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Synthesis and thermal stability of the new copper oxide carbonate $Ba_4ScCu_2O_{7-x}CO_3$ and other members of the series $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$

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We report the synthesis of a new perovskite-type oxide carbonate, $Ba_4ScCu_2O_{7-x}CO_3$. This phase has a tetragonal cell ($a=b\approx7.99$ Å, $c\approx4.10$ Å) based on a doubling of the basic perovskite subcell in the *a* and *b* directions. A possible structural model based on an ordering of Sc, Cu and C in the small cation sites is proposed. Experiments on the thermal stability of this phase have shown that raising the synthesis temperature from 940 to 1000 °C results in partial carbonate loss and a change in cell to a $\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell as previously observed for $Ba_4YCu_{2.27}O_{7.08}(CO_3)_{0.53}$. In addition we show that $Ba_4ScCu_2O_{7-x}CO_3$ may be classed as the $x=1$ member of the series, $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$ and we also report the synthesis of other new phases in this series.

Introduction

Cuprate systems have attracted unprecedented interest over the last 12 years, due to the observation of high temperature superconductivity in these systems, first reported by Bednorz and Müller.[1] This research has expanded our knowledge of the chemistry of cuprates immensely and has led to some remarkable and surprising results. One example has been the demonstration that small oxyanions (CO_3^{2-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}) can partially substitute for the small cation sites in materials with the perovskite structure.[2–10] This has led to a large body of new phases (see, for example, the review by Francesconi and Greaves[11]).

This paper concerns further work on the synthesis and characterisation of perovskite phases of the type $Ba_4MCu_{2+x}O_y(CO_3)_z$ (M = alkaline or rare earth),[5,6] which were found to have an ordered arrangement of M, Cu and C (from CO_3^{2-}) in the small cation sites. This arrangement was similar to the ordering (tetragonal $\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell where a_p and c_p are the basic perovskite subcell lengths) observed in $Ba_4LiBi_3O_{12}$.[12] Structural studies of $Ba_4MCu_{2+x}O_y(CO_3)_z$ showed three unique Cu sites, one of these sites being only partially occupied, with an essentially random distribution of Cu ions, CO_3^{2-} ions and vacancies (Fig. 1). This will be referred to as structure 1 throughout the paper. The presence of CO_3^{2-} ions was found to be vital for the formation of these phases, with no sign of the phase when synthesis was attempted from the metal oxides in an oxygen atmosphere. Instead the oxide $Ba_4MCu_3O_{8+y}$ (M = alkaline or rare earth) (cubic $2a_p\times2a_p\times2a_p$ cell) was observed[13,14] displaying an ordered arrangement on the small cation sites similar to that observed for $Ba_4LiSb_3O_{12}$.[15]

We have continued to study the oxide carbonate system and have examined the rare earth size limits that are possible for the formation of this phase. It has been found that the oxide carbonate forms for rare earths with ionic radii[16] ranging from 0.73 Å (Sc^{3+}) to 0.96 Å (Sm^{3+}). For larger rare earths such as Nd and La, there was no sign of the required phase. We report here the results for the smallest rare earth Sc. We have found a new ordered cell in this system, and a possible structural model is presented. The thermal stability of this phase is also discussed. In addition we show that the Sc content and carbonate content can be varied, so that it is possible to synthesise a range of phases of the form $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$.

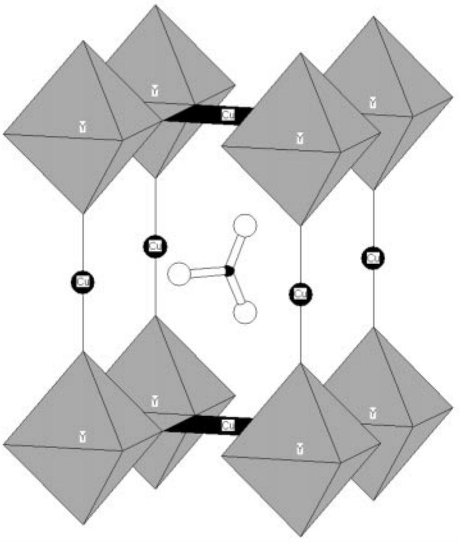

Fig. 1 Structure of $Ba_4YCu_{2+x}O_{6+4x}(CO_3)_y$ ($\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell) showing the unit cell when the central site is occupied by CO_3^{2-} (orientation of CO_3^{2-} shown arbitrarily).

