Thermochimica Acta, 174 (1991) 9–25
Elsevier Science Publishers B.V., Amsterdam

STRUCTURAL PROPERTIES AND THERMOCHEMICAL REACTIVITY OF SUPERCONDUCTING MIXED COPPER OXIDE PHASES

ARMIN RELLER and STELLA CASAGRANDE

Institute for Inorganic Chemistry, University of Zürich, Winterthurersrasse 190, 8057 Zürich (Switzerland)

(Received 1 November 1989)

ABSTRACT

A selection of published results on superconducting mixed copper oxides, focussing on the interrelationship between their thermochemical reactivity and their structural properties, is presented. The role of thermal analysis in the field of superconductivity is briefly discussed.

INTRODUCTION

When in 1986 Bednorz and Müller [1] published their experimental findings on extraordinary physical properties of a Ba–La–Cu–O system under the title "Possible high T_c superconductivity in the Ba–La–Cu–O system" nobody would have predicted the enormous amount of research activity that has been invested in the elucidation of the compositional, structural and physical properties of this system or in all the new superconducting mixed copper oxide phases which have been found in the meantime. Up to now several thousand (!) scientific contributions have been published and the pace with which further ones follow is as high as in the first year. Thus, the sheer amount of data available restricts any compilation of a review article to a rather personal choice and consequently to a limited spectrum of the knowledge about this fascinating family of mixed copper oxides.

Superconducting mixed copper oxides certainly represent a class of compositionally and structurally complex materials. In Fig. 1 we attempt to show the complicated interrelation between the different features describing and/or characterizing the 'form' or the 'Realstruktur' of these perovskite-related phases. The term 'form' seems to be adequate in this context because it refers to the sum of intrinsic and extrinsic interrelated features of any solid material (see e.g. refs. 2 and 3). Therefore, any physical or chemical characterization of these compounds should include its relative significance.

0040-6031/91/$03.50

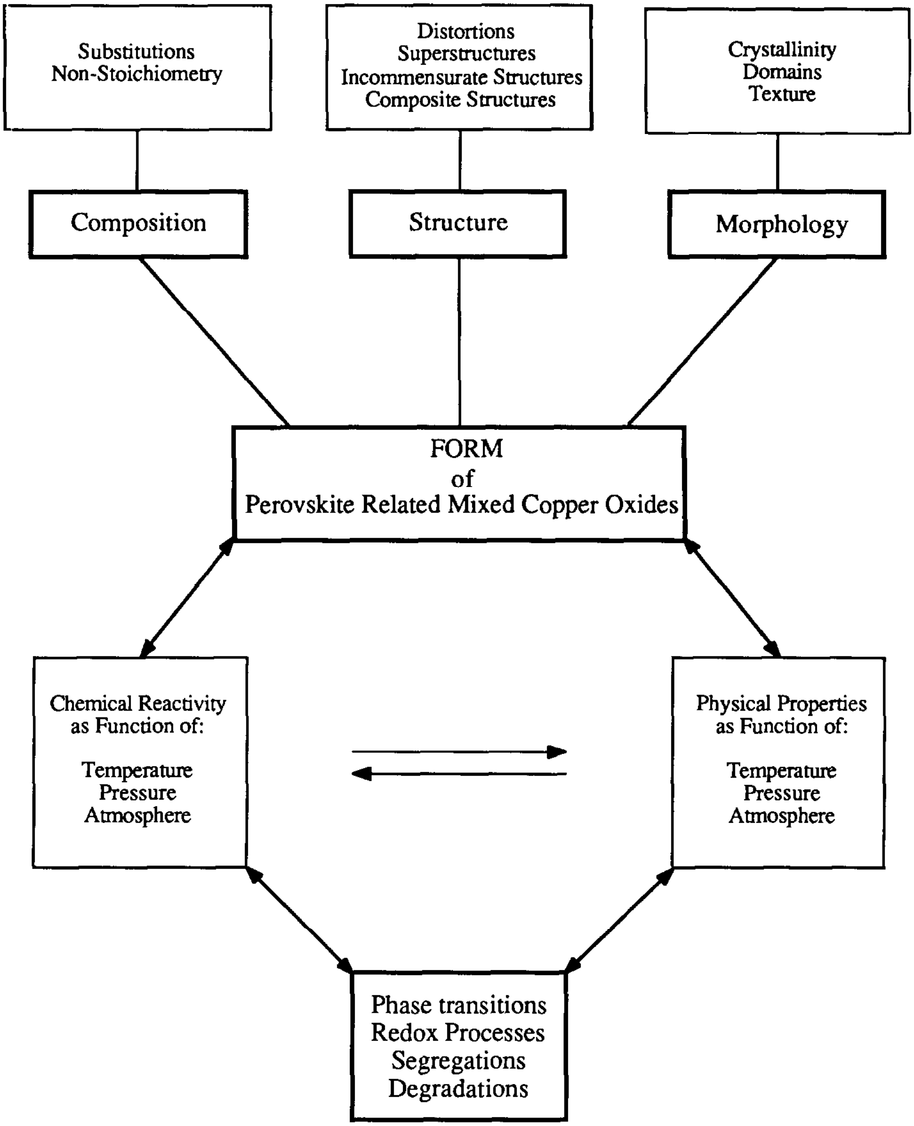

Fig. 1. Schematic representation of the 'form' of perovskite-related mixed copper oxides, referring to the interrelation and/or interdependence of compositional, structural and morphological features with the physical properties and with the (time-dependent) chemical reactivity, both as functions of external parameters such as temperature (energetic potential), pressure (mechanical potential) and atmospheric (chemical potential).

