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Relationships between the chemical composition and properties of the high-temperature superconductor $Bi_{2+x}Sr_{2-y}Ca_{1+y}Cu_2O_{8+d}$

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Samples of the high-temperature superconducting solid-solution $Bi_{2+x}Sr_{2-y}Ca_{1+y}Cu_2O_{8+d}$ (2212 phase, $T_c \leqslant 95$ K) were prepared with different cation concentrations in order to study the influence of the cation concentration on the crystal structure, oxygen content and on several other physical properties. The measurements show that the *c*-axis parameter, the critical temperature, T_c, the resistivity, R, and the oxygen ion conductivity, $\sigma_{O^{2-}}$ of the phase decrease with increasing calcium content. With increasing bismuth content, T_c and R decrease, whereas the *c*-axis parameter increases. $\sigma_{O^{2-}}$ is not strongly dependent on the bismuth content of the phase. The oxygen content of the phase increases with increasing bismuth and calcium content.

1. Introduction

Since the discovery of the high-temperature superconducting compound $Bi_{2+x}Sr_{2-y}Ca_{1+y}Cu_2O_{8+d}$ (2212) [1] great efforts have been made to describe the crystal structure and chemistry of the phase [2, 3]. The variations of the Sr : Ca ratio [4–10] and of total bismuth content [4, 5], as well as the oxygen content [11–13] of the phase have been studied extensively (for an Overview, see [14]). From the stoichiometric formula $Bi_{2+x}Sr_{2-y}Ca_{1+y}Cu_2O_{8+d}$, the parameters x, y and d can be defined to be $0 \leqslant x \leqslant 0.3$, $-0.3 \leqslant y \leqslant 0.8$ and $0 \leqslant d \leqslant 0.4$. From this information it is possible to prepare 2212 ceramics with defined cation ratio and oxygen content which is important for optimizing the 2212 in terms of T_c and critical current density.

Owing to its extended homogeneity region, 2212 is an excellent example to point out that physical properties are very sensitive to variations of the chemical composition of the compound and that a knowledge of the phase relations and solubility limits is essential for optimizing a desired property.

2. Experimental procedure

The starting materials (Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO, purity > 99%) were weighed, mixed, homogenized and calcined at 750 °C for 24 h, and at 800 °C for 48 h. Samples with different Sr : Ca ratios and bismuth contents were prepared (Table I, Fig. 1). The calcined powders were pressed (625 MPa) and sintered for 24 h at 820 °C in air, except for the strontium-rich samples ($y = 0.1$–0.3) which were sintered at 870 °C, because these compositions are not within the single-phase regions at 820 °C, but at 870 °C [14]. Subsequently, the samples were reground, pressed, sintered at the same temperature for 60 h and furnace cooled. Finally the samples were annealed at 650 °C in flowing nitrogen for 15 h in order to achieve high T_c values [11–13]. Phase identification has been performed by a scanning electron microscope with energy dispersive analysis of X-rays (EDX; Cambridge Instruments S 200), X-ray diffraction, (XRD; Philips PW 1050, CuK_α) and optical microscopy (Zeiss Axiomat) with polarized light. The chemical composition of 2212 in the prepared samples was analysed by EDX. From each, sample, five to ten 2212 grains were analysed. The oxygen content was measured by carrier gas hot extrusion (Leco Inst. N/O-analysator TC 436, sample mass per analysis: about 2 mg; analysis per sample: 5–10). The CO_2 content of the samples was measured using the Rosemount carbon/hydrogen analysator 5003 (sample mass per analysis: about 2 mg; analysis per sample: 3). The critical temperatures were determined by a.c. susceptibility measurements. The error in the T_c measurements was about ± 1 K. The resistivity measurements were performed at 4–290 K using the four-point method. The oxygen conductivity of 2212 was determined from the stationary response of an electrochemical polarization measurement on the cell O_2–platinum–[Y_2O_3-doped $ZrO_2|2212|Y_2O_3$-doped ZrO_2]–platinum–O_2 (for further details, see [15, 16]).

