

Synthesis and thermal properties of superconducting copper oxides

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Abstract - Aspects of the synthesis and of the characterization of the thermochemical properties of high- T_c mixed copper oxides, in particular of the Y-Ba-Cu-O system and of the Bi-Ca-Sr-Cu-O system are discussed. Related studies are based on conventional thermoanalytical tools such as thermogravimetry and differential thermal analysis. Facilities for the determination of the partial pressures of the gases establishing the ambient gas atmosphere during the formation as well as during the thermal treatment of these phases are indispensable. Thus, combined methods of investigation such as thermogravimetry/mass spectrometry are applied. The elucidation of mechanism and kinetics of temperature dependent changes of the structural frameworks are discussed in terms of reversible reduction/reoxidation processes. Specific details of morphological properties as well as of structural features such as superstructures or incommensurate structures evoked by non-stoichiometry are described by studies obtained from scanning electron microscopy (SEM) as well as high resolution electron microscopy (HREM). These studies allow more detailed insights into the relation between the *real structure of superconducting ceramics* and their *physicochemical properties*. The role of thermoanalytical techniques is discussed with respect to its present potential as well as to its future development for the characterization of the temperature dependent physicochemical properties of these challenging materials.

INTRODUCTION

During the last two years the rather small family of metal oxides exhibiting superconducting properties, i.e. the Li-Ti-O system with an onset temperature $T_c = 13.7$ K (ref. 1) and the Ba-Bi-Pb-O system with $T_c = 13$ K (ref. 2), has remarkably grown by the discovery of a mixed copper oxide adopting a perovskite related K_2NiF_4 structure, i.e. the Ba-La-Cu-O system of Bednorz and Müller (ref. 3). One of the main reasons for the enormous interest into this phase originated from the fact, that it showed T_c 's higher than the ones reported for *A 15* transition metal alloys such as Nb_3Ge with a $T_c = 23.3$ K (ref. 4,5). Thereafter, worldwide scientific activities lead to the discovery of further mixed copper oxides with T_c 's above the boiling point of liquid nitrogen, i.e. the RE-Ba-Cu-O system (RE = rare earth metals) (ref. 6) as well as the Bi-Sr-Cu-O system (ref. 7), the Bi-Ca-Sr-Cu-O system (ref. 8,9) and the Tl-Ca-Ba-Cu-O system (ref. 10).

Whereas for the elucidation of the theory of superconductivity in ceramics materials without copper as 'essential metallic ingredient' such as the recently published Ba-K-Bi-O system (ref. 11) will be of importance, the copper systems are of remarkable interest with respect to their high T_c 's as well as with respect to the variety of perovskite-related structural frameworks, within which Cu can be stabilized under adoption of different oxygen coordinations as well as unusual (formal) oxidation states. These features lead to the specific electronic structures, i.e. the prerequisites for superconductivity.

This contribution focusses on aspects of the synthesis and of the thermochemical reactivity of high- T_c mixed copper oxides, in particular of the Y-Ba-Cu-O system and of the Bi-Ca-Sr-Cu-O system. Owing to the fact, that they represent rather complex materials with respect to their structures as well as to their limited thermodynamic and chemical stability, detailed investigations on the different possibilities for the generation of pure phases as well as quantitative studies on their thermal degradation are of decisive importance. Therefore, related studies require not only the conventional thermoanalytical tools such as

thermogravimetry and differential thermal analysis, but also facilities for the elucidation of the partial pressures of the gases establishing the ambient gas atmosphere during the formation as well as during the thermal treatment of these ceramics. Combined methods of investigation such as thermogravimetry/mass spectrometry are applied.

The determination of temperature dependent structural properties of the obtained phases as well as the changes of the structural frameworks as result of reduction/reoxidation processes represent important features of this class of materials. Moreover, the kinetics of reduction/reoxidation processes, in particular of the Y-Ba-Cu-O-system, require quantitative thermogravimetric measurements using well-defined samples. As it will be shown, the morphology of the actual crystallites, i.e. their shape influences the kinetics decisively.