Moreover, it is of paramount importance to obtain detailed insights into the mutual relations between microscopic and macroscopic properties. This means that the microstructure and the 'microcomposition' on one hand influence decisively physical properties like electrical conductivity. On the other hand, however, they cannot be fully characterized by any bulk analysis. This is made obvious by the often-made correlation between a stoichiometry of, say, $YBa_2Cu_3O_{6.942}$ and the corresponding structural and physical properties. Such a stoichiometry only reflects a punctiliously performed overall bulk analysis but gives no indication of the previously mentioned form or Realstruktur of the material in question. Consequently, a correlation between easily comparable and therefore necessary quantitative measurements and qualitative features such as textural, microstructural, etc. features certainly allows a more specific characterization. Such a correlation is essential for reproducibility, which is the indispensable prerequisite for any research activity in materials science.

At this point it has to be emphasized that the characterization of the form or the Realstruktur of a solid includes its potential or actual reactivity or 'interactivity' with the ambient. This proves to be particularly important for these metastable mixed copper oxides accommodating not only metal cations in highly reactive, unusual oxidation states but also forming complicated structural frameworks which only can be stabilized in a narrow range in terms of thermodynamic stability.

The following selection of published results on superconducting mixed copper oxides focusses on the interrelation between their thermochemical reactivity and their structural properties. The methods of investigation include above all thermoanalytical techniques allowing not only the determination of partial or complete phase diagrams but also the reactive behaviour as a function of temperature, pressure and atmosphere. The results, however, prove to be valuable and comparable only if they can be interpreted in terms of the above-mentioned criteria, i.e. if they can be specified in terms of qualitative arguments. Consequently, these specifications have to be obtained from investigations by means of spectroscopy, diffraction techniques, microscopy and conventional chemical analysis. This should lead finally to a more comprehensive understanding of such a challenging physico-chemical phenomenon as superconductivity in ceramic materials.

This article is divided into a first section comprising the general structural features, three further sections covering the thermochemical reactivity of $YBa_2Cu_3O_7$ and its related compounds, of phases crystallizing in the K_2NiF_4 structure and of materials adopting complex composite structural frameworks. Finally, a short discussion is presented in order to reconsider the role of thermal analysis in the field of superconductivity.

STRUCTURAL FEATURES OF SUPERCONDUCTING MIXED COPPER OXIDES

Layers of corner-sharing square-planar CuO_4 units have been found to be the indispensable structural element and therefore the crucial ingredient of the superconducting mixed copper oxide phases. As is schematically summarized in Fig. 1 such elements can be found in the basic cubic perovskite structure and its strongly oxygen-deficient modification $YBa_2Cu_3O_{7-x}$ [4], including closely related phases with partial cationic substitution as well as the homologous series $Y_2Ba_4Cu_{6+n}O_{14+n}$ [5,6], in the perovskite-related K_2NiF_4 modification [1,7–9], and in the more complicated composite structural frameworks of the Bi–Sr–Cu–O phases [10], the Bi–Sr–Ca–Cu–O series [11,12], in the Tl–Ba–Ca–Cu–O series [13] and the Pb–Sr–A–Cu–O series (where A is a lanthanide or a mixture of lanthanide with Sr or Ca) [14].

The schematic structural framework, however, only gives an average arrangement of the atomic positions. The microstructure of practically all superconducting phases proves to be very complicated. "All of the high T_c perovskite superconductors appear to show disorder of certain oxygen atoms. In $(La, Sr)_2CuO_4$ and perhaps also in $YBa_2Cu_3O_7$ this is associated with a structural transition. The Bi and Tl superconductors, for which we have neutron structural data on four different phases, also show oxygen 'disorder' which may be associated with valence fluctuations. In $Tl_2Ba_2CuO_6$, electron holes are created by the absence of one-eighth of the atoms in the TlO plane, producing a marked superstructure. However, this material is not superconducting if the superstructure is well ordered, with an orthorhombic (strictly monoclinic) structure. The T_c appears to depend on the disordering of the superstructure to produce a pseudotetragonal metric in which the oxygens atoms within the TlO plane are distributed over four equivalent sites about the center of the Tl square." This is the abstract of a paper entitled "Oxygen 'disorder' and the structures of high-T_c superconductors by neutron powder diffraction" [15] and it gives an introductory taste of the problems with which one is confronted.

The general structural features of the superconducting mixed copper oxide phases discovered and characterized up to the end of 1988 is summarized in comprehensive reviews by Rao and Raveau [16] and Sleight [17]. A more general overview on perovskite-related structures including the superconducting ceramics has been compiled by Reller and Williams [18]. A comprehensive article by De Leeuw [19] covers the interdependence between structure and conductivity of copper oxide based compounds.

Although the structural investigations on this class of materials are based on data obtained by different diffraction techniques (above all X-ray and neutron diffraction techniques) at different levels of sophistication the resulting frameworks always correspond to a more or less detailed average structure. In the field of conduction, even more critical for superconducting materials, however, the texture, the microcomposition and the microstructure are of paramount importance. Thus, it is not surprising that from the beginning of research work in this field, the full potential of electron microscopic techniques was used for the detailed study of these features. The results of these investigations allowed a more accurate interpretation of the crucial role of oxygen ordering and oxygen deficiency, on the formation of domain structures, twins, superstructures and incommensurate structures. Soon after the publication of the work of Bednorz and Müller [1] electron microscopic and electron diffraction studies were carried out at different temperatures, revealing structural phase transitions and distorted structures [20,21]. For the characterization of all the recent ceramic superconductors electron microscopy was established as a key method [22–27]. Complicated structural features were recently observed in the novel electronic superconductors of the Nd–Ce–Cu–O system with K_2NiF_4-type frameworks. In these phases superstructures are formed as a result of cation ordering and/or oxygen vacancy ordering effects [28]. In turn, these features depend on the experimental conditions under which the actual compounds were synthesized.