TABLE I Prepared samples

Sample	Bi	Sr	Ca	Cu	Analyzed Sr:Ca ratio Analyzed Bi content	Comment	Nominal y-value	 x-value
1	2.18	2.3	0.7	2	2.26:0.74	$Bi_2Sr_2CuO_6$, $Sr_3Bi_2O_6$, $Sr_{14}Cu_{24}O_{41-x}$	− 0.3	0.18
2	2.18	2.2	0.8	2	2.18:0.82	single phase	− 0.2	0.18
3	2.18	2.1	0.9	2	2.10:0.90	traces of $Sr_3Bi_2O_6$ and $Sr_{14}Cu_{24}O_{41-x}$	− 0.01	0.18
4	2.18	2	1	2	2:1	single phase	0	0.18
5	2.18	1.9	1.1	2	1.88:1.12	single phase	0.1	0.18
6	2.18	1.8	1.2	2	1.80:1.20	single phase	0.2	0.18
7	2.18	1.75	1.25	2	1.77:1.23	single phase	0.25	0.18
8	2.18	1.7	1.3	2	1.67:1.33	traces of Ca_2CuO_3	0.3	0.18
9	2.18	1.6	1.4	2	1.60:1.40	single phase	0.4	0.18
10	2.18	1.55	1.45	2	1.56:1.44	single phase	0.45	0.18
11	2.18	1.5	1.5	2	1.5:1.5	single phase	0.5	0.18
12	2.18	1.4	1.6	2	1.38:1.62	single phase	0.6	0.18
13	2.18	1.3	1.7	2	1.28:1.72	Ca_2CuO_3, CuO, $Sr_{1-x}BiO_{2.5}$	0.7	0.18
14	2.18	1.2	1.8	2	1.23:1.77	traces of Ca_2CuO_3	0.8	0.18
15	2.1	2	1	2	2.09	single phase	0	0.1
16	2.125	2	1	2	2.13	single phase	0	0.125
17	2.18	2	1	2	2.18	single phase	0	0.18
18	2.2	2	1	2	2.21	single phase	0	0.2
19	2.25	2	1	2	2.25	single phase	0	0.25
20	2.275	2	1	2	2.27	$Bi_2Sr_2CuO_6$, CuO	0	0.275

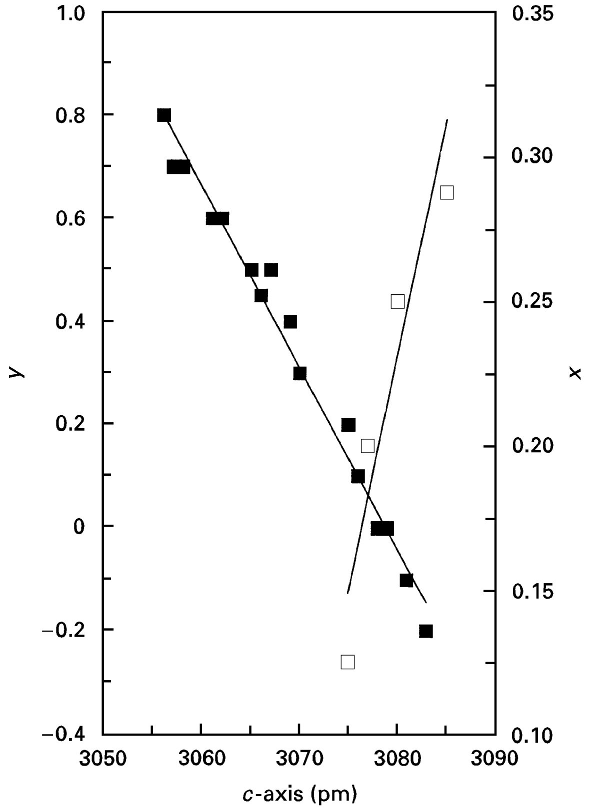

Figure 1 The (■) Ca (y) and (□) Bi (x) content versus the c-axis parameter.