As a consequence morphological studies by light and scanning electron microscopy are correlated with the synthetic parameters in order to optimize the form of such materials with respect to specific requirements, be it for application or for purely scientific purposes.

Temperature dependent structural characterizations by means of X-ray diffraction or neutron diffraction in the temperature range from liquid helium up to 1200 K prove to be indispensable tools. Complementary informations on the microstructure and/or on specific structural features such as superstructures or incommensurate structures evoked by non-stoichiometry enable a more detailed correlation between the *real structure of superconducting ceramics* and their *thermochemical and physical properties*. The observation and detailed characterization of these abovementioned phenomena require studies by means of analytical and high resolution electron microscopy and the correlation of the so-obtained findings with measurements of the temperature dependent changes of the physical properties including the transition into the superconducting state in the range between 4 K and room temperature.

As a matter of fact, the following statements only represent extracts of experimental investigations on these challenging materials. They are thought as contribution illustrating the potential as well as the limitations of thermal analysis in the field of materials science.

INVESTIGATIONS ON $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ($0 \leq x \leq 1$)

The first preparations were carried out by simply mixing the binary oxides or carbonates of the metal constituents of the Y-Ba-Cu-system and subsequent calcining in the temperature range of 1200 - 1250 K in air. Subsequent annealing procedures at various temperatures yielded considerable amounts of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ phase with T_c 's above 90 K. After these sensational findings an exponentially growing number of scientists got occupied with the more tedious work of detailed investigations on the structural and compositional features of this phase by means of x-ray and neutron diffraction, spectroscopy, optical, scanning and high resolution electron microscopy, thermal analytical techniques and various kinds of chemical analysis. As the recently determined phase diagram of the BaO-CuO-Y₂O₃-system reveals (ref. 11), the crucial phase $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ only exists in a narrow array. Thus, the careful control of experimental parameters during the synthesis is decisive.

Our interests were focussed on the decomposition of selected precursor systems in order to avoid the formation of by-products as well as to control the morphological features of the superconducting phase. Therefore, by coprecipitation techniques mixed hydroxides, carbonates, formates and oxalates were prepared and their thermal degradation was monitored by thermogravimetry under well-controlled atmospheres. As it turned out, the use of coprecipitated precursor materials proved to be advantageous with respect to the degree of purity of the product phase $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. Moreover, the morphology can be directly influenced by the type of the selected precursor system: Starting with a carbonate precursor, plate-like crystals of the superconductor are obtained. The use of formate precursors leads to the formation of small, isotropically shaped crystallites in a relatively fast reaction (ref. 12). As it will be mentioned later on, the morphology of the yielded products is important with respect to the annealing behaviour.

The compound $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ adopts a strongly oxygen-deficient, perovskite-related structural framework (ref. 13). As it is shown schematically in fig. 1, this layered and consequently highly anisotropic phase undergoes reversible reduction/reoxidation processes evoked by thermally induced loss respectively gain of bulk oxygen anions (see e.g. ref. 14). The reversibility can be ascribed to the conservation of the perovskitic metal cation positions. Similar behaviour has been observed in related perovskites such as CaMnO_{3-x} (ref. 15).