In summary, one can conclude that the structural types of the superconducting mixed copper oxides described so far are well known. The Realstruktur, i.e. the form of these challenging phases, including compositional, structural, textural and morphological details and anomalies, is clearly not yet fully understood. For the time being and for the rest of this article, only average structures and average properties are investigated and characterized. The results of the cited research activities, however, certainly lead to an improved description and may finally lead to a better understanding of the phenomenon of superconductivity.

PHASE DIAGRAMS

Before referring to selected publications on the thermochemical reactivity of superconducting mixed copper oxides, the present state of knowledge of the thermodynamic stability ranges of these phases, i.e. the partial or complete phase diagrams, has to be presented. Owing to the increasing complexity of the structural features, the lanthanum cuprates adopting the K_2NiF_4 structure will be mentioned first. The systems related to $YBa_2Cu_3O_{7-x}$ (YBCO) will then be discussed, and finally the composite phases containing Bi, Tl and Pb will be described.

Soon after the discovery of superconductivity in the La–Ba–Cu–O and La–Sr–Cu–O systems, data on related phase diagrams at various temperature ranges were published [29]. Moret et al. [30,31] investigated the phase diagram of $La_{2-x}Sr_xCuO_{4-y}$ at the phase transition. The superconducting behaviour and the phase diagram of $La_{2-x}Ba_xCuO_{4-y}$ were characterized by Fujita et al. [32] with regard to temperature and composition. Depending on the x value, two different types of phase transitions were found to compete in the T–x plane. Detailed characterizations of magnetic phase diagrams were accomplished by Kitaoka et al. [33] and by Aharony et al. [34]. In a theoretical study on the phase diagram of superconducting glass phases, computer simulations were performed based on a two-dimensional system of superconducting clusters [35]. The authors concluded that in low fields (≤ 10 G) real high T_c granular systems are three-dimensional and behave in a much more complicated manner than expected from an idealized model.

Finally, and probably the most familiar investigation for researchers working in the field of thermal analysis, the compounds and phase compatibilities in the system La_2O_3–SrO–CuO were determined at 950 °C by De Leeuw et al. [36]. The authors investigated the subsolidus phase diagram under 1 bar of oxygen and a new ternary compound, $La_{1+x}Sr_{2-x}Cu_2O_{5.5-y}$ was identified among the various compounds. Many more phase diagram determinations were published on the YBCO system. This fact can certainly be explained by the more attractive properties of this system, above all the high T_c. A detailed and reliable phase diagram of the YBCO system was accomplished by Roth et al. [37] as early as 1987. It was published under the title "Phase equilibria and crystal chemistry in the system Ba–Y–Cu–O" and still represents one of the most detailed investigations. Further investigations entitled "Phase equilibria in the system Ba–Y–Cu–O–CO_2 in air" by the same group were not published, although these results would be of importance.

X-ray diffraction and neutron diffraction studies on the structural features of YBCO required single crystals. Therefore, phase compatibilities were determined, which allowed controlled crystallization of single phase material. Moreover, further details on the thermodynamic stability ranges of YBCO and related phases were obtained by Schneemeyer et al. [38] and by Bykov et al. [39]. Additional data on the YBCO phase diagram were determined by American groups [40,41] as well as by a Chinese group [42]. The latter collected data on the La–Ba–Cu–O, the La–Sr–Cu–O and the YBCO systems. Experimental data supplying the basis for a partial pseudobinary phase diagram for the orthorhombic–tetragonal phase transition of YBCO was determined by Meuffels et al. [43]. A phase diagram of the pseudobinary $BaCuO_2$–$YBa_2Cu_3O_{6.5}$–$YCuO_{2.5}$ system was investigated by means of differential thermal analysis (DTA) and X-ray diffraction by Nevriva et al. [44]. The same team carried out quenching experiments on YBCO and found, in addition to the then known phases, unidentified compounds [45]. The acquisition of data on the YBCO–CuO_x phase diagram characterized by DTA, thermogravimetry, hot-stage microscopy and X-ray diffraction revealed that a small excess of CuO leads to a decrease in the decomposition temperature of YBCO by about 60 °C [46]. This result is important, inasmuch as YBCO crystallization out ot a CuO flux must be performed under careful control of the actual temperature.

A summary of the currently available knowledge on "Binary and ternary compounds, phase diagrams and contaminations in the $Y_{1.5}$–BaO–CuO system auxiliary to superconducting ceramics" as well as on "Preparation of YBCO polycrystalline materials through melt solidification and glass formation" has been compiled by Šesták [47] and Šesták and Strnad [48]. "Phase equilibria and crystal chemistry in the quaternary system Ba–Sr–Y–Cu–O in air" has recently been published by Roth et al. [49]. They found that Sr may substitute Ba by up to 60%. There exist, however, no ternary compounds in the Sr–Y–Cu–O system equivalent to the three ternary phases in the Ba–Y–Cu–O analogue. A new phase with the formal stoichiometry $Sr_{14}Cu_{24}O_{41}$ could be identified, which in turn can also incorporate considerable amounts of Ba, Ca and many other large cations.