3. Results

Most of the prepared samples are single phase (⩾ 99 vol. %) as determined by optical and electron microscopy, as well as XRD. The Sr/Ca ratio and varying bismuth content of the 2212 grains of the different samples were analysed to be significantly homogeneous within the standard error of the EDX measurement in one sample indicating that 2212 phase can be easily synthesized. The second phase content of the multi-phase samples constituted less than 5 vol % (Table I). The variation of the Sr/Ca ratio and bismuth content can be monitored by a pronounced change of the c-axis parameter of the phase (Fig. 1).

The measurements of the resistivity, R, at 4–290 K clearly show that R at room temperature increases with increasing calcium and bismuth content (Fig. 2). The effect of increasing calcium content on R is significantly larger than the effect of increasing bismuth. In

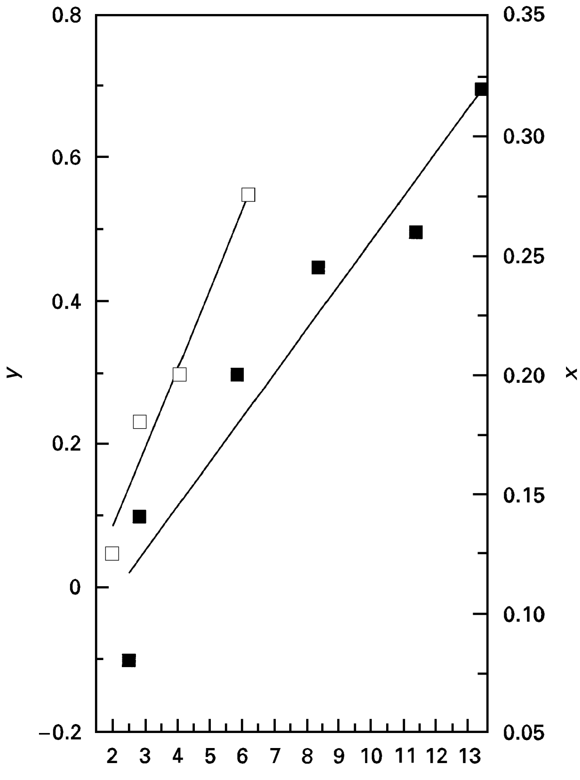

Figure 2 The (■) Ca (y) and (□) Bi (x) content versus R.

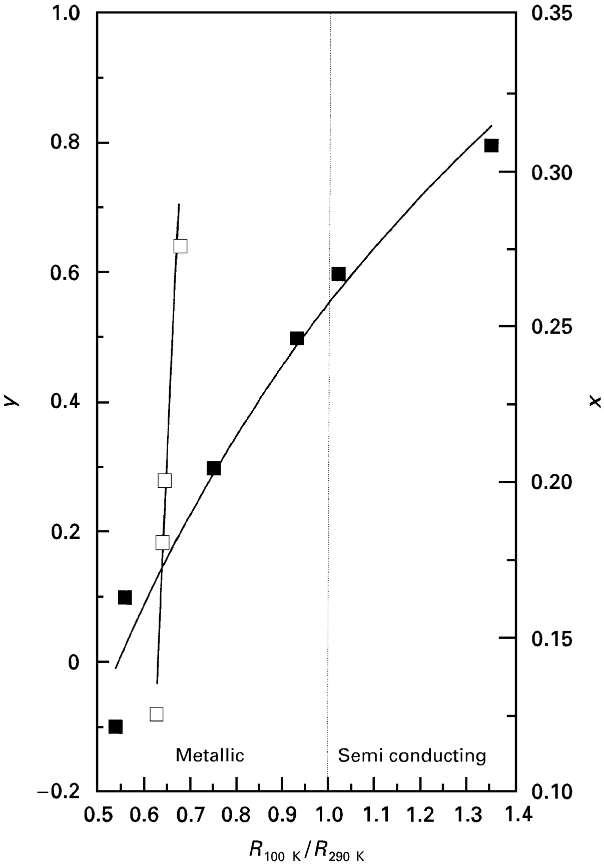

Figure 3 The (■) Ca (y) and (□) Bi (x) content versus the ratio of the resistivity at 100 and 290 K.