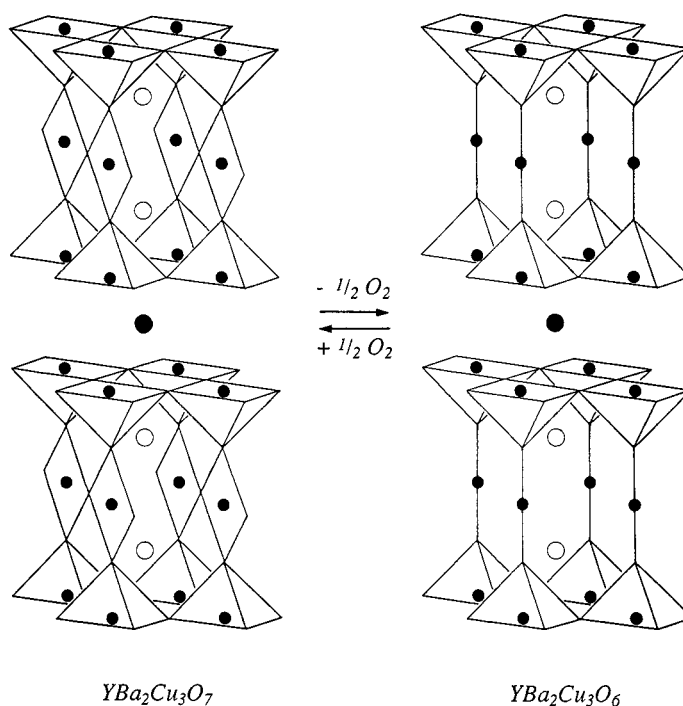


Fig. 1. Schematic representation of the reversible topotactic structural reaction mechanism of the thermally induced reduction/reoxidation of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $0 \leq x \leq 1$. (Cu: small filled circles; Ba: large full circles; Y: large filled circles; the oxygen anions occupy the corners of the copper-oxygen-polyhedra)

The described redox processes not only change the coordination of the copper cations including their formal oxidation states, but also alter the electric, magnetic and the superconducting properties of the bulk material. Owing to the fact that at the calcination temperatures, i.e. in the range of 1200 - 1250 K, the oxygen content is not optimal, annealing procedures at lower temperatures (around 700 K) in pure oxygen lead to the formation of the superconducting material with stoichiometries close to the ideal value of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The detailed characterization of the oxygen ordering and of the *real structure* of these phases has been investigated by high resolution electron microscopy (see e.g. ref. 16).

In order to optimize the annealing procedures we carried out computer simulations of the kinetics of the thermal oxidation of freshly prepared $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ crystallites. Owing to the topotactic structural reaction mechanism one can assume that the oxygen mobility parallel to the $(\text{CuO}_2)_\infty$ -layers, i.e. parallel to the crystallographic [001]-plane, is rate-limiting. Consequently, a model based on a two-dimensional reaction-mechanism can be applied. As the computer simulation of thermogravimetric measurements of the reduction or reoxidation of an isolated single crystal, of various single crystals or of a powder-like sample show (figure 2), that the morphological features of the actual material prove to be decisive for kinetics controlled by either a diffusion mechanism or by a phase boundary reaction mechanism (ref. 17).

The experimental confirmation using single crystals with well defined morphology will be published elsewhere. As an important consequence for any applications the control of the morphology of the calcination product as well as of the crystallographic orientation of the primary domains being exposed at the surface has to be achieved by careful selection of the precursor systems and by the thermal treatment. Only then highly oxidized superconducting material can be formed under optimally controlled experimental conditions.

As mentioned above the superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ easily undergoes thermal reduction. Moreover this compound exhibits a high reactivity towards humidity, carbon dioxide as well as reducing agents. Recent investigations proved the presence of considerable fractions of hydroxyl groups within

