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THERMOCHEMICAL REACTIVITY OF SUPERCONDUCTING MIXED COPPER OXIDES

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The importance of thermoanalytical methods for the investigation of superconducting mixed copper oxides is discussed. The thermochemical reactivity of ceramic superconductors adopting the structures of $YBa_2Cu_3O_{7-x}$, of K_2NiF_4 as well as of the composite structural frameworks is characterized in dependence of various gas atmospheres. The results give evidence, that depending on the ambient gas atmosphere most of these phases turn out to be remarkably reactive. Moreover, the oxygen stoichiometry proves to be of paramount importance for the superconducting properties. In turn, the range of stability of a superconducting phase with a given oxygen stoichiometry is often very narrow. Therefore, the thermoanalytical monitoring of redox processes and the determination of phase diagrams are indispensable.

Although a rather small family of superconducting metal oxides with onset temperatures below 15 K, i.e. the Li-Ti-O system with $T_c = 13.7$ K [1] and the Ba-Bi-Pb-O system with $T_c = 13$ K [2], has been known for more than ten years, it was the discovery of the mixed copper oxides with perovskite-related structures, i.e. the Ba-La-Cu-O system of Bednorz and Müller [3] and the Y-Ba-Cu-O system of Wu *et al.* [4] leading to far-reaching expectations into the production and application of these materials. In contrast to the practically tested superconducting metal alloy phases (see e.g. [5]), the preparation, the characterization of physical and chemical properties as well as of the thermochemical reactivity of these new ceramic superconductors is not yet fully established. This fact may be due to the complex interrelation between the compositional, structural and morphological features and the physical, above all the superconducting properties. In order to achieve detailed insights into the mentioned properties independent but complementary methods of investigations are indispensable.

This contribution aims in presenting experimental investigations on the thermochemical reactivity of the superconducting mixed copper oxides. As the number of such phases has increased with a tremendous pace during the

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last three years, a rough classification into groups containing similar structural elements appears to be necessary. As a consequence, the historic development of the discovery of the corresponding compounds cannot be maintained. In the first group, the thermochemical reactivity of phases with oxygen-deficient perovskite structure is presented. The second group relates to phases adopting the K_2NiF_4 structures and the third group comprises the more complex phases made up of several different structural elements.

Superconducting mixed copper oxides exhibiting oxygen-deficient perovskite structure

Soon after the discovery of superconducting properties of the $YBa_2Cu_3O_{7-x}$ phase with a T_c above 90 K [4] its structure was determined by various techniques such as X-ray and neutron diffraction as well as high resolution electron microscopy (see e.g. [6]). It was found, that the structural framework can be described by a grossly oxygen deficient (hypothetical) perovskite $AA_2'B_3O_9$ with Y and Ba in the A and A' positions and Cu in the B positions. It also turned out that the oxygen content of this phase was decisive for its physical properties. By means of thermoanalytical techniques performed under defined atmospheres it could be established that this metal oxide is metastable and that its oxygen stoichiometry can be adjusted by annealing procedures. As it is known from investigations on perovskite metal oxides, a number of representants of this class of materials undergoes reversible reduction/reoxidation by conserving the metal positions (see e.g. [7]). Depending on the actual oxygen stoichiometry the formal oxidation states of the present metal cations and thus the physical properties can be altered. Consequently, for the optimization of the superconducting properties of the mentioned Y-Ba-Cu-O phase, i.e. the preparation of material with a stoichiometry as close as possible to $YBa_2Cu_3O_7$ leading to a maximum amount of Cu cations in the formal oxidation state + III, the temperature and atmosphere dependence of the oxygen stoichiometry has been determined by comparative structural and thermoanalytical measurements (see e.g. [8, 11]). Moreover, the temperature dependent kinetics of the reduction/reoxidation is of paramount importance for any practical application of this compound. Therefore we set out to develop a model for the kinetic course of this reversible process [12]. Based on the highly topotactic reaction mechanism implicating a two-dimensional diffusion of the oxygen parallel to the crystallographic *a*-*b*-plane, the influence of the geometric dimensions of the real crystallites on the course of the temperature and time dependent thermogravimetric curves has been studied. These model calculations clearly show that the mentioned geometric dimensions are decisive parameters for the formation of highly oxidized, i.e. superconducting material. As a consequence the morphology of this type of highly anisotropic ceramic superconductors has to be taken into account for an optimal annealing procedure.

At this point it should be mentioned that materials adopting perovskite related structures and undergoing reversible uptake and release of oxygen are important with respect to their selective catalytic activity for conversions of organic compound such as the oxidation of methanol, etc. (see e.g. [13, 14]).