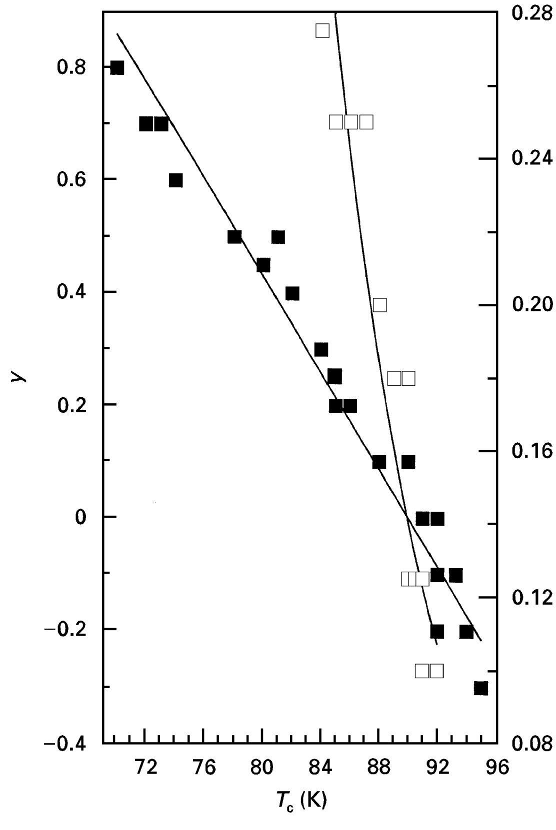

Figure 4 The (■) Ca (y) and (□) Bi (x) content versus T_c.

addition, it is remarkable that the phase exhibits a transformation from metallic to semiconducting above T_c with increasing calcium content (Fig. 3).

