JOURNAL OF Materials CHEMISTRY

Oxygen content analysis of functional perovskite-derived cobalt oxides

M. Karppinen,[a,b] **M. Matvejeff,**[a,b] **K. Salomäki**[a,b] **and H. Yamauchi**[b]

[a]*Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02015 Espoo, Finland*
[b]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan. E-mail: karppinen@rlem.titech.ac.jp; Fax: +81-45-924-5365*

Received 21st January 2002, Accepted 8th March 2002
First published as an Advance Article on the web 4th April 2002

We have evaluated the possible redox chemical methods for precisely determining the oxygen content in complex cobalt oxides that are being studied increasingly for their interesting electric and magnetic properties. For the evaluation, $BaNdCo_2O_{5+\delta}$ and $Sr_2(Ca,Y)Co_2O_{6+\delta}$ phases are selected as reference materials to elucidate the capabilities of the different analysis methods. Two redox methods so far commonly applied, *i.e.* thermogravimetric H_2 reduction and iodometric titration, are tested and two other, as yet unapplied, methods, *i.e.* cerimetric titration and Cu^+/Cu^{2+} coulometric titration, are introduced for the analysis of functional cobalt oxides. The three different titration methods are found to reveal consistent values for the oxygen content with good reproducibility. The results of thermogravimetric H_2 reduction analysis agree with the titration results but show a wider scattering. Of the four analytical methods, the Cu^+/Cu^{2+} coulometric titration method is considered most recommendable, since it is precise and may, furthermore, be applied to *e.g.* Cu and Fe substituted cobalt oxide samples.

"Non-stoichiometry" and "doping" are important concepts in modern inorganic materials science and technology. For transition metal (*T*) oxides that are increasingly being applied as electronic and other functional materials, non-stoichiometry in terms of the oxygen content is highly possible, and furthermore is crucially important in controlling the desired properties, *e.g.* electric and ionic conductivity, superconductivity, magnetoresistivity and strong thermoelectricity. "Oxygen engineering"—which should cover techniques for both controlling and determining the precise oxygen content—is therefore one of the most important tools for on-demand tailoring of functional oxides into optimized performances.[1] Tunability of oxygen non-stoichiometry and thereby the transition metal valency is especially common with perovskite-derived structures of 3d transition metal oxides. No real interpretation of the material characteristics of these oxides can be made without reliable knowledge of the absolute oxygen content of the samples studied.

The most accurate methods for establishing the precise oxygen contents of transition metal oxides are all based on redox reactions. In these methods, the high-valent cation(s) of the studied sample are reduced by a suitable reductant, *e.g.* I^-, Fe^{2+}, Cu^+ or H_2, followed by the determination of the exact amount of reductant left over or the oxidized form of the reductant formed, or even the weight change related to the reduction reaction, using an appropriate analysis technique. So far the most versatile set of analytical methods has been developed to determine the oxygen content in copper oxides of a perovskite-derived structure (see refs. 1–3 and references therein). This is due to the fact that during the last fifteen years unprecedented research efforts have been focused on these materials as many of them exhibit high-T_c superconductivity when appropriately doped.

Recently magnetoresistivity was revealed for cobalt oxide perovskites, $(La,Sr)CoO_{3-\delta}$[4–7] and $Ba\mathit{RE}Co_2O_{5+\delta}$ (*RE* = rare earth element).[8,9] This has already sparked intensive studies of spin, charge and orbital orderings in these materials.[10–17] Also a related Ruddlesden–Popper system, $Sr_2(Sr,Ca,Y)Co_2O_{6+\delta}$, has been studied because of its interesting magnetic properties.[18–21] The physical properties, including magnetoresistivity, have been found to be very sensitive to the oxygen content of the samples. As these and related complex cobalt oxides are anticipated to be the focus of intensive research in the near future, it is important to search for methods of precisely determining their oxygen contents. In the present contribution, the suitability of two redox methods that have so far been commonly applied to the oxygen content analysis of complex cobalt oxides [*i.e.* thermogravimetric (TG) reduction and iodometric titration], is evaluated. Furthermore, two other methods, *i.e.* cerimetric titration and Cu^+/Cu^{2+} coulometric titration, so far used for the oxygen content analysis of iron and/or copper oxides, are also tested and successfully extended to the analysis of cobalt oxides. For this study, $BaNdCo_2O_{5+\delta}$ and $Sr_2(Ca,Y)Co_2O_{6+\delta}$ phases are used as reference materials to demonstrate the capabilities of the different analysis methods.