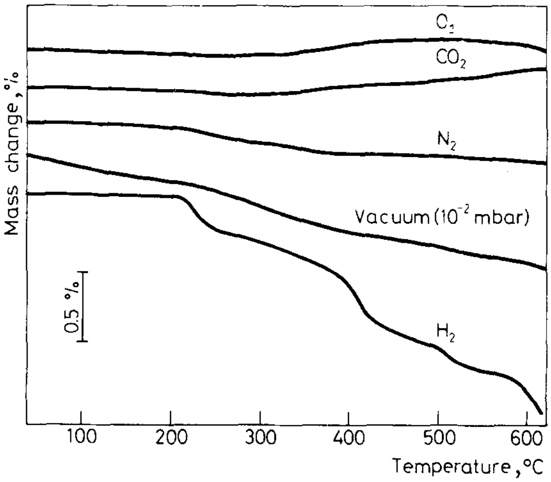

Fig. 1 Thermogravimetric measurements of the thermal behaviour of freshly calcined $YBa_2Cu_3O_{7-x}$ in various gas atmospheres (heating rate: 10 deg/min).

The thermochemical reactivity of the superconducting Y-Ba-Cu-O phase and of the related isostructural RE-Ba-Cu-O phases (RE = rare earth metals) is an important factor for their longtime stability. Therefore, not only the thermodynamical range of stability has to be determined by thermoanalytical techniques (see e.g. [15]), but also their reactivity in various gas atmospheres. This is demonstrated by thermogravimetric measurements in well defined gas atmospheres (Fig. 1 [16]).

Together with complementary investigations the following main results have been obtained:

- In oxygen atmosphere a weight gain is registered up to 800 K. Above 900 K the loss of oxygen is observed. These weight changes refer to the mentioned reversible reduction and reoxidation of $YBa_2Cu_3O_{7-x}$. Owing to the fact that freshly calcined material was used as initial material (calcination temperature around 1200 K), the weight gain below 800 K corresponds to the oxidation and thus to an increase of the maximally oxidized superconducting phase.
- In inert gas atmospheres and ambient pressure the compound is stable up to 700 K. At higher temperatures oxygen is evolved and above 1250 K phase segregations into the more stable binary metal oxide phases is observed.
- In CO_2 atmosphere the formation of the thermodynamically stable $BaCO_3$ leads to an increase of the weight (see also [17]). This result is of particular interest since the synthesis of these phases is often based on the use of metal carbonate precursors. Therefore, the thermal treatment of the precursor has to be well controlled in order to produce pure product phase.
- In hydrogen or further reducing atmospheres reduction processes are observed at low temperatures. Such type of measurements, however, cannot be applied for the determination of the oxygen stoichiometry, as the products formed not only contain well defined metals or binary metal oxides.
- Under reduced pressure the evolution of oxygen is registered at room temperature.
- Finally, in the presence of humidity these phases readily degrade under formation of metal hydroxides [18].

In summary, the understanding of the thermochemical reactivity of these most interesting phases represents the prerequisite for any application. Owing to the fact that they contain at least three different metal cations exhibiting partly mixed valence states, and, moreover, adopt various oxygen stoichiometries, a comprehensive interpretation of the interrelation between composition, structure, morphology on one side and chemical reactivity and physical properties on the other side is necessary. As it is described in the following chapters, this proves to be equally true for superconducting mixed copper oxide phases made up of different structural elements.

Superconducting mixed copper oxide phases adopting the K_2NiF_4 structure

The Ba-La-Cu-O phase established by Bednorz and Müller – which initialized the development of superconducting mixed copper oxide phases [3]

– is made up of alternating layers of elements of the perovskite structure and the rock-salt structure. The substitution of La by two-valent Ba or Sr leads to the formation of Cu cations with a formal oxidation state of +III (as present in the mentioned Y-Ba-Cu-O system). Thermoanalytical investigations of These K_2NiF_4-type phases give no evidence for similar reduction and reoxidation processes as found for the oxygen-deficient perovskite related compounds. Consequently their thermochemical reactivity is not as pronounced.