Experimental

Samples were synthesised from intimately ground mixtures of high purity $BaCO_3$, Sc_2O_3 and CuO, which were subjected to two heat treatments at 940 °C in air for 14 h with intermediate regrinding and then furnace cooled. Examination using powder X-ray diffraction (Philips X'Pert PW3020 diffractometer) indicated that single phase samples were obtained for a Ba : Sc : Cu ratio of 4 : 1 : 2. Thermogravimetric analysis (H_2–N_2 reduction) was performed using a Stanton Redcroft STA-780 thermal analyser. Samples (*ca.* 30 mg) were heated at 10 °C min^{-1} to 950 °C and held at this temperature for 10 min in H_2–N_2 (5–95%). Under these conditions the Cu in the sample is reduced to Cu metal. Cu oxidation states were determined by iodometric titration. Two complementary titrations were performed for each sample. The first titration involved dissolving *ca.* 0.05 g of the sample in 50 cm^3 of distilled water by the addition of dilute 2 M HCl. The solution was then boiled to ensure complete conversion of any Cu^{3+}/Cu^{+} to Cu^{2+}, before

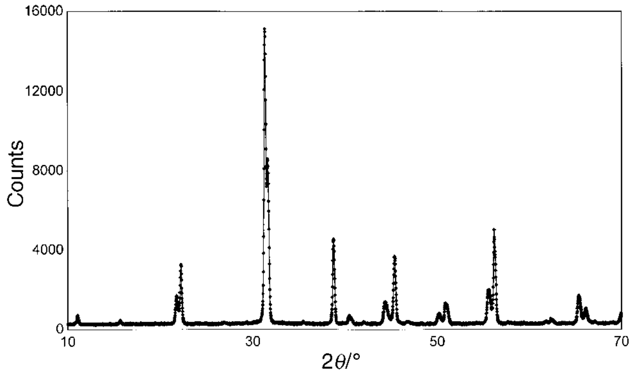

Fig. 2 XRD pattern for $Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}$ (sample A).

excess KI was added. The I_2 generated was then titrated under N_2 against standard 0.02 M $Na_2S_2O_3$ solution. This titration determines the total amount of Cu in the sample. The second titration involved dissolving under N_2 the same mass of sample in excess KI solution by addition of dilute HCl. The liberated I_2 was then titrated as before. From the difference in the titration values obtained, the copper oxidation state could be determined.

Results

The sample with cation composition Ba_4ScCu_2 was single phase with an XRD pattern similar to that observed previously for $Ba_4YCu_{2.27}O_{7.08}(CO_3)_{0.53}$, except for the fact that the intensities for the peaks associated with the tetragonal splitting were reversed (Fig. 2). Attempts to index the pattern on a similar tetragonal cell to that observed for the Y containing compound (*i.e.* $a=b\approx5.8$ Å, $c\approx8$ Å, $a=b=\sqrt{2}a_p$, $c=2c_p$) were unsuccessful. Instead a different cell with size $a=b\approx8.0$ Å, $c\approx4.1$ Å (*i.e.* $2a_p\times2a_p\times c_p$) was obtained.

TGA and iodometric titrations were used to determine the sample composition. It was necessary to determine two variables, the CO_3^{2-} content and the oxygen content, and unique values for these could be obtained by solving simultaneous equations using the two sets of analytical data. Such calculations indicated a sample composition of $Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}$. Approximate errors are ±0.1 in both oxygen and carbonate content.

Proposed structural model

A new structural model is required to account for the unit cell observed for $Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}$ (sample A). It was assumed that as in the previous model (structure 1) the rare earth (Sc) was octahedrally coordinated and that vacancies or carbonate ions were located in sites which were surrounded only by Cu. The structure (structure 2) shown in Fig. 3 (ideal composition $Ba_4ScCu_2O_7CO_3$) has therefore been proposed. Preliminary structural refinement using powder X-ray diffraction (Table 1, Rietveld method using program LX15LS based on the Cambridge Crystallography Subroutine Library CCSL[17,18]) supports the general cation ordering proposed showing a low occupancy of the Cu2 site (the proposed site for the location of C from the carbonate group). Owing to the fact that X-rays are insensitive to light atoms such as oxygen and carbon in the presence of heavy atoms such as Ba, it is, however, inappropriate to carry out a detailed analysis using X-ray diffraction. This is particularly the case for these oxide carbonates due to the complexity of the carbonate orientation.[5,6] A neutron diffraction structural study is, however, planned to confirm the proposed structure and obtain reliable oxygen positions as well as an indication of the presence of any ordering of the CO_3^{2-} groups.