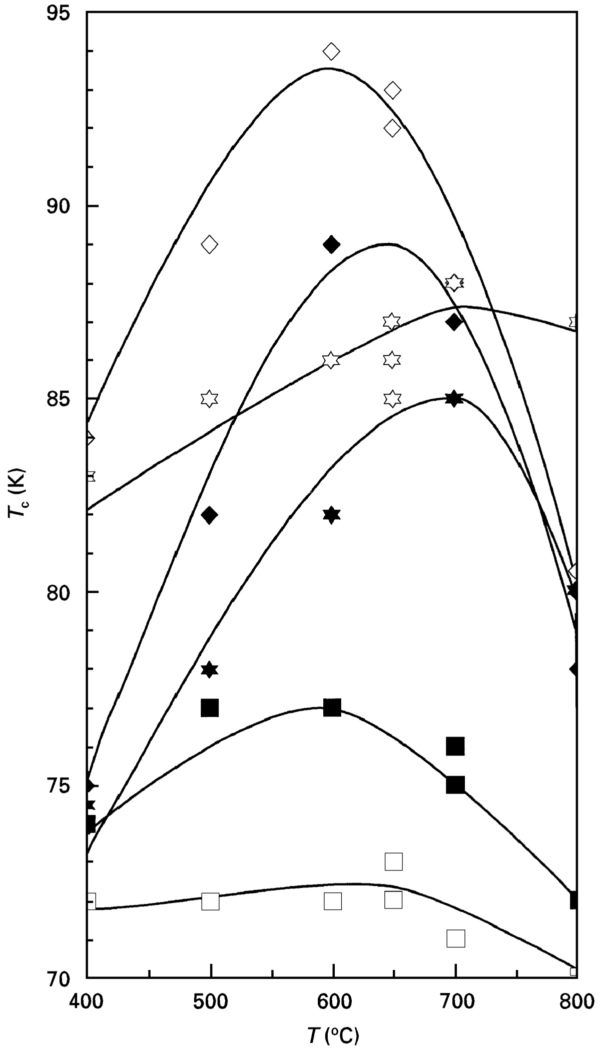

Figure 5 T_c of the standard samples (◇, ◆, $y = -0.1$, $x = 0.1$), that of the calcium-rich 2212 phase (□, ■, $y = 0.7$, $x = 0.18$) and that of the bismuth-rich 2212 phase (☆, ★, $y = 0$, $x = 0.25$) versus the post-annealing temperatures. (◆, ■, ★) $p_{O_2} = 1$ bar, (◇, □, ☆) $p_{O_2} = 10^{-4}$ bar.

The critical temperature, T_c, decreases with increasing calcium and bismuth content of the 2212 phase (Fig. 4). However, the decrease of T_c with increasing calcium content is much more pronounced compared to that for increasing bismuth content. It is well known that the T_c of the 2212 phase can easily be optimized by a heat treatment at lower temperatures and oxygen partial pressures [11–13] which correlates with an optimization of the oxygen content and that of the charge carrier concentration. The optimum conditions have been reported to be 500–600 °C and oxygen partial pressures of 10^{-5}–10^{-4} bar [12, 13]. In Fig. 5 the results of the low-temperature heat treatments at oxygen partial pressures of 1 (flowing oxygen) and 10^{-5}–10^{-4} (flowing nitrogen) are presented indicating that the T_cs of standard 2212 samples (calcium- and bismuth-poor) are significantly affected by these treatments ($\Delta T_c \approx 14$ K). For calcium- or bismuth-rich samples, the effect is smaller ($\Delta T_c \approx 5$–10 K). In addition, in contrast to the standard sample, the highest T_c values of the calcium-rich samples were obtained by annealing in oxygen and the maximum T_c values of the bismuth-rich samples were observed after annealing at 700 °C.

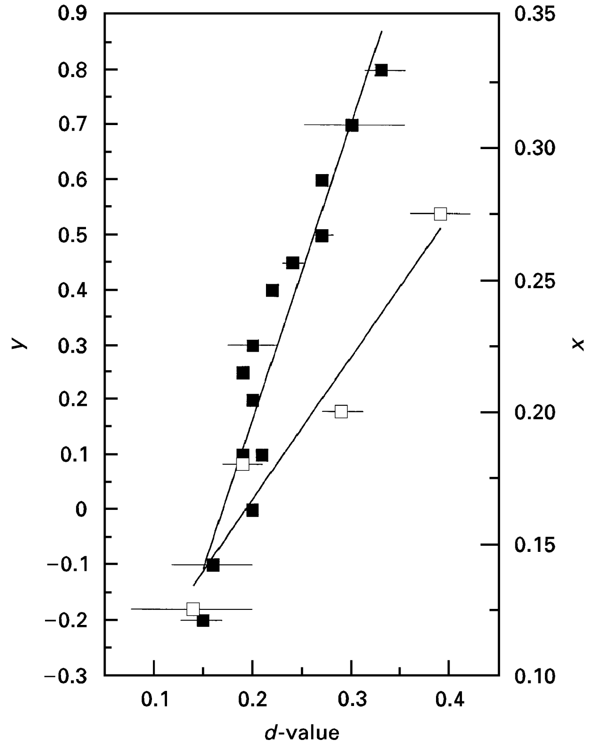

Figure 6 The oxygen content versus the (■) Ca (y) and (□) Bi (x) content.