As this short overview on phases in the Y–Ba/Sr/Ca–Cu–O system reveals, one is confronted with a remarkable number of compositionally and structurally different compounds. Moreover, the identified compounds can be modified by partial substitutions of the cations or by modification of the oxygen content via annealing, reduction or reoxidation procedures. The preparation of superconducting mixed copper oxides was performed under somewhat extreme conditions by Karpinski and co-workers [50–52]: They determined the YBCO phase diagram under high oxygen pressure (up to 3000 bar). Under these conditions two new superconducting phases were obtained: $YBa_2Cu_{3.5}O_{7+x}$ with a T_c of 40 K and $YBa_2Cu_4O_{8+x}$ with a T_c of around 80 K.

For the compositionally and structurally most complicated composite superconductors, i.e. the Bi–Sr–Ca–Cu–O system and its Tl and Pb analogues or the Pb–Sr–A–Cu–O system, only a few data on phase diagrams are available. Vaile et al. [53] studied superconductivity in the Bi–Sr–Ca–Cu oxide compositional diagram and they detected a wide range of materials exhibiting superconducting transitions in the temperature range 60–110 K. The samples investigated turned out to be multiphased with a number of common compounds that are responsible for superconductivity. Among these the 2212 composition was identified as a previously known phase and two new phases with compositions 2213 and 2215 were observed.

More detailed data on the structure and composition of Bi–Sr–Ca–Cu–O phases were obtained by Kajitani et al. [54]. They investigated the partial phase diagram of the pseudoternary system Bi_2O_3–SrO–CaO–CuO at 1133 K. The range in chemical composition, where a structure with a c-axis of around 30 Å is adopted was found in the vicinity of the metal ratio of Bi/(Sr, Ca)/Cu between 2/3/2 and 2/2/3. For the phase with a c-axis of around 36 Å (with a T_c of around 110 K) a unique metal ratio of 5/8/8 was identified. The phases studied, however, were not pure, i.e. they did not show 100% diamagnetism at 4 K, or they were made up of both low T_c and high T_c compounds. Additional data on the phase diagram of $Bi_nSrCaCu_{3-n}O_y$ ($n = 1$–2) were obtained by Tomomatsu et al. [55].

This compilation of studies of the phase diagrams of superconducting mixed copper oxides may reflect the complexity of the topic with which one is confronted. It also gives an idea how carefully any qualitative or quantitative study on the thermochemical reactivity of these compounds has to be interpreted. From the outset one should keep in mind that the specimens under consideration do not represent single crystals or even pure phases (see e.g. electron microscopic studies!). Therefore, any measurement, above all bulk measurements carried out by means of e.g. thermogravimetry or differential thermal analysis, should be judged with respect to its significance. For any finding, the question of reproducibility and reliability arises. This situation requires the most concise descriptions of the experimental conditions under which investigations were carried out and under which new phenomena were found. In particular, any thermoanalytical measurements should be optimally defined with respect to the specimen used, to the material of the crucible and apparatus used, as well as to the atmosphere and pressure conditions applied.

THERMOCHEMICAL REACTIVITY

The important role of thermoanalytical methods of investigation is evidenced by the remarkable number of contributions to the field of controlled formation and studies on the thermochemical reactivity of superconducting ceramics. As mentioned above, the most attractive system for this type of investigation turns out to be the YBCO and its analogues. Soon after its discovery by Wu et al. [4] thermoanalytical investigations on the formation processes starting from different precursors, and on annealing procedures, were presented by several research groups [56–63]. A brief review of related studies was recently published by Niinistö and Karppinen [64]. The controlled preparation of highly oriented superconducting oxides and improvement of their durability as well as the precise determination of the redox state was characterized by Wu and Ruckenstein [65] and by Murugaraj et al. [66]. As will be shown below, the role of the oxygen content relative to the redox state of these compounds cannot be underestimated. This proves to be equally true for single crystal growth conditions, which were described by Schneemeyer et al. [38], Wojcik et al. [67] and others.

Kinetic studies on the formation of YBCO using various precursor phases were carried out by Ozawa [68] and by Krebs [69]. Depending of the type of precursor system, i.e. coprecipitated carbonates or oxalates, powder mixtures of the metal oxides, etc., Ozawa identified phase boundary contracting reactions or multiple parallel processes. Krebs worked with in situ X-ray diffraction, DSC under various pressures of oxygen and with thermogravimetry. The smallest oxygen partial pressure necessary for the formation of the orthorhombic phase was determined at various temperatures and the kinetics of the tetragonal-to-orthorhombic transition were studied. A diffusion constant for oxygen in YBCO at 400 °C of about 1×10^{-11} cm^2 s^{-1} and an activation energy of the diffusion of about 1.6 eV were determined. These studies were carried out using polycrystalline samples.

More general thermoanalytical studies on temperature-dependent structural and compositional features were published by—among many others—Rodriguez and Llopiz [70], Costa et al. [71] and Kikuchi et al. [72]. In a theoretical study, Chechetkin and Sigov [73] tackle the problem of the thermal stability of superconducting magnetic systems. The authors discuss probably the most important stability problems for conventional superconducting magnets based on intermetallic materials and for the novel ceramic materials, i.e. the problem of thermal disturbances. In addition, the problem of thermomechanical instability is discussed.