The most recently discovered class of superconducting mixed copper oxides is the Nd-Cu-O system with K_2NiF_4-related structure, where Nd is substituted by various other metal cations like Ce or Sr [19, 20]. Although these phases do not show high T_c values, they are of importance for the understanding of superconductivity in ceramic materials: In contrast to the mentioned Y-Ba-Cu-O-type, the La-Ba-Cu-O-type as well as to the complex phases mentioned in the following chapter, these novel Nd-Cu-O-type compounds are electron superconductors, i.e. Cu adopts the formal oxidation states +I and +II, but not +III. The chemical reactivity of these phases is not yet fully characterized. Preliminary results of investigations by means of high resolution electron microscopy and selected area electron diffraction techniques show, however, that thermal treatment leads to the formation of superstructural features [21]. Whether these superstructures, which are decisive for the superconducting properties, can be explained by metal cation ordering and/or by oxygen vacancy ordering is not yet confirmed. Answers to this problem are achieved by complementary thermoanalytical and structural methods of investigations. In the La-Ba-Cu-O-type phases, no indication for metal cation ordering and consequently for superstructures was found. Therefore the understanding of the role of these structural features of the Nd-Cu-O-type compounds may shed light on the theory of the electron hole superconductors (with formal Cu^{+III}) as well as the known electron superconductors.

Owing to the fact that the oxygen vacancies in the substituted Nd-*M*-Cu-O phases (where M = Ce, Sr) lead to a much more "open" structure than the one of the La-Ba-Cu-O-type compounds, the thermochemical reactivity of these novel materials proves to be much more pronounced. Thus, the investigations of the thermal behavior in oxidizing, inert as well as reducing atmospheres still need to be carried out in order to get detailed insights into the interrelation between this type of superconductivity and compositional and structural features of the actual ceramic material (this work is in progress).

Superconducting mixed copper oxides adopting composite structral frameworks

After the discovery of the high-T_c phases of the mentioned Y-Ba-Cu-O-type structure, the intensive search for other systems led to the discovery of further ceramic superconductors adopting complex layered structures made up two or more different structure fragments: Apart of the mentioned compounds based on the $LnBa_2Cu_3O_7$ structure (with Ln = Y, Ho, Dy, ...) and the $(M_{2-x}M'_x)CuO_4$ structure (with M = La, Nd and M' = Ba, Sr, Ce, ...) two more classes of compounds with the nominal stoichiometries $(Tl, Bi)_m(Ba, Sr)_2Ca_{n+1}Cu_nO_{2+m+2n}$ [6] as well as $Pb_2Sr_2ACu_3O_{8+\partial}$ [22] have been characterized. The preparation of pure phases of these two last mentioned systems causes, however, serious problems: As a consequence of the volatility of binary metal oxides of Bi, Pb around the afforded temperature of calcination, the use of selected precursor systems is necessary. Moreover, these materials exhibiting complicated compositional features can only be stabilized in a narrow temperature range. As differential thermal analysis shows phase segregations and decomposition processes occur above 1050 K. In the case of the Bi-Ca-Sr-Cu-O system the member with a double perovskite layer can be transformed into a compound with a triple perovskite layer by relatively long annealing procedures at temperatures around 1050 K. This phase shows a higher T_c than the double layered starting material. Obviously, during this process bismuth oxide is evolved. Owing to the fact that this conversion is very slow, its monitoring by on-line thermal analysis (TG or DTA) proves to be difficult. Complementary investigations of the concomitant structural changes by means of diffraction techniques yields a more detailed characterization of these processes.

The thermochemical reactivity as function of the gas atmosphere proves to be equally complicated: Detailed investigations on the Bi-Ca-Sr-Cu-O system containing the double layer of the perovskite fragment by means of thermogravimetric measurements in oxidizing and inert gas atmospheres reveal that reversible reduction/reoxidation processes take place at temperatures above 1070 K [23]. In oxygen a weight loss in the range of 0.3% is observed in the temperature range of 1160-1200 K. By cooling this partly reduced material in oxygen, the reoxidation occurs at slightly lower temperatures. This reduction/reoxidation process is reversible. In nitrogen the analogous reduction is observed. The temperature onset, however, is at 1070 K and the weight loss is more than 1%. Moreover, in both athmospheres melting occurs simultaneously to the reduction.

Conclusions

Superconducting mixed copper oxides represent a challenging class of compounds provided with a hitherto scarcely encountered complexity of compositional and structural features. It is therefore quite plausible that not only the preparation of these phases but also the characterization of their *Realstruktur* as well as of their thermochemical reactivity affords investgations by many different, but complementary methods. In this field thermal analysis plays a particular role: It offers not only the mere monitoring of weight changes as function of temperature, but also allows the determination of phase diagrams. This possibility is of paramount importance since the interesting superconducting phases often exhibit a very narrow range of stability. For both, the thermochemical reactivity as well as the determination of phase diagrams, the best possible definition of the actual pressure and of the actual gas atmosphere, under which measurements are performed, is of decisive necessity. For any application, be it in fundamental science or in applied sciences and materials research, the possible interactions between gases and the matter of interest, i.e. the superconducting material, must be elucidated in the full temperature range of stability, i.e. from the lowest possible up to the decomposition temperature. In may cases this requirement goes beyond the possibilities of the nowadays available thermoanalytical equipments. Above all, the development and establishment apparatus allowing measurements under well defined oxidizing, inert or reducing atmospheres as well as pressures from high vacuum up to several bars must be provided. Moreover, the materials used in any experimental set-up as e.g. crucibles, thermocouples as well as furnaces, have to be carefully selected, since during preparation, annealing procedures and measurements of thermochemically induced processes volatile binary metal oxides of e.g. Bi and Pb are evolved, may react and thus damage parts of the equipment.