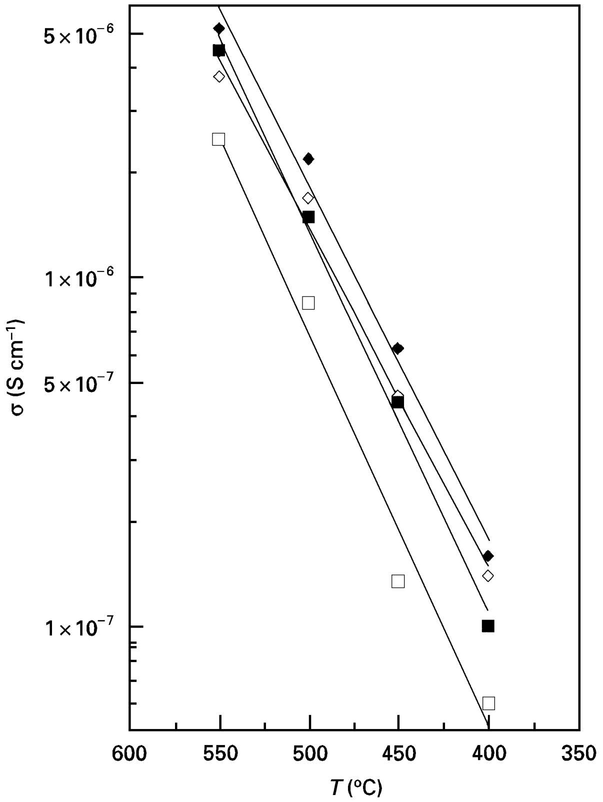

Figure 7 The oxygen conductivity versus the calcium and bismuth content. (■) $y = 0$, (□) squares: $y = 0.5$, (♦) $x = 0.1$; (◇) $x = 0.275$. In comparison with Y_2O_3-doped ZrO_2 the oxygen conductivity of the 2212 phase is about two orders of magnitude lower at 500 °C.

The measurements of the oxygen content and the oxygen ion conductivity, $\sigma_{O^{2-}}$, of the 2212 phase show that both depend on the calcium content of the phase. With increasing calcium, the oxygen content increases and the oxygen conductivity decreases. With increasing bismuth content, the oxygen content also significantly increases but a decrease of the oxygen conductivity is not observed (Figs 6 and 7).

4. Discussion

The electrical conductivity of a compound depends on the charge carrier concentration and the amplitude of lattice vibrations. Increasing the amplitude of the lattice vibrations by substituting calcium on the strontium site is assumed to be less significant than changing the carrier concentration, because the difference in the calcium and strontium masses is moderate. Therefore, the decrease in conductivity with calcium substitution is likely to be due to a decrease of the charge carrier concentration. However, because there is a large difference between the mass of bismuth and strontium or calcium, an influence on the lattice vibration by bismuth-substitution cannot be excluded.

The T_c also depends on the charge carrier concentration. However, the dependence is not linear, but exhibits a maximum at a certain charge carrier concentration. With increasing concentrations (overdoped, i.e. by annealing 2212 at low temperatures and $p_{O_2} = 1$ bar) or decreasing concentrations (underdoped, i.e. by annealing 2212 at high temperatures and $p_{O_2} = 10^{-5}$ bar) the T_c decreases (Fig. 8). Although the charge carrier concentration decreases with increasing calcium content, the results do not show that the calcium- and bismuth-rich samples are simply underdoped compared to the calcium-poor samples, because it was impossible to shift the low T_c values of