Soon after the discovery of the YBCO system it became evident that this material is metastable and readily undergoes reversible loss and uptake of bulk oxygen. Furthermore it was confirmed by many research groups that the oxygen stoichiometry (and hence the dependent (formal) oxidation state of the copper cations) represents a decisive parameter for superconductivity. Consequently, numerous studies on the oxygen stoichiometry and its temperature- and pressure-dependent fluctuations were published. Derouane et al. [74] and Gabelica et al. [75] performed thermogravimetric, DTA and X-ray diffraction studies on the YBCO system in order to obtain detailed correlations between oxygen content, crystal structure and superconducting properties. Insights into the relationship between oxygen stoichiometry and phase formation and/or phase transitions were accomplished by Dharwadkar et al. [76], Klamut et al. [77] and Vogel et al. [78]. The latter authors also describe a method for establishing the oxygen stoichiometry by measuring weight change as a function of temperature and ambient pressure. Oxygen stoichiometry, microstructure and the orthorhombic-to-tetragonal phase transition were investigated by Button et al. [79] using thermogravimetric and X-ray techniques and polarized light microscopy. Structural changes induced by oxygen evolution from YBCO were monitored by Strauven et al. [80] using temperature-dependent neutron diffraction and X-ray diffraction experiments. Using desorption relations, a value of 0.16 eV could be assigned to the oxygen–oxygen repulsion energy, which is responsible for the order–disorder transition in the linear Cu–O chains. Pavlyukhin et al. [81–83] followed the gas exchange and its implications for YBCO using differential scanning calorimetry/DTA and structural analysis under different heat and gas treatment procedures.

Barometric measurements revealing the relationship between stoichiometry and oxygen potential were correlated with X-ray diffraction experiments by Krabbes et al. [84] in the temperature range 300–1000 °C. The non-superconducting phase Y_2BaCuO_5 was included in the studies and was found to be antiferromagnetic with a T_N of around 30 K. Microstructural changes in YBCO were monitored by Balek and Šesták [85] using emanation thermal analysis. It is suggested that this technique is a suitable tool for quality testing procedures of the intermediate products of superconducting ceramics.

Investigations on phases with partially substituted cations were performed by Kaisersberger et al. [86] on the (Y, Eu)$Ba_2Cu_3O_{7-x}$ system, and by Shimakawa et al. [87] on YBCO with various contents of Cu and Ba. These authors monitored the effect of Cu/Ba variations on the electrical and chemical properties using DTA and resistivity measurements. Fujiwara et al. [88] studied the YBa_2 $(Cu_{3-x}Fe_x)O_{7-x}$ compound by thermogravimetry and X-ray diffraction. They identified a marked discontinuity in the slope for a plot of the oxygen content vs. *c*-cell parameter.

Rather specific measurements on the oxygen content and the structural features of YBCO below 525 °C were carried out by O'Bryan and Gallagher [89]. Further results on the diffusion of oxygen and related kinetics of YBCO were reported by several research teams [57,90–95].

As this compilation of studies on temperature-dependent changes of structural and compositional features in YBCO prove, this phase not only represents a highly reactive material with respect to reduction or reoxidation but requires careful inspection of its reactivity in the presence of other reactive gases or solvents. Any technical application can only be guaranteed if its reactive behaviour is known and if its properties can be 'tailored' and 'fine-tuned' (see e.g. refs. 96 and 97). Whereas thermal analysis is well suited to quantifying compositional changes and heats of enthalpy of bulk material, the first steps of thermochemical reactions including changes of the redox state need investigations using spectroscopic and surface specific methods as shown by e.g. Ramsey and Netzer [98] or Schlögl et al. [99]. Scanning tunnelling microscopy, as performed by Naukkarinen et al. [100] or electrochemical methods, as used by Bormann and Nölting [101] may also elucidate minute changes of compositional features and therefore represent highly sensitive techniques for the study of the thermochemical reactivity of YBCO at various ambient conditions.

Specific data on the thermochemical reactivity of YBCO in carbon dioxide, carbon monoxide and water were collected by Gallagher et al. [102]. Experiments performed under these atmospheres, but also in hydrogen and ammonia were performed by Langer and Di Chiara [103], Shelby et al. [104], Bhargava et al. [105] and Reller [94]. The findings of these studies support the above-mentioned statement that YBCO readily undergoes reactions with various gases, and non-superconducting phases are obtained as solid products. Among these products, alkaline earth metal carbonates might be the most prominent and the most abundant.

As reported by Matthews et al. [106] YBCO absorbs helium. Because helium occupies interstitial positions in the YBCO lattice, internal pressure effects may result, which in turn influence the electrical properties.

The stability of YBCO in the presence of water or water vapour has to be discussed as one of the most important topics with respect to possible deterioration or degradation processes. Several authors followed the interaction of water with YBCO using various techniques. Schlögl [107] found by XPS measurements that hydroxyl groups can easily be accommodated within the YBCO lattice. Barns and Laudise [108] and Dominec et al. [109] observed that YBCO reacts with water at room temperature. Hydrolytic and deliquescent properties were found by Dexin et al. [110]. The reaction of YBCO with water at 0 ° C and its protection from water corrosion at 100 ° C were investigated by Jin et al. [111]. Deteriorated or corroded YBCO specimens can be recovered by reheating procedures, as reported by Hwang et al. [112]. As a rather surprising effect, Salvador et al. [113] observed spontaneous O_2 release from the YBCO analogue $SmBa_2Cu_3O_{7-x}$ in contact with water. They conclude that these findings indicate the presence of O^- and/or O^{2-} ions stabilized in the superconductor lattice.