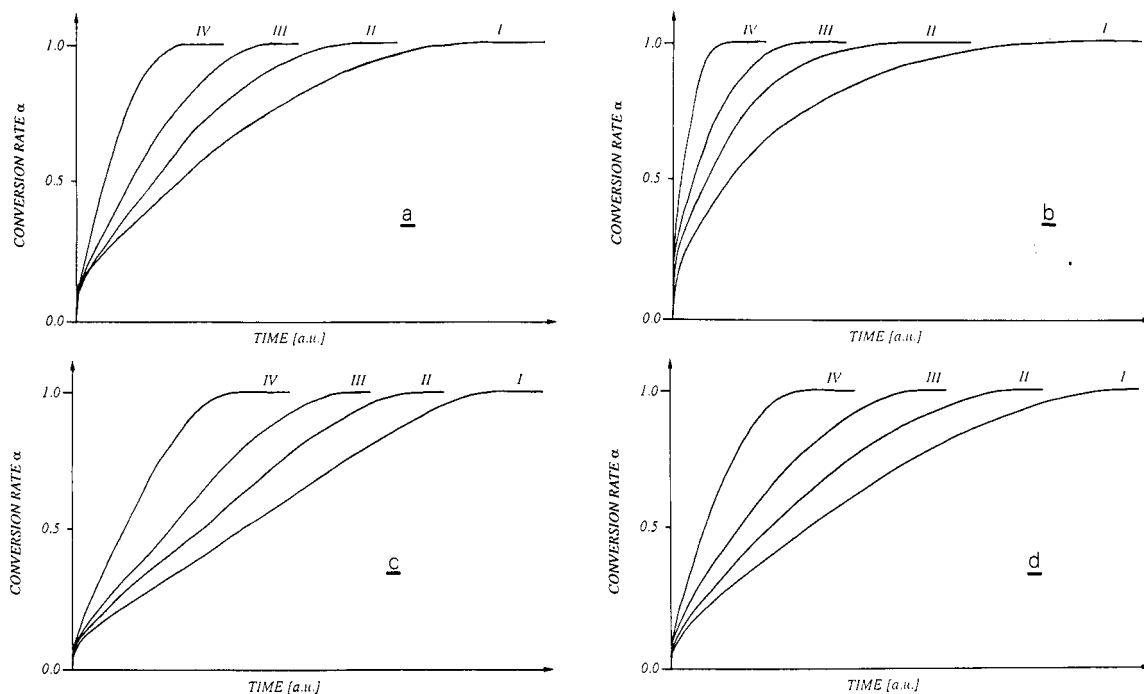


Fig. 2: Computer-simulated thermogravimetric measurements of reversible topotactic reduction and reoxidation processes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ based on a two-dimensional macroscopic reaction mechanism with the following assumptions: In figure 2a, 2b, 2c and 2d I refers to a measurement using one isolated single crystal, II to two single crystals, III to four single crystals, IV to sixteen single crystals. The weights of the samples are equal, i.e. the weight of an isolated single crystal (curve I) corresponds to the weight of sixteen single crystals (curve IV). Abbreviations used: $k \equiv$ rate constant, depending on temperature and crystallographic direction (see e.g. ref. 18); $T \equiv$ reaction temperature; $x \equiv$ relative metric dimension along the crystallographic axes a and b .

Fig. 2a: $k(100) = k(010) = f(T)$; endothermal process controlled by phase-boundary reaction mechanism. Fig. 2b: $k(100) = k(010) = f(T,x)$; endothermal process controlled by diffusion. Fig. 2c: $k(100) = k(010) = f(T)$; exothermal process controlled by phase-boundary reaction mechanism. Fig. 2d: $k(100) = k(010) = f(T,x)$; exothermal process controlled by diffusion.