The correlation of thermoanalytical measurements including the determination of magnetic and electronic properties with the concomitant compositional, structural and morphological changes leads finally to a better knowledge on the thermochemical reactivity of superconducting ceramic materials. Moreover, it improves and completes a comprehensive understanding of the reactivity of metal oxide phases and of solids in general (see also [24- 26]). The fact that superconducting ceramics represent compounds exhibiting a high degree of complexity with respect to the described features and that they are of enormous scientific as well as practical importance implies far-reaching developments in this field.

References

1 D. C. Johnston *et al.*, Mater. Res. Bull., 8 (1973) 777.
2 A. W. Sleight, J. L. Gillson and F. E. Bierstedt, Solid State Commun., 17 (1975) 27.
3 J. G. Bednorz and K. A. Müller, Z. Phys., B 64 (1986) 189.
4 M. K. Wu *et al.*, Phys. Rev. Lett., 58 (1987) 908.
5 T. G. Geballe and J. K. Hulm, Science, 239 (1988) 367.
6 C. N. R. Rao and B. Raveau, Acc. Chem. Res., 22 (1989) 106.
7 A. Reller, Ber. Bunsenges. Phys. Chem., 90 (1986) 742.
8 R. J. Cava *et al.*, Phys. Rev. Lett., 58 (1987) 1676.
9 A. Santoro *et al.*, Mater. Res. Bull., 22 (1987) 1007.
10 H. Eickenbusch *et al.*, Angew. Chem., 99 (1987) 1201.
11 R. Schöllhorn, Angew. Chem., 100 (1988) 1446.
12 C. Gurtner and A. Reller, unpublished results.
13 V. S. Komarov *et al.*, Zhurnal Prikladnoi Khimii, 56 (1986) 2409.
14 S. Hansen *et al.*, Nature, 334 (1988) 143.
15 R. S. Roth, K. L. Davis and J. R. Dennis, Adv. Ceram. Mater., 2 (1987) 303.
16 A. Reller, J. Pure Appl. Chem., in press.
17 P. K. Gallagher, G. S. Grader and H. M. O'Bryan, Mater. Res. Bull., 23 (1988) 1491.
18 J. Dominec *et al.*, Solid State Commun., 65 (1988) 373.
19 Y. Tokura, H. Takagi and S. Uchida, Nature, 337 (1989) 345.
20 H. Sawa *et al.*, Nature, 337 (1989) 347.
21 T. B. Williams *et al.*, to be published.
22 R. J. Cava *et al.*, Nature, 336 (1988) 211.
23 S. Casagrande, Diploma Thesis, University of Zürich, 1989.
24 H. R. Oswald and A. Reller, Thermochim. Acta, 95 (1985) 311.
25 H. R. Oswald and A. Reller, J. Thermal Anal., 33 (1988) 67.
26 H. R. Oswald and A. Reller, J. Pure Appl. Chem., in press.

Zusammenfassung — Es wird die Bedeutung thermoanalytischer Methoden für die Untersuchung supraleitender Kupfermischoxide beschrieben. In Abhängigkeit verschiedener Gasatmosphären wird die thermochemische Reaktivität von keramischen Supraleitern charakterisiert, die sowohl die Strukturen von $YBa_2Cu_3O_{7-x}$, von K_2NiF_4 oder auch von Verbundstrukturgerüsten annehmen. Die Ergebnisse zeigen eindeutig, daß in Abhängigkeit von der umgebenden Gasatmosphäre die meisten von ihnen eine bemerkenswerte Reaktivität aufweisen. Weiterhin scheint der Sauerstoffanteil von äußerster Wichtigkeit für die supraleitenden Eigenschaften zu sein. Der Stabilitätsbereich von supraleitenden Phasen mit einem gegebenen Sauerstoffanteil ist hingegen oft sehr schmal. Eine thermoanalytische Überwachung von Redoxprozessen und die Erstellung von Phasendiagrammen ist somit unentbehrlich.