Finally, comparative data on the reactivity of YBCO and the Bi–Sr–Ca–Cu–O system with various solvents were compiled by Liu et al. [114] using electrochemical methods. No information on the temperature dependence of the observed processes was given. The authors found, however, that in both compounds superconductivity apparently depends on a high oxidation state of Cu. Endo et al. [115] carried out thermoanalytical measurements under various oxygen partial pressures in order to determine the thermal stability of the superconducting phases in the Bi–Sr–Ca–Cu–O system in the temperature range 800–900 ° C. They state that, depending on the oxygen partial pressure, the high T_c phase ($T_c = 110$ K) can be generated or degraded. Thus, under oxygen partial pressures of more than 0.2 atm and a temperature of 870 ° C the amount of this high T_c phase is markedly increased by the possible disproportionation of the low T_c phase ($T_c = 80$ K).

Thermal analysis was performed by Park and Kim [116] in order to investigate the formation and the thermal stability of various compositions of the Bi–Sr–Ca–Cu–O system. Hwang et al. [117] described the effect of atmosphere on the formation of low T_c and high T_c materials in the Bi–Pb–Sr–Ca–Cu–O system. They worked in two kinds of sintering atmospheres, i.e. in N_2 and in air. The annealing temperatures were 810 ° C (N_2) and 850 ° C (air). Compared with air, N_2 enhanced the formation of the low T_c phase and inhibited the formation of the high T_c phase. Multiple transitions in bismuth-based superconductors were reported by Gupta et al. [118]. They detected possible superconducting transitions at 133, 117 and 105 K in samples prepared by calcining and annealing Bi_2O_3, $Sr(NO_3)_2$, $CaCO_3$ and CuO powders. The products were (most probably) multiphase and no precise data on compositional and structural features nor on the reactive behaviour were given. As reported by Liu et al. [119] complicated quenching and annealing procedures at various temperatures led to Bi–Sr–Ca–Cu–O phases exhibiting reversible phase transitions from semiconductivity to superconductivity. The thermally treated specimens were characterized by X-ray diffraction and DTA. The results revealed that specimens quenched from above 900 ° C were semiconducting. Annealing procedures at 820 ° C for 40 h under O_2 atmosphere converted these semiconductors into superconductors with two nominal compositions. Influences of the atmosphere on the composition and on the superconducting properties in Bi-based systems were observed by Casagrande [120]. Using thermogravimetric techniques, X-ray diffraction, electron microscopy and resistivity measurements it was found that small changes in oxygen content at temperatures around 850 °C, which can be fully or partially reversible (depending on the ambient atmosphere and on the heat treatments), have a marked effect on the structural and superconducting properties.

As Kawasaki et al. [121] observed, UV light irradiation in an oxygen atmosphere changed the critical temperature of Bi–Sr–Ca–Cu–O thin films. The change was reversible between 80 K after annealing and 60 K after photo-irradiation. These findings show how reactive Bi-based superconductors may be and how carefully any chemical or energetic impact on these phases have to be taken into account. A rather sophisticated study on the thermal behaviour of the structural features of Bi-based superconductors with various compositions was performed by Gasgnier and Ruault [122] in the temperature range 15–1000 K using electron microscopy. They demonstrated the coexistence of two orthorhombic structures, one of them showing incommensurate spacings. No structural changes or transitions were found in the range 15–300 K. On annealing the specimens up to 350 K, a structural transition into a new orthorhombic phase was observed. Between 500 and 1000 K disproportionations into different metal oxides were detected.

Hydrogen absorption in single crystalline $Bi_2Sr_2CaCu_2O_8$ and its effects on superconductivity were investigated by Coey et al. [123]. They found that absorption at 1 bar hydrogen occurs in three stages at approximately 275, 500 and 600 °C. Only the first step did not lead to decomposition processes. The effect of the absorbed hydrogen on the structure and the superconducting properties was discussed.

The preparation and thermal characteristics of Tl–Ba–Ca–Cu–O superconductors were studied by Zhang et al. [124]. The formation and degradation as a function of time of the $T_c = 120$ K phase in the Tl–Ba–Sr–Ca–Cu–O system was analysed by Itoh and Uchikawa [125] using several complementary techniques. The authors showed that the $T_c = 80$ K phase can be converted into the high T_c phase. The resulting material, however, converts again into the low T_c phase upon heat treatment in the presence of an excess amount of Tl_2O_3.

CONCLUSIONS

Superconducting ceramics certainly belong to the most complicated synthetic metal oxides known. In contrast to compositionally comparable systems such as mineral oxides or sulphides, they turn out to be fairly unstable and show in many cases vigorous chemical reactivity. Therefore, the establishment of reliable structural and compositional data (see e.g. refs. 126 and 127), the determination of complete or partial phase diagrams, the definition of reproducible synthetic routes and the characterization of the thermochemical reactivity requires an enormous amount of experimental investigation. Unfortunately, and probably characteristic for research activities in this young field, the pressure of publishing new findings as early as possible overcame many conventions for the serious reporting of scientific data. Up to now routine procedures such as proper definition of experimental conditions, and the declaration of all findings, including the less successful ones, have been increasingly neglected. The personal responsibility for the reproducibility of the published results became increasingly meaningless. After the 'superconductor rush' of the past three years it is time to recapitulate, to sort out the reliable studies and data and to continue research activities at a probably slower and less sensational, but nevertheless more efficient pace. The aim of these research activities should be directed towards a better understanding of the relationship between composition, structure and morphology of a phase, on the one hand, and chemical reactivity or physical properties, in particular superconductivity, on the other. This understanding of the initially mentioned 'form' of a solid certainly includes a sound knowledge of temperature-dependent and temperature-induced effects and/or phenomena. Their characterization requires adequate facilities for qualitative and quantitative measurements. Unfortunately, only a few of the present commercially available instruments are satisfactory with respect to accurate temperature control, thermochemical inertia of furnaces and crucibles, sensitivity of balances and thermocouples and versatility of gas control systems. Manufacturers may change this situation in the near future according to the demands of the users. It will be worthwhile, as research in the field of superconducting ceramics turns out to be a challenge for many laboratories and it is equally demanding with respect to the development of new scientific concepts as well as sophisticated technological understanding.