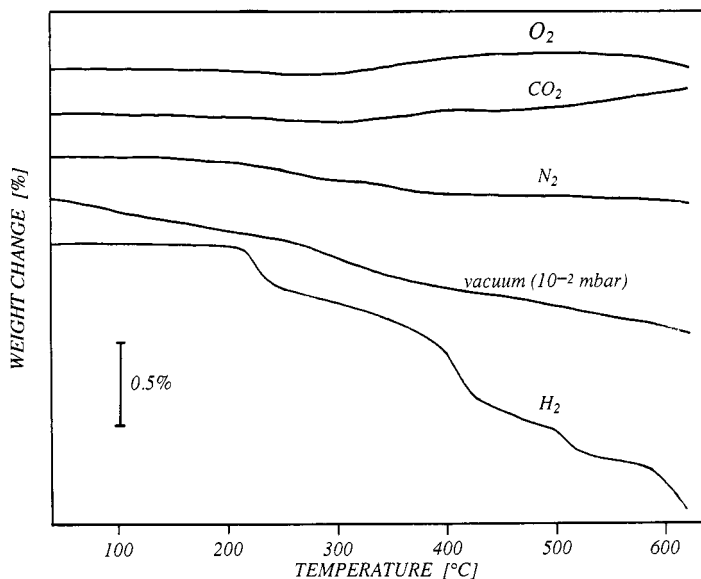


Fig. 3. Thermogravimetric measurements of the thermochemical reactivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in various gas atmospheres and under reduced pressure (heating rate: $10 \text{ K}\cdot\text{min}^{-1}$). Depending on the morphological features of the primary particles making up the bulk material the time and temperature dependence of the processes occurring are decisively influenced.

the structure of samples, which were treated in the conventional manner (ref. 19). As figure 3 demonstrates, thermogravimetric measurements are crucial in order to get informations on the reactivity of the material under consideration. There is, however, one paramount parameter accounting for the reproducibility and reliability of such studies: the gas atmosphere present during any temperature dependent experiment must be well-defined. This implies the construction of thermoanalytical equipment which can not only be evacuated but which is in addition equipped with accurate control units for gas pressure and gas atmosphere. e.g. a thermomicrobalance coupled to a simultaneously working mass spectrometer.

The measurements reveal that in pure oxygen the material undergoes oxidation and subsequent reduction. This phenomenon might be of future interest for the use of such type of phases as selective oxidation catalysts. In CO_2 , $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ takes up weight at relatively low temperatures. This result refers to the formation of the thermodynamically stable carbonate BaCO_3 , i.e. concomitantly occurring phase segregations lead to the degradation of the superconducting phase. Consequently thermal treatments should be carried out in CO_2 -free atmospheres. In pure nitrogen freshly prepared samples evolve oxygen at elevated temperatures according to the mechanism presented in figure 1. Loss of oxygen is registered at nearly ambient temperature, if the material is kept under reduced pressure. This fact gets very important with respect to any application under specific pressure conditions. Finally, in pure hydrogen $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ undergoes reduction in a multi-step process. An accurate determination of the oxygen stoichiometry by fully reducing a given sample is not possible, since the final products are not well-defined, i.e. together with metallic copper, barium oxide and yttria, stable binary and ternary metal oxide phases might be formed as side-products.

SYNTHESIS AND THERMAL REACTIVITY OF THE Bi-Ca-Sr-Cu-O-SYSTEM

In common with the method used for the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ metal oxides of the Bi-Ca-Sr-Cu-O-system are usually synthesized by calcining mixtures of the binary carbonates and oxides. Very often, however, biphasic or multiphasic products form. This certainly reflects the narrow range of the thermodynamical stability of such complex metal oxides. Consequently a phase diagram or parts of a phase diagram of this system are still to be accomplished.

In order to yield pure product phases mixed hydroxide/carbonate precursors were prepared by coprecipitation methods. In contrast to the described Y-Ba-Cu-O-system one needs to start with acidic solutions of the metal nitrates, since otherwise basic bismuth salts precipitate immediately and a homogeneous mixture of all metal carbonates or metal hydroxides is prevented. Thermogravimetric measurements of the thermal decomposition of this kind of precursor materials show, that at 1050 K the mixed phases readily form. Starting with mechanically mixed binary carbonates and binary oxides leads to relatively long calcination times. Owing to the fact that Bi_2O_3 exhibits a finite volatility at temperatures above 1050 K. however, short reaction times are certainly preferable. Moreover, the fine-tuning of compositional features are eased by the precursor method.