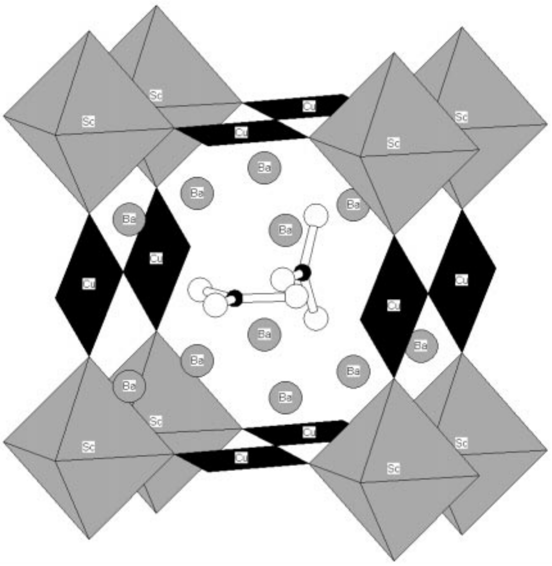

Fig. 3 Proposed structure for the ideal composition $Ba_4ScCu_2O_7(CO_3)$ ($2a_p\times2a_p\times c_p$ cell) (orientation of CO_3^{2-} shown arbitrarily).

Thermal stability

Heating sample A to higher temperature (1000 °C for 14 h) in air resulted in a change in the XRD pattern, with peak intensities now similar to those observed for $Ba_4YCu_{2.27}O_{7.08}(CO_3)_{0.53}$.[6] In agreement with this, the pattern could be indexed on a $\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell [$a=b=5.742(2)$, $c=7.975(3)$ Å] (Fig. 4). The pattern also showed the presence of a small amount of $BaCuO_2$ impurity, the amount of which increased if the temperature was increased further. From TGA and iodometric titrations a composition of $Ba_4ScCu_2O_7(CO_3)_{0.5}$ was determined for this sample (sample B). From these results we can write an equation for the partial loss of carbonate [eqn. (1)]

$$Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}\rightarrow Ba_4ScCu_2O_7(CO_3)_{0.5}+0.4CO_2+0.05O_2 \qquad (1)$$

The presence of a $BaCuO_2$ impurity however should be noted, and this will have an effect on the composition calculations, and also more importantly suggests that the cation composition may have changed. In this respect it is relevant to note the higher Cu content observed previously for the Y containing system.[6]

If sample B was then annealed at 920 °C for 24 h, a conversion back to the $2a_p\times2a_p\times c_p$ cell was observed. A composition of $Ba_4ScCu_2O_{6.8}(CO_3)_{0.8}$ was determined from the analytical data for this annealed sample, indicating a pick up of CO_2 according to eqn. (2)

$$Ba_4ScCu_2O_7(CO_3)_{0.5}+0.3CO_2+0.05O_2\rightarrow Ba_4ScCu_2O_{6.8}(CO_3)_{0.8} \qquad (2)$$

It should be noted, however, that if the sample had been heated to too high a temperature (>1000 °C) and so there was a large amount of $BaCuO_2$ impurity, then the pattern remained as the $\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell, thus indicating an irreversible change under these conditions, probably associated with a cation composition change.

These thermal stability results raised an interesting question, specifically that if for M = Sc a structural transformation and partial loss of carbonate occurred on heating to higher temperature, would it be possible to obtain a similar transition for larger rare earths such as Y. This was found to be the case; synthesis of $Ba_4YCu_2O_x(CO_3)_y$ at 940 °C resulted in a $\sqrt{2}a_p\times\sqrt{2}a_p\times2c_p$ cell as previously reported,[6] while synthesis

Table 1 Results from preliminary refinement of X-ray diffraction data for $Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}$ (sample A)[a]

Atom	Position	x	y	z	B/Å^2	Unit cell occupancy
Ba	8r	0.2419(2)	0.2419(2)	0.4756(9)	1.3(1)	0.5
Sc	1a	0	0	0	2.1(1)	1.0
Cu(1)	2f	0	0.5	0	2.1(1)	0.91(2)
Cu(2)	1c	0.5	0.5	0	2.1(1)	0.21(3)
O(1)	4l	0	0.257(4)	0	3.5(6)	1.0
O(2)	1b	0	0	0.5	3.5(6)	1.0
O(3)	2e	0.5	0	0.5	3.5(6)	0.91(5)
O(4)	4n	0.339(5)	0.5	0	3.5(6)	0.55(4)
O(5)	2h	0.5	0.5	0.35(2)	3.5(6)	0.34(5)

[a]Tetragonal, space group $P4/mmm$, $a=b=7.9926(2)$ Å, $c=4.0980(1)$ Å, $R_I=8.9\%$, $R_p=7.0\%$, $R_{wp}=9.2\%$, $R_E=4.6\%$.