Experimental

Synthesis of reference samples

An air-synthesized $BaNdCo_2O_{5+\delta}$ sample was obtained through solid-state reaction from $BaCO_3$, Nd_2O_3 and Co_3O_4. Before synthesis Nd_2O_3 was decarbonated at 900 °C overnight. Stoichiometric amounts of the powders were ground thoroughly and calcined at 1000 °C in air for 24 hours. After cooling and regrinding the sample was reheated at 1100 °C in air for 24 hours and slowly cooled down to room temperature. The $Sr_2(Ca_{1-x}Y_x)Co_2O_{6+\delta}$ sample was synthesized with a stoichiometry of $x = 0.7$ from $SrCO_3$, $CaCO_3$, Y_2O_3 and Co_3O_4. The heat treatments were carried out in air at 800, 1000 and 1100 °C, and twice at 1200 °C, each for 20 hours. After each heat treatment the sample was cooled down to room temperature and reground.

The oxygen non-stoichiometry of the $BaNdCo_2O_{5+\delta}$ and $Sr_2(Ca_{0.3}Y_{0.7})Co_2O_{6+\delta}$ samples was modified by

DOI: 10.1039/b200770n

thermogravimetric oxygenation and deoxygenation treatments performed for small portions of the as-air-synthesized powders in flowing oxygen and argon atmospheres, respectively, using a thermobalance of high sensitivity (Perkin Elmer TGA System 7 or MAC Science TG-DTA 2000S). In these TG annealings a powder sample of *ca.* 100 mg was heated at a slow enough rate (2 °C min^{-1}) to the desired temperature to guarantee an essentially equilibrium situation during the annealing. At the final annealing temperature, a one-hour isothermal heating period was applied after which the sample was cooled down to room temperature, slowly in the case of O_2 annealing (0.5 °C min^{-1}) and fast in the case of Ar annealing (20 °C min^{-1}). All the samples prepared were checked for phase purity by X-ray diffraction using a MAC Science M18XHF[22] or Philips PW 1830 diffractometer operating with Cu-Kα radiation.

Oxygen content analyses

The oxygen contents of the $BaNdCo_2O_{5+\delta}$ samples were determined by iodometric, cerimetric and Cu^+/Cu^{2+} coulometric titrations as well as by the thermogravimetric hydrogen (TG/H_2) reduction method, while for the $Sr_2(Ca_{0.3}Y_{0.7})Co_2O_{6+\delta}$ samples only cerimetric and coulometric titrations were applied. For each analysis, three to five parallel experiments were carried out. All the titration methods are based on dissolution of the sample in acidic solution and subsequent reduction of the high-valent cobalt species, Co^{III} and Co^{IV}, with an appropriate reductant. To prevent oxidation of the reductant by oxygen, the acidic solution used as a solvent and titration medium was freed from dissolved oxygen before each experiment by Ar bubbling. Also, it was important to perform the titrations in an air-tight cell under an Ar atmosphere.

In iodometric titrations[22] *ca.* 50 mg of the sample studied were dissolved in 1 M HCl solution (*ca.* 100 ml) containing an excess of KI (*ca.* 2 g), resulting in reduction of tri- and tetravalent cobalt species of the sample to Co^{2+} ions and formation of a stoichiometric amount of iodine in the solution. Iodine was titrated with $Na_2S_2O_3$ solution using starch as the indicator. Starch (1 ml; 0.2 w%) was added just before the end-point to avoid the end-point from being diffuse. For the same reason, KSCN (*ca.* 2 g) was added near the end-point. The end-point was detected visually as the blue colour of the starch complex disappeared and the solution turned white due to the formation of solid CuI. The concentration of the $Na_2S_2O_3$ solution (*ca.* 0.015 M) was standardized against both KIO_3 and CuO.

