb yields $V(\text{Co})$ at 2.99/3.60. From structural and chemical considerations the valence of Pb is likely to be closer to IV than II. Therefore, the actual $V(\text{Co})$ is believed to be closer to 3.0 than 3.6 in our $\text{Pb}_{0.32}\text{SrCo}_{1.05}\text{O}_{3.21}$ sample.

4. OXYGEN-CONTENT TUNABILITY

The possibility to tune the oxygen contents of the as-air-synthesized samples was investigated by means of oxygenation and deoxygenation annealings performed in a thermobalance in a 1-atm gas flow of O_2 and N_2 , respectively. In these experiments a small (10~40 mg) portion of the sample was heated to 800~1000 °C. A slow heating rate (0.5~2 °C/min) was used to guarantee an essentially equilibrium situation during the annealing. Substantial variation in the oxygen content upon such an annealing was observed only for the $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9.24}$ sample, in agreement with a previous report¹⁷ showing a variation range of approximately 0.2 oxygen atoms per " $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ formula unit". For the other samples, the observed changes in weight/oxygen content were negligible.

In Fig. 3, we show TG curves for the as-air-synthesized $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9.24}$ sample recorded upon first heating in N_2 up to 750 °C, then cooling back to room temperature in N_2 , and subsequently subjecting the same sample to heating up to 850 °C and cooling back to room temperature in O_2 . Note that from preliminary TG experiments it was found that the misfit-layered phase decomposes in N_2 above 750 °C (to a mixture of $\text{Ca}_3\text{Co}_2\text{O}_6$ and CoO) and melts in O_2 above 900 °C. From Fig. 3, upon heating in N_2 oxygen depletion starts in $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9.24}$ 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 $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ phase. The steady decrease seen in weight within 350-750 °C indicates that the oxygen content of $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ can be tuned in a continuous manner. Here it is useful to recognize that from the TG curve for the N_2 annealing it is possible 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.* TCOD (temperature-controlled oxygen depletion) annealing.^{16,18} From Fig. 3 we also notice that 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 $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ phase from 750 °C in N_2 the oxygen content remains low (Fig. 3). On the other hand, by recycling in O_2 oxygen is incorporated into the $\text{Ca}_3\text{Co}_{3.95}\text{O}_{9+\delta}$ phase again. Upon heating in O_2 oxygen incorporation starts about 300 °C.

The maximum in oxygen content is reached about 400 °C after which the phase again starts to lose oxygen. In comparison to the behaviour in N₂ atmosphere, in O₂ the oxygen loss occurs more moderately. It is interesting to note that in O₂ 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 O₂ when the recycling is carried out slowly enough (here 0.5 °C/min). As a result of the slow cooling in O₂ the oxygen content in Ca₃Co_{3.95}O_{9+ δ} is increased back to the original level of $\delta \approx 0.24$ (Fig. 3).

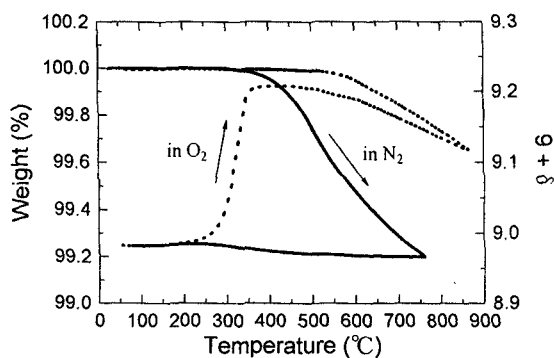


Fig. 3. TG curves for Ca₃Co_{3.95}O_{9+ δ} showing its deoxygenation and oxygenation characteristics. First as-air-synthesized Ca₃Co_{3.95}O_{9.24} is deoxygenated by heating (up to 750 °C) and cooling in N₂ (solid line) and subsequently oxygenated by heating (up to 850 °C) and cooling in O₂ (broken line). The mass of the sample was ~60 mg and the heating and cooling rates were 0.5 °C/min.

5. DISCUSSION AND CONCLUSIONS

The presently investigated misfit-layered and related cobalt-oxide phases that contain the hexagonal CoO₂ layer as a common building block have been recognized for their unexpectedly high characteristics of thermoelectric power. On the basis of Heikes formula and its extension to high-valent Co oxide systems by Koshibae *et al.*⁷ the thermoelectric power in these oxides should depend on the valence of cobalt, increasing with decreasing magnitude of $V(\text{Co})$. Here we have systematically elucidated the valence state of cobalt in the four representative CoO₂-layer oxides, Na _{y} CoO_{2+ δ} , Ca₃Co_{3.95}O_{9+ δ} , Bi_{2.1}Sr_{2.15}Co₂O_{8+ δ} and Pb_{0.32}SrCo_{1.05}O_{3+ δ} , by means of wet-chemical and thermogravimetric redox analysis methods. The value of $V(\text{Co})$ was revealed to lie approximately in the range of 3.1 to 3.3. In general, the present values may be regarded to be lower than those previously proposed for these systems. Among the different systems, the valence of cobalt seemed to be the highest in Na _{y} CoO_{2+ δ} ($y = 0.72$ or 0.77) in agreement with the fact that this phase typically shows the lowest room-temperature thermo-

electric power values.¹⁹

Only for Ca₃Co_{3.95}O_{9+ δ} , further tuning of oxygen content and thus the (average) value of $V(\text{Co})$ was found possible by means of oxygenation/deoxygenation annealings. In respect to its tailorable oxygen content the Ca₃Co_{3.95}O_{9+ δ} phase strongly resembles the most famous category of multi-layered oxide phases, *i.e.* copper oxides with high- T_c superconductivity.

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