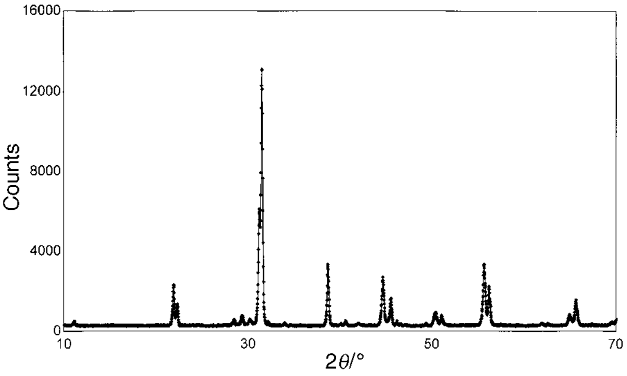

Fig. 4 XRD pattern for $Ba_4ScCu_2O_7(CO_3)_{0.5}$ (sample B).

at a lower temperature (880–900 °C) resulted in a $2a_p \times 2a_p \times c_p$ cell. It is however difficult to avoid some $BaCO_3$ impurity at these lower temperatures, and further research is ongoing to prepare single phase samples for structural characterisation and sample composition determination.

Variation of the Sc content

It is interesting that $Ba_4ScCu_2O_{7-y}CO_3$ may be classed as the $x=1$ member of the series $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$ with both endmembers already known, *i.e.* $Ba_2CuO_2CO_3$ ($x=0$),[19] $Ba_2ScCuO_{4.5}$ ($x=2$).[20] Attempts were therefore made to prepare other members of this series. Similar experimental conditions were used, and it was found that it was possible to prepare single phase samples for almost the complete series, $0 \leqslant x \leqslant 2$; small impurities were observed for the samples with $x=0.25$ ($BaCO_3$ impurity) and $x=1.25$ ($BaCuO_2$ impurity). For samples with low Sc contents, x, and consequently high CO_3^{2-} contents, synthesis under O_2 was required to obtain complete reaction, with $BaCO_3$ impurity being observed otherwise. Cell parameters for the single phase samples are given in Table 2. TGA and iodometric titrations confirmed that the compositions were in agreement with those expected, and these are also reported in Table 2.

Table 2 Cell parameters for $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$

Cation composition, x	$a=b$/Å	c/Å	Composition from TGA + iodometric titrations
0[a]	5.660(1)	7.974(3)	$Ba_4Cu_2O_4(CO_3)_2$
0.5	8.025(2)	4.001(1)	$Ba_4Sc_{0.5}Cu_2O_{5.6}(CO_3)_{1.3}$
0.75	8.003(2)	4.071(1)	$Ba_4Sc_{0.75}Cu_2O_{6.0}(CO_3)_{1.2}$
1.0	7.993(2)	4.098(1)	$Ba_4ScCu_2O_{6.7}(CO_3)_{0.9}$
1.5	4.099(1)	7.942(2)	$Ba_4Sc_{1.5}Cu_2O_{8.0}(CO_3)_{0.4}$
1.75	4.111(1)	7.944(2)	$Ba_4Sc_{1.75}Cu_2O_{8.6}(CO_3)_{0.2}$
2.0[b]	4.131(1)	7.977(2)	$Ba_4Sc_2Cu_2O_9$

[a]Data from ref. 19. [b]Data from ref. 20.

Conclusions

We have prepared a series of oxide carbonates of composition $Ba_4Sc_xCu_2O_y(CO_3)_{2-x}$ ($0 \leqslant x \leqslant 2.0$), demonstrating the versatility and extent to which CO_3^{2-} can be substituted into the small cation sites in perovskite cuprates. Particular attention has been focused on the $x=1$ member. For this phase it has been shown that synthesis at 940 °C results in a $2a_p \times 2a_p \times c_p$ cell, for which we have proposed a model (structure 2) with a new type of cation ordering in the small perovskite sites. We have also shown that a relatively small increase in synthesis temperature (from 940 to 1000 °C) results in partial carbonate loss to give a composition $Ba_4ScCu_2O_7(CO_3)_{0.5}$ which has a $\sqrt{2}a_p \times \sqrt{2}a_p \times 2c_p$ cell (structure 1) as previously observed for $Ba_4YCu_{2.27}O_{7.08}(CO_3)_{0.53}$.[6] It therefore appears as if the structure formed depends on the temperature of synthesis/carbonate content, with a $2a_p \times 2a_p \times c_p$ cell (structure 2) favoured at low temperatures/high carbonate content while the $\sqrt{2}a_p \times \sqrt{2}a_p \times 2c_p$ cell (structure 1) is favoured at higher temperatures/low carbonate content. In addition the temperature stability range depends on the size of the rare earth, with a small rare earth (*e.g.* Sc) favouring the former cell to higher temperatures than for larger rare earths (*e.g.* Y).

The change in structure can probably be attributed to a combination of factors, including carbonate content, rare earth size and oxygen content. Further work is however required, including powder neutron diffraction data, to fully characterise this interesting system, confirm the proposed structural model and obtain detail such as the orientation of the CO_3^{2-} groups. Electron microscopy studies would also be of potential interest, as it is likely, owing to the fact that the difference in synthesis conditions for the two compounds is small, that there may be regions showing intergrowths of the two different structures.

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