In cerimetric titrations[22] a *ca.* 50 mg portion of the studied sample was dissolved in 1 M HCl solution (*ca.* 100 ml) containing an excess of $FeCl_2 \cdot 4\,H_2O$ (*ca.* 100 mg). Cobalt with high oxidation states in the sample was reduced by divalent iron and the remaining excess of Fe^{2+} ions was titrated with $Ce(SO_4)_2$ solution using ferroin (one drop) as the indicator. The end-point was detected visually as the orange colour turned to green. The concentration of the cerium sulfate solution (*ca.* 0.015 M) was determined using Mohr's salt $[(NH_4)_2SO_4\text{-}FeSO_4 \cdot 6\,H_2O]$ as a reference and additionally standardized against As_2O_3.

Coulometric Cu^+/Cu^{2+} titrations[23] were carried out using Cu_2O as the reductant for Co^{III} and Co^{IV}. About 50 mg of the sample were dissolved in 1 M HCl solution (*ca.* 200 ml) containing an excess of Cu^+ ions (*ca.* 20 mg of Cu_2O) and the remaining excess of them was determined by means of electrochemical oxidation, *i.e.* coulometric titration. The anodic oxidation of Cu^+ to Cu^{2+} was performed with a dc current of 5 mA. Platinum plates were used as electrodes and the cathode was separated from the cell solution with a salt bridge. The potential was measured against an Ag/AgCl reference electrode (Horiba pH Meter F-22). The end-point of the titration was determined at 930 mV. Before each titration, a pre-titration with a small amount of Cu_2O (2–3 mg) was done to standardize the starting potential of the cell solution. Several blank titrations were carried out with the Cu_2O powder to standardize the titration.

Thermogravimetric hydrogen reduction[24] was performed in a Perkin Elmer TGA System 7 thermobalance. A sample of *ca.* 20–50 mg was heated at a rate of 2 °C min^{-1} to 700 °C in a 5% H_2–95% Ar atmosphere. The oxygen content of the sample was calculated from the weight loss resulting from the complete reduction of the complex oxide.

Results and discussion

Among the redox analysis methods used for the determination of the oxygen content of functional transition metal oxides, thermogravimetric reduction of the complex oxide to a mixture of metals and binary metal oxides is probably the most straightforward approach and has previously been applied to mixed cobalt oxides.[25,26] Hydrogen (H_2–Ar) is the most commonly used reductant. Following the reduction reaction by means of a thermobalance of high sensitivity and determination of the weight loss *in situ* at the temperature corresponding to the complete reduction are indispensable since many of the reduction products, *e.g.* BaO, react with moisture and/or CO_2, such that during cooling the mass of the decomposed sample gradually increases. In the present study the TG/H_2 reduction method was first applied to the oxygen content determination of the air-synthesized $BaNdCo_2O_{5+\delta}$ sample. Five parallel experiments were carried out. A typical TG/H_2 reduction curve is shown in Fig. 1. The complex oxide is reduced and decomposed in a stepwise reaction to a mixture of BaO, Nd_2O_3 and Co according to the overall reaction equation below

$$\begin{aligned} &BaNdCo_2O_{5+\delta}(s) + (2.5+\delta)\,H_2(g) \rightarrow BaO(s) \\ &\quad + 0.5\,Nd_2O_3(s) + 2\,Co(s) + (2.5+\delta)\,H_2O(g). \end{aligned} \qquad (1)$$

From Fig. 1, it can be seen that the reaction is complete around 550 °C. From the overall weight loss the amount of excess oxygen, δ, in the air-synthesized $BaNdCo_2O_{5+\delta}$ sample was calculated to be 0.64 with a reproducibility of ± 0.05. The other $BaNdCo_2O_{5+\delta}$ samples obtained through different post-annealing treatments from the air-synthesized material were also analyzed by the TG/H_2 reduction method. The results are given in Table 1.