REFERENCES

1 J.G. Bednorz and K.A. Müller, Z. Phys. B, 64 (1986) 189.
2 N.E. Emerton, The Scientific Reinterpretation of Form, Cornell University Press, Ithaca, NY, 1984.
3 H.R. Oswald and A. Reller, Thermochim. Acta, 33 (1988) 67.
4 M.K. Wu, J.R. Ashburn and C.J. Torng, Phys. Rev. Lett., 58 (1987) 908.
5 P. Bordet, C. Chaillout, J. Chenavas, J.L. Hodeau, M. Marezio, J. Karpinski and E. Kaldis, Nature, London, 334 (1988) 596.
6 R.J. Cava, J.J. Krajewski, W.F. Peck Jr., B. Batlogg, L.W. Rupp Jr., R.M. Fleming, A.C.W.P. James and P. Marsh, Nature, London, 338 (1989) 328.
7 D. Balz and K. Plieth, Z. Elektrochem., 59 (1955) 545.

8 Y. Tokura, H. Takagi and S. Uchida, Nature, London, 337 (1989) 345.
9 H. Sawa, S. Suzuki, M. Watanabe, J. Akimitsu, H. Matsubara, H. Watabe, S. Uchida, K. Kokusho, H. Asano, F. Izumi and E. Takayama-Muromachi, Nature, London, 337 (1989) 347.
10 C. Michel, M. Hervieu, M.M. Borel, A. Grandin, F. Deslandes, J. Provost and B. Raveau, Z. Phys. B, 68 (1987) 421.
11 H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, Jpn. J. Appl. Phys., 27 (1988) L209.
12 H.G. von Schnering, L. Walz, M. Schwarz, W. Becker, M. Hartweg, T. Popp, B. Hettich, P. Müller and G. Kämpf, Angew. Chem., 100 (1988) 604.
13 Z.Z. Sheng and A.M. Hermann, Nature, London, 332 (1988) 55.
14 R.J. Cava, B. Batlogg, J.J. Krajewski, L.W. Rupp, L.F. Schneemeyer, T. Siegrist, R.B. van Dover, P. Marsh, W.F. Peck, Jr., P.K. Gallagher, S.H. Glarum, J.H. Marshall, R.C. Farrow, J.V. Waszczak, R. Hull and P. Trevor, Nature, London 336 (1988) 211.
15 A.W. Hewat, E.A. Hewat, P. Bordet, J.-J. Capponi, C. Chaillout, J. Chenavas, J.-L. Hodeau, M. Marezio, P. Strobel, M. Francois, K. Yvon, P. Fischer, J.-L. Tholence, IBM Res. Dev., 33 (1989) 220.
16 C.N.R. Rao and B. Raveau, Acc. Chem. Res., 22 (1989) 106.
17 A.W. Sleight, Science, 242 (1988) 1519.
18 A. Reller and T.B. Williams, Chem. Br., 25 (1989) 1227.
19 D.M. De Leeuw, J. Less-Common Met., 150 (1989) 95.
20 T. Onozuka, M. Omori, M. Hirabayashi and Y. Syono, Jpn. J. Appl. Phys., 26 (1987) L1714.
21 K. Oh-Ishi, K. Kikuchi, Y. Syono, K. Hiraga and Y. Morioka, Jpn. J. Appl. Phys., 26 (1987) L484.
22 T.E. Mitchell, J. Electron Microsc. Tech., 8 (1988) 339.
23 K. Hiraga, T. Oku, D. Shindo and M. Hirabayashi, J. Electron Microsc. Tech., 12 (1989) 228.
24 G. van Tendeloo, H.W. Zandbergen, J. Van Landuyt and S. Amelinckx, Ultramicroscopy, 29 (1989) 115.
25 P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, M. Godinho, A.W. Hewat, E.A. Hewat, J.L. Hodeau, A.M. Spieser, J.L. Tholence and M. Marezio, J. Less-Common Met., 150 (1989) 109.
26 S. Amelinckx, G. Van Tendeloo, H.W. Zandbergen and J. Van Landuyt, J. Less-Common Met., 150 (1989) 71.
27 M.A. Alario-Franco, C. Chaillout, J. Chenavas and M. Marezio, J. Less-Common Met., 150 (1989) 117.
28 T.B. Williams, Y. Maeno, I. Mangelschots, A. Reller and J.G. Bednorz, Z. Phys. C, 161 (1989) 331.
29 P.J. Picone, H.P. Jenssen and D.R. Gabbe, J. Cryst. Growth, 91 (1988) 463.
30 R. Moret, J.P. Pouget and G. Collin, Europhys. Lett., 4 (1987) 365.
31 R. Moret, J.P. Pouget, C. Noguera and G. Collin, Physica C, 153 (1988) 968.
32 T. Fujita, Y. Aoki, Y. Maeno, J. Sakurai, H. Fukuba, H. Fujii, T. Okamoto, K. Kumagai and M. Kurisu, Jpn. J. Appl. Phys., 26 Suppl. (1987) 1041.
33 Y. Kitaoka, K. Ishida, T. Kobayashi, K. Amaya and K. Asayama, Physica C, 153 (1988) 733.
34 A. Aharony, R.J. Birgeneau, A. Coniglio, M.A. Kastner and H.E. Stanley, Physica C, 153 (1988) 1211.
35 C. Giovanella, C. Chappert and P. Beauvillain, Europhys. Lett., 5 (1988) 535.
36 D.M. De Leeuw, C.A.H.A. Mutsaers, G.P.J. Geelen and C. Langereis, J. Solid State Chem., 80 (1989) 376.
37 R.S. Roth, K.L. Davis and J.R. Dennis, Adv. Ceram. Mater., 2 (1987) 303.
38 L.F. Schneemeyer, J.V. Waszczak, T. Siegrist, R.B. van Dover, L.W. Rupp, B. Batlogg, R.J. Cava and D.W. Murphy, Nature, London, 328 (1987) 601.