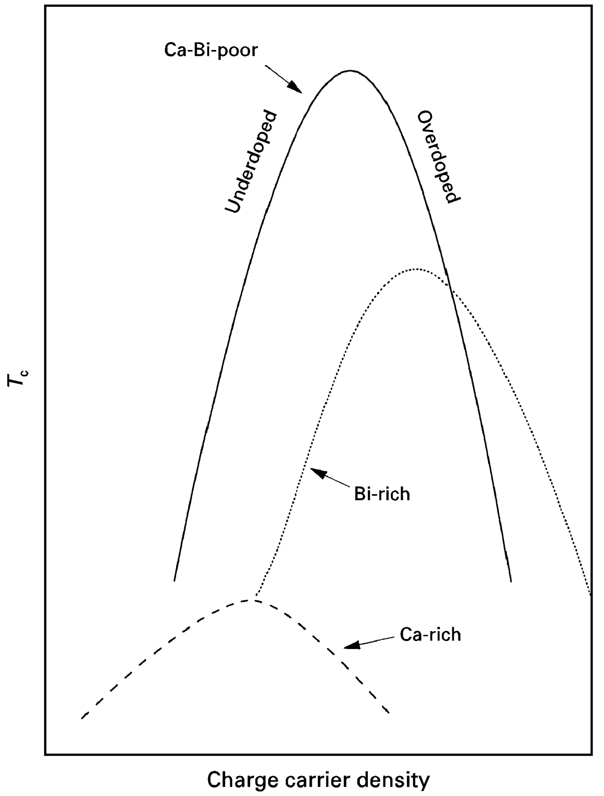

Figure 8 Schematical representation of the correlation between T_c and the charge carrier concentration. The positions of the peaks are arbitrary.

the calcium-rich samples up to the high T_c values of the calcium-poor samples. However, it is possible to shift the T_c of calcium-rich 2212 phase by about 5 K by heat treatment at 600 °C in 1 bar oxygen, which indicates that calcium-rich 2212 can have an underdoped, optimum and overdoped region. Therefore, we believe that there is no universal doping curve for 2212, but rather there are several, depending on the 2212 composition, which is schematically shown in Fig. 8.

The increase in the oxygen content with increasing bismuth can easily be explained by the charge balance, because the three-valent bismuth ion substitutes for the two-valent strontium and calcium ions. A calculation of the excess oxygen due to an increase of the bismuth content from $x = 0.1$ to $x = 0.3$ results in a d-value of 0.3 which fits with the observed increase of the d value with increasing bismuth content. The excess oxygen is believed to enter interstitials [17–19]. However, an increase in the oxygen content with increasing calcium is not expected because both the calcium ion and the substituted strontium ion are both two-valent. The artificially increased oxygen content of the calcium-rich samples by the formation of $CaCO_3$ can also be excluded as the carbon content of calcium-rich and calcium-poor samples were measured to be identical (0.05 wt %). Therefore, the enhanced oxygen content of the calcium-rich samples cannot be explained chemically. However, it can be assumed that the excess oxygen increases the valency of the bismuth and copper ions which has been shown for calcium-poor 2212 with different oxygen contents [12].

The ion conductivity depends on the mobility of the ion and the defect density within the crystal lattice. The mobility of the oxygen ion (O^{2-}) within 2212 is not affected by an increased calcium content. However, owing to the increased oxygen content of calcium-rich 2212, the number of oxygen interstitials is increased. Therefore, both the oxygen vacancy concentration and the oxygen ion conductivity are decreased [17–19]. However, with increasing bismuth content, a significant increase in the oxygen content is observed without a decrease in the oxygen conductivity. Therefore, it can be assumed that the oxygen conductivity is related to certain oxygen lattice sites, i.e. within the Cu–O layers of the perovskite-like "$Sr_2CaCu_2O_{5-d}$" units, which are probably affected by increased calcium contents but not by enhanced bismuth contents.

5. Conclusion

The measurements show that superconducting, normal state and ion-conducting properties of 2212 are significantly affected by the cation composition. In addition, substitution of equivalent cations also can significantly affect physical and chemical parameters, i.e. the charge carrier concentration and oxygen content resulting in a change of properties. For the advanced processing of materials, a knowledge of the homogeneity region and solubility limits of the phase and that of the dependence between properties and chemical composition is essential, because relationships between the desired property and the chemical composition of a material have to be taken into account.

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