Of the redox titrations, iodometric titration, *i.e.* titration using I^- as a reductant, is probably the most widely used method to determine the high oxidation states of transition metals and thereby the oxygen contents of their oxides.[1–3] Iodometry is also frequently applied to the oxygen content analysis of perovskite-related cobalt oxides.[8,9,27,28] In the present study, iodometric titration analysis was carried out

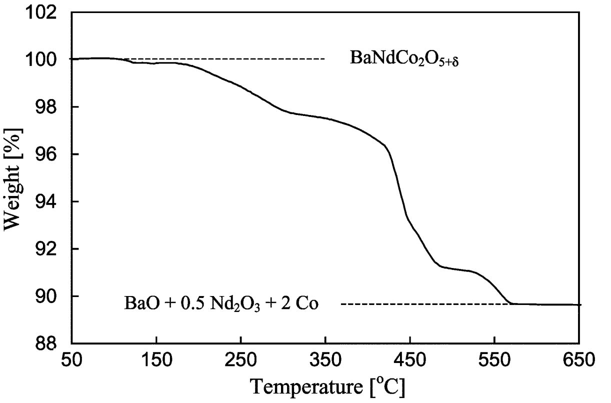

Fig. 1 A typical TG curve for the reduction of $BaNdCo_2O_{5.75}$ measured in a 5% H_2–95% Ar atmosphere at a heating rate of 2 °C min^{-1}.

Table 1 Results of oxygen content analyses for the $BaNdCo_2O_{5+\delta}$ samples[a]

	Method			
Sample	TG/H_2 reduction	Iodometric titration	Cerimetric titration	Coulometric titration
O_2-annealed (250 °C)	0.78	0.80	—	—
Air-synthesized	0.64	0.75	0.74	0.76
Ar-annealed (350 °C)	0.52	0.54	—	—
Ar-annealed (830 °C)	0.11	0.20	—	—

[a] The numbers given are values for the excess oxygen, δ, based on five parallel experiments with a reproducibility of *ca.* ±0.005 for the titration methods and *ca.* ±0.05 for the TG/H_2 reduction method. Note that the Co valence varied from +2.7 to +3.3 in the samples studied.

Table 2 Results of oxygen content analyses for the $Sr_2(Ca_{0.3}Y_{0.7})Co_2O_{6+\delta}$ samples[a]

	Method	
Sample	Cerimetric titration	Coulometric titration
O_2-annealed (360 °C)	0.48	0.47
Air-synthesized	0.27	0.29

[a] The numbers given are values for the excess oxygen, δ, based on three or more parallel experiments with a reproducibility of *ca.* ±0.005. Note that the Co valence varied from +2.9 to +3.1 in the samples studied.

for all the $BaNdCo_2O_{5+\delta}$ samples and was found to reveal the oxygen content values with a reproducibility of about ±0.005. The results are summarized in Table 1. Although the oxygen contents for the various $BaNdCo_2O_{5+\delta}$ samples as established by means of TG/H_2 reductions and iodometric titrations are quite consistent, the absolute values differ by ±0.1 (Table 1).

Cerimetric titration utilizing the reduction power of divalent iron against high-valent transition metal species and a subsequent determination of the remaining amount of Fe^{2+} ions by tetravalent cerium has been widely applied to the determination of oxygen content in complex iron oxides.[29–32] In the present study, we successfully applied the method to the oxygen content analysis of cobalt oxides. Five parallel cerimetric titration experiments carried out for the air-synthesized $BaNdCo_2O_{5+\delta}$ sample gave an oxygen content value of $\delta = 0.74$ with a reproducibility of about ±0.005. As shown in Table 1, the values obtained for the air-synthesized $BaNdCo_2O_{5+\delta}$ sample by the cerimetric and iodometric titration methods agree within the error limits of the two methods.

For the oxygen content analysis of copper oxides a redox method utilizing the reduction capability of monovalent copper in acidic solution has been successfully applied. As a final analysis step the remaining excess of the reducing agent is determined by means of electrochemical oxidation, *i.e.* coulometric titration[3,33,34] or constant-potential electrolysis[3,35,36] of Cu^+ to Cu^{2+}. The method is applicable to iron oxides as well.[1,34,37,38] In the present study, we applied Cu^+/Cu^{2+} coulometric titrations to the analysis of complex cobalt oxides for the first time. The method turned out to be completely quantitative for Co^{III} and Co^{IV}. The result obtained for the air-synthesized $BaNdCo_2O_{5+\delta}$ sample was exactly the same as those revealed by iodometric and cerimetric titrations within the error limits of the three methods (Table 1). In terms of accuracy, the Cu^+/Cu^{2+} coulometric titration method was found to be on the same level as the other two titration methods, *i.e.* five parallel experiments revealed the value of δ with a reproducibility of *ca.* ±0.005. To further demonstrate the applicability of the Cu^+/Cu^{2+} coulometric titration method to the analysis of high-valent cobalt oxides, the oxygen contents of two $Sr_2(Ca_{0.3}Y_{0.7})Co_2O_{6+\delta}$ samples were determined three times by Cu^+/Cu^{2+} coulometric and cerimetric titrations. As with the $BaNdCo_2O_{5+\delta}$ samples, both titration methods revealed essentially same values for the oxygen content. The results of the oxygen content analysis of the $Sr_2(Ca_{0.3}Y_{0.7})Co_2O_{6+\delta}$ samples are presented in Table 2.