Differential thermal analysis as well as thermogravimetric studies prove, the thermochemical reactivity of the Bi-Ca-Sr-Cu-O-system not only depends on the Ca:Sr ratio but also on the gas atmosphere, within which thermal treatments are performed. It has been shown (ref. 20) that increasing the Ca content leads to a lowering of the melting point. Moreover, in pure nitrogen melting and decomposition processes including phase segregations occur at lower temperatures than in pure oxygen. This finding is of importance for any annealing procedures. The determination of a phase diagram of the Bi_2O_3 -CaO-SrO-CuO-system would be extremely important. The problem, however, of identifying and characterizing all the additional thermodynamically stable or metastable ternary and quaternary metal oxide phases can only be solved by an enormous expenditure of mostly thermoanalytical studies. Whether or not this tedious work will be carried out certainly depends on the potential applicability of these phases.

The structure of the superconducting Bi-Ca-Sr-Cu-O-oxides is made up of alternating of bismuth oxide layers and two or three perovskitic copper layers (ref. 21, 22). Strontium and calcium occupy interlayer sites. Owing to a metric mismatch between the interlinked layers, incommensurate superstructures have been observed by high resolution electron microscopy (ref. 23, see also figure 4). As it has been pointed out in an early publication (ref. 11), the oxygen stoichiometry within the bismuth oxide layer is not stoichiometric, i.e. there exist oxygen vacancies between the bismuth cations. Thermal treatment of this type of material leads to a loss of small amounts of oxygen in the temperature range close to the melting point. As mentioned above, the exact temperature of the melting point depends on the actual composition. This decomposition process is reversible if the heat treatment is performed in the presence of oxygen (see also ref. 24). The influence of these phenomena on the physical properties of this material are not yet fully understood.

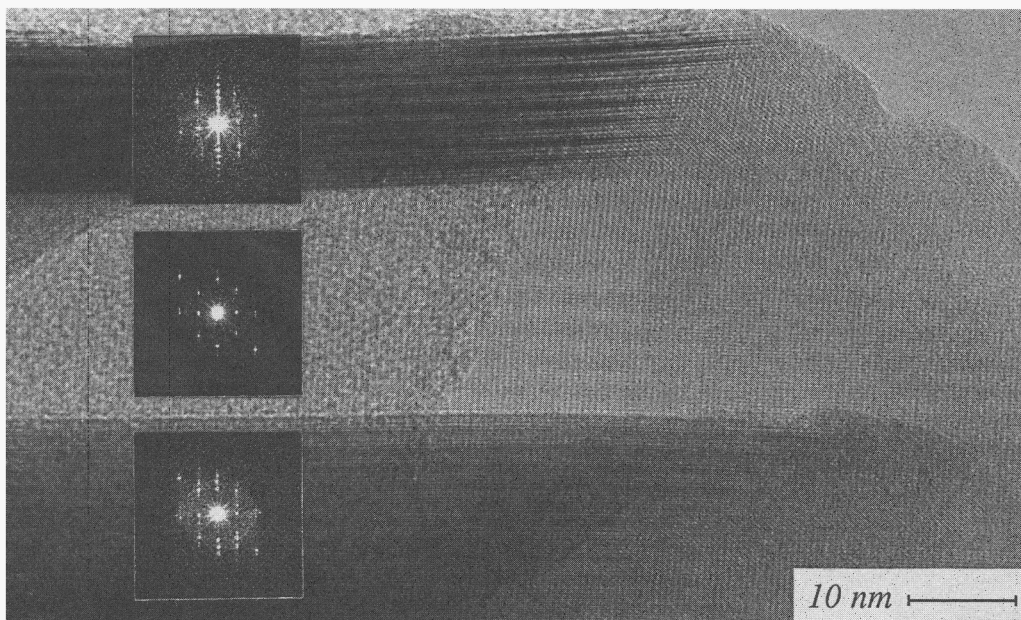


Fig. 4. High resolution electron micrograph of an array of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{8+y}$ (projection along [001]). The three inset optical diffraction patterns refer to the structural and textural differences among the micro-domains.