Of the three different titration methods that were all found to reveal consistent oxygen content values with good reproducibility, the Cu^+/Cu^{2+} coulometric titration method has the advantage of being applicable to the widest range of 3d transition metals. It may thus be applied to the oxygen content analysis of cobalt oxides substituted with *e.g.* Fe and/or Cu. These kinds of samples with multiple transition metals are believed to possess potential as both scientifically and technologically interesting functional oxide materials. In Table 3, a short summary is given of the three different titration methods applied/developed in the present study for the accurate oxygen content analysis of complex cobalt oxides.

Finally, we demonstrate that once the exact oxygen content of an as-synthesized sample has been precisely determined by any of the redox titration methods, considerably good estimaions for the oxygen contents of the post-annealed samples can be obtained from *in-situ* detection of the corresponding weight changes if the post-annealings are carried out in a thermobalance of high sensitivity.[1,24] In Fig. 2 are presented representative TG curves for post-annealings performed for the as-air-synthesized $BaNdCo_2O_{5+\delta}$ (δ determined to be 0.75 by iodometric titrations) sample in O_2 and Ar atmospheres. The results calculated for the changes in the oxygen content upon post-annealings, *i.e.* $\Delta\delta = \delta_{ann} - \delta_{as\text{-}syn}$, from the thermograms agree reasonably well with those obtained by means of iodometric titration analysis of the post-annealed samples (Table 4). The sample annealed in Ar at 830 °C seemed to have a tendency to absorb some oxygen as soon as it was taken into open air, explaining the slightly higher value obtained by iodometry for the oxygen content than that calculated from the TG curve.

Table 3 Summary of the different titration methods applied/developed

	Iodometric titration	Cerimetric titration	Coulometric Cu^{2+}/Cu^+ titration
Reduction reactions	$2\,Co^{III} + 6\,I^- \rightarrow 2\,CoI_2 + I_2$ $Co^{IV} + 4\,I^- \rightarrow CoI_2 + I_2$	$Co^{III} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$ $Co^{IV} + 2\,Fe^{2+} \rightarrow Co^{2+} + 2\,Fe^{3+}$	$Co^{III} + Cu^+ \rightarrow Co^{2+} + Cu^{2+}$ $Co^{IV} + 2\,Cu^+ \rightarrow Co^{2+} + 2\,Cu^{2+}$
Titration reaction	$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$	$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$	$Cu^+ \rightarrow Cu^{2+} + e^-$
End-point detection	Visually[a] using starch as an indicator	Visually[a] using ferroin as an indicator	Measuring voltage against an Ag/AgCl reference electrode
Reproducibility for δ in parallel experiments	±0.005	±0.005	±0.005
Comments	Applicable to Co and Cu oxides, not Fe oxides	Applicable to Co and Fe oxides, not Cu oxides	Applicable to Co, Cu and Fe oxides

[a] It should be noted that instead of visual end-point detection, it is also possible to follow cerimetric and iodometric titrations potentiometrically.