In summary, the study of the Bi-Ca-Sr-Cu-O-system is a challenge for thermoanalytical investigations inasmuch as the controlled preparation of monophasic material affords accurate heat treatments under well-defined atmospheric conditions. Together with supplementary methods of characterization the *real structure* and its influence on the chemical and physical properties including the perhaps most interesting feature, i.e. the superconductivity, should be achievable even for such a complicated material. Owing to the fact, however, that thermal analysis as well as many other techniques such as X-ray and neutron diffraction, spectroscopy, etc., yield data on a relatively large amount of material, complementary studies on the microstructural features of these phases by means of high resolution and analytical electron microscopy get indispensable. As figure 4 demonstrates, the details of the structure and morphology of these complex metal oxides include the presence of intergrown domains, which exhibit partly highly ordered, partly twinned and ill-defined arrays in the submicron range. To cope with this sum of complex and mutually interrelated features is very demanding and certainly requires a great deal of intensive phenomenological studies and quantitative measurements.

DISCUSSION

The discovery, the synthesis and the detailed characterization of high- T_c ceramic superconductors has opened up a wide field of applications for thermoanalytical techniques. Not only the conventional methods comprising thermogravimetry, differential thermal analysis or differential scanning calorimetry prove to be indispensable tools for the study of these exciting metal oxides, but owing to the complexity of their composition as well as to their thermochemical and thermophysical behaviour, the combination of simultaneously working methods is required. It is most probable that the study of ceramic superconductors leads to a major improvement of the versatility and of the reliability of thermoanalytical equipment.

Thermobalances have to be constructed in such a manner, that the controlled synthesis of samples exhibiting specific textural and morphological features, the reproducible heat treatment procedures as well as the characterization of their thermochemical reactivity can be measured under ambient or reduced pressure, under well-defined inert, oxidizing or reducing atmospheres in a range between room temperature and at least 1300 K. Moreover, the sensitivity of the balances used should be below one microgram in order to enable the quantitative measurement of weight changes of less than 1% of the

sample weight. Since the known superconducting ceramics exhibit only narrow stability ranges, the accuracy of the temperature measurement should be in the range of ± 3 K. Owing to the presence of reactive volatile compounds the furnaces as well as the crucibles have to be constructed on the basis of highly inert materials. Moreover, the coupling of pressure control devices and simultaneously registering mass spectrometers has to be further developed and the evacuation or gas exchange systems have to be improved. Most probably none of the nowadays purchasable equipments fulfil these requirements. Consequently, new types of thermobalances have to be constructed in the near future.

Equally strict requirements have to be fulfilled by the new generations of calorimeters, magnetometers, apparatus for differential thermoanalytical measurements as well as differential scanning calorimeters, since heat capacity changes or enthalpies of structural phase transitions, in particular any changes of thermal properties being related to the transition into the superconducting state, are often extremely difficult to measure quantitatively and reproducibly. However, the results of such measurements are of fundamental importance for the understanding of the interrelation between the temperature-dependent compositional and structural features and the temperature-dependent physical properties of these ceramics.

Thermoanalytical techniques suffer from the disadvantage of only yielding data specifying the characteristics of a given amount of material. Therefore, complementary data obtained by means of structure- or element-specific investigations, i.e. by diffraction, microscopy or spectroscopy, prove to be indispensable.

In conclusion, the future development of research in the field of superconductive ceramics and concomitantly in the field of modern materials science demands not only the knowledge and creativeness of dedicated scientists but also an enormous amount of reproducible experiments obtained by means of reliable methods and equipments. Thomas Huxley may have foreseen this when he said around hundred years ago: '*The investigation of nature is an infinite pasture-ground, where all may graze, and where the more bite, the longer the grass grows, the sweeter is its flavour, and the more it nourishes.*'

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