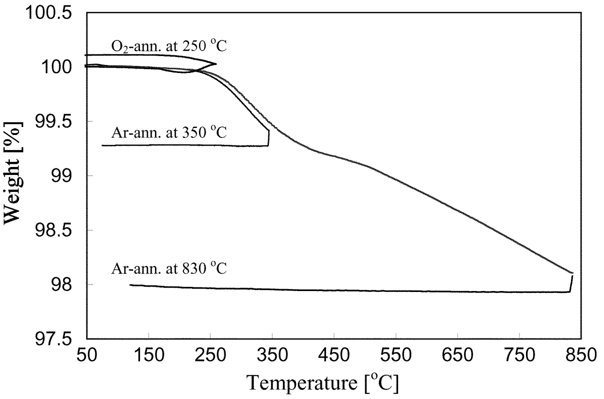

Fig. 2 TG curves for the oxygenation (at 250 °C) and deoxygenation (at 350 and 830 °C) of the air-synthesized $BaNdCo_2O_{5.75}$ material measured in an O_2 flow at a heating rate of 0.5 °C min^{-1} and in an Ar flow at a heating rate of 2 °C min^{-1}, respectively.

Table 4 Change in the oxygen content, $\Delta\delta = \delta_{ann} - \delta_{as\text{-}syn}$, detected for the air-synthesized $BaNdCo_2O_{5.75}$ material upon annealing in Ar and O_2 atmospheres by means of *in-situ* TG detection and iodometric titration

	Annealing		
Method	O_2 (250 °C)	Ar (350 °C)	Ar (830 °C)
TG detection	0.03	−0.23	−0.64
Iodometric titration	0.05	−0.21	−0.55

Conclusions

In the present study, four different methods of chemical analysis were evaluated in terms of their applicability for precise determination of the oxygen content in complex cobalt oxides. For the evaluation, two different perovskite-derived phases, *i.e.* $BaNdCo_2O_{5+\delta}$ and $Sr_2(Ca,Y)Co_2O_{6+\delta}$, were used as reference materials. In the samples studied, the valence of cobalt varied between +2.7 and +3.3. The three redox titration methods applied/developed, *i.e.* iodometric, cerimetric and Cu^+/Cu^{2+} coulometric titrations, were found to yield consistent values for the oxygen content with excellent accuracy, while the results of thermogravimetric H_2 reduction analysis showed considerably more scattering, even though being on average parallel to the titration results. Of the titration methods, the Cu^+/Cu^{2+} coulometric titration provides the widest possibilities, since it is applicable to a large number of 3d transition metals thereby enabling for instance analysis of Cu and/or Fe substituted cobalt oxide samples.

Acknowledgement

The present work has been supported by the Academy of Finland (Decision No. 46039), by a Grant-in-Aid for Scientific Research (contract No. 11305002) from the Ministry of Education, Science and Culture of Japan, and also by an International Collaborative Research Project Grant-2000 of the Materials and Structures Laboratory, Tokyo Institute of Technology.

References

1 M. Karppinen and H. Yamauchi, in International Book Series: *Studies of High Temperature Superconductors*, Vol. **37**, A.V. Narlikar (Ed.), Nova Science Publishers, New York, 2001, pp. 109–143.
2 M. Karppinen and H. Yamauchi, *Mater. Sci. Eng., R*, 1999, **26**, 51.
3 M. Karppinen, A. Fukuoka, L. Niinistö and H. Yamauchi, *Supercond. Sci. Technol.*, 1996, **9**, 121.
4 R. Mahendiran, A. K. Raychaudhuri, A. Chainani and D. D. Sarma, *J. Phys. Condens. Matter*, 1995, **7**, L561.
5 R. Mahendiran and A. K. Raychaudhuri, *Phys. Rev. B*, 1996, **54**, 16044.
6 G. Briceno, H. Chang, X. Sun, P. G. Schultz and X. D. Xiang, *Science*, 1995, **270**, 273.
7 S. Yamaguchi, H. Taniguchi, H. Takagi, T. Arima and Y. Tokura, *J. Phys. Soc. Jpn.*, 1995, **64**, 1885.
8 C. Martin, A. Maignan, D. Pelloquin, N. Nguyen and B. Raveau, *Appl. Phys. Lett.*, 1997, **71**, 1421.
9 A. Maignan, C. Martin, D. Pelloquin, N. Nguyen and B. Raveau, *J. Solid State Chem.*, 1999, **142**, 247.
10 T. Vogt, P. M. Woodward, P. Karen, B. A. Hunter, P. Henning and A. R. Moodenbaugh, *Phys. Rev. Lett.*, 2000, **84**, 2969.
11 E. Suard, F. Fauth, V. Caignaert, I. Mirebeau and G. Baldinozzi, *Phys. Rev. B*, 2000, **61**, R11871.
12 Y. Moritomo, T. Akimoto, M. Takeo, A. Machida, E. Nishibori, M. Takata, M. Sakata, K. Ohoyama and A. Nakamura, *Phys. Rev. B*, 2000, **61**, R13325.
13 H. Wu, *Phys. Rev. B*, 2000, **62**, R11953.
14 S. K. Kwon, J. H. Park and B. I. Min, *Phys. Rev. B*, 2000, **62**, R14637.
15 M. Paraskevopoulos, J. Hemberger, A. Krimmel and A. Loidl, *Phys. Rev. B*, 2001, **63**, 224416.
16 J. Wang, W. Zhang and D. Y. Xing, *Phys. Rev. B*, 2001, **64**, 64418.
17 H. Wu, *Phys. Rev. B*, 2001, **64**, 92413.
18 S. E. Dann and M. T. Weller, *J. Solid State Chem.*, 1995, **115**, 499.
19 K. Yamaura, Q. Huang and R. J. Cava, *J. Solid State Chem.*, 1999, **146**, 277.
20 K. Yamaura, Q. Huang, R. W. Erwin, J. W. Lynn and R. J. Cava, *Phys. Rev. B*, 1999, **60**, 9623.
21 K. Yamaura, D. P. Young and R. J. Cava, *Phys. Rev. B*, 2001, **63**, 64401.
22 G. D. Christian, *Analytical Chemistry*, 5th edn., John Wiley & Sons Inc., New York, 1994, pp. 284–383.
23 G. Kawamura and M. Hiratani, *J. Electrochem. Soc.*, 1987, **134**, 3211.
24 M. Karppinen, L. Niinistö and H. Yamauchi, *J. Therm. Anal.*, 1997, **48**, 1123.
25 N. V. Kasper, I. O. Troyanchuk, D. D. Khalyavin, N. Hamad, L. Haupt, P. Fröbel, K. Bärner, E. Gmelin, Q. Huang and J. W. Lynn, *Phys. Status Solidi B*, 1999, **215**, 697.
26 W. S. Kim, E. O. Chi, H. S. Choi, N. H. Hur, S.-J. Oh and H.-C. Ri, *Solid State Commun.*, 2000, **116**, 609.
27 J. E. Sundstrom IV, K. V. Ramanujachary and M. Greenblatt, *J. Solid State Chem.*, 1998, **139**, 388.
28 H. W. Brinks, H. Fjellvåg, A. Kjekshus and B. C. Hauback, *J. Solid State Chem.*, 1999, **147**, 464.
29 J. Lindén, M. Lippmaa, P. Karen, A. Kjekshus and M. Karppinen, *J. Solid State Chem.*, 1998, **138**, 87.
30 P. Karen and M. Woodward, *J. Mater. Chem.*, 1999, **9**, 789.
31 J. Lindén, P. Karen, A. Kjekshus, J. Miettinen, T. Pietari and M. Karppinen, *Phys. Rev. B*, 1999, **60**, 15251.
32 H. W. Brinks, H. Fjellvåg, A. Kjekshus and B. C. Hauback, *J. Solid State Chem.*, 2000, **150**, 233.
33 K. Kurusu, H. Takami and K. Shintomi, *Analyst*, 1989, **114**, 1341.
34 M. Karppinen, H. Yamauchi and S. Tanaka, *J. Solid State Chem.*, 1993, **104**, 276.
35 M. Karppinen, *Ann. Acad. Sci. Fenn., Ser. A2*, 1993, **249**, 51.
36 A. Fukuoka, M. Karppinen, M. Itoh, K. Hamada and H. Yamauchi, *Phys. Rev. B*, 1995, **51**, 12759.
37 K. Lehmus, M. Kochi, M. Karppinen, H. Yamauchi and L. Niinistö, *Int. J. Inorg. Mater.*, 2000, **2**, 203.
38 K. Lehmus, M. Karppinen, M. Matvejeff, J. Lindén, T. Pietari and H. Yamauchi, *Int. J. Inorg. Mater.*, 2001, **3**, 803.