39 A.B. Bykov, L.N. Demyanets, I.P. Zibrov, G.V. Kanunnikov, O.K. Mel'nikov and S.M. Stishov, J. Cryst. Growth, 91 (1988) 302.

40 K.G. Frase, E.G. Liniger and D.R. Clarke, J. Am. Ceram. Soc., 70 (1987) C-204.

41 J. Hahn, T.O. Mason, S.J. Hwu and K.R. Poeppelmeier, Chemtronics, 2 (1987) 126.

42 G. Che, J. Liang, W. Chen, S. Xie, Y. Yu, H. Li, Q. Yang, Y. Ni, G. Liu and G. Chen, Sci. Sin. Ser. A, 31 (1988) 1079.

43 P. Meuffels, B. Rupp and E. Poerschke, Physica C, 156 (1988) 441.

44 M. Nevriva, E. Pollert, J. Šesták, L. Matejkova and A. Triska, Thermochim. Acta, 136 (1988) 263.

45 J. Šesták, M. Nevriva, E. Pollert, J. Hejtmanek, A. Triska and M. Simeckova, Thermochim. Acta, 132 (1988) 35.

46 F. Licci, P. Tissot and H.J. Scheel, J. Less-Common Met., 150 (1989) 201.

47 J. Šesták, Thermochim. Acta, (1989) in press.

48 J. Šesták and Z. Strnad, Proc. XV. Congress on Glass, 1989, Leningrad, U.S.S.R., in press.

49 R.S. Roth, C.J. Rawn, J.D. Whitler, C.K. Chiang and W.K. Wong-Ng, J. Am. Ceram. Soc., 72 (1989) 395.

50 J. Karpinski and E. Kaldis, Nature, London, 331 (1988) 242.

51 J. Karpinski, E. Kaldis and S. Rusiecki, J. Less-Common Met., 150 (1989) 207.

52 J. Karpinski, E. Kaldis, S. Rusiecki and E. Jilek, J. Less-Common Met., 150 (1989) 129.

53 R. Vaile, S. Bosi, T. Puzzer, A. Bailey, J. Cochrane, N. Mondinos, K. Sealey and G.J. Russell, J. Cryst. Growth, 91 (1988) 450.

54 T. Kajitani, M. Hirabayashi, M. Kikuchi, K. Kusaba, Y. Syono, N. Kobayashi, H. Iwasaki and Y. Muto, Jpn. J. Appl. Phys., 27 (1988) L1453.

55 K. Tomomatsu, A. Kurosaka, H. Tominaga, T. Takayama, O. Fukuda and H. Osanai, Appl. Phys. Lett., 55 (1989) 298.

56 Z. Gabelica, G. Demortier, G. Deconninck, F. Bodart, A.A. Lucas, M. Renier, Ph. Lambin, J.P. Vigneron and E.G. Derouane, Solid State Commun., 64 (1987) 1137.

57 W.P. Brennan, M.P. Di Vito, R.F. Culmo and C.J. Williams, Nature, London, 330 (1987) 89.

58 P.P. Edwards, M.R. Harrison and R. Jones, Chem. Br., October (1987) 962.

59 A. Reller, Thermochim. Acta, 137 (1988) 11.

60 M. Kamimoto, R. Sakamoto, A. Negishi, Y. Takahashi and M. Hirabayashi, Thermochim. Acta, 142 (1989) 281.

61 M. Heuberger, A. Bhargava and R.L. Snyder, Mater. Lett., 5 (1987) 489.

62 J. Šesták, T. Hanslik, M. Nevriva, D. Zemanova, E. Pollert, A. Triska and J. Tlaskal, J. Thermal Anal., 33 (1988) 947.

63 G.R. Paz-Pujalt, A.K. Mehrotra, S.A. Ferranti and J.A. Agostinelli, Solid State Ionics, 32 (1989) 1179.

64 L. Niinistö and M. Karppinen, J. Thermal Anal., 35 (1989) 319.

65 N.L. Wu and E. Ruckenstein, Mater. Lett., 5 (1987) 432.

66 P. Murugaraj, J. Maier and A. Rabenau, Solid State Ionics, 32 (1989) 1183.

67 J. Wojcik, M. Rosochowska, H. Niculescu and A. Pajaczkowska, J. Cryst. Growth, 91 (1988) 255.

68 T. Ozawa, Thermochim. Acta, 133 (1988) 11.

69 H.-U. Krebs, J. Less-Common Met., 150 (1989) 269.

70 G. Rodriguez and J.C. Llopiz, Rev. Cubana Fis., 7 (1987) 21.

71 G.A. Costa, M. Ferretti, E.A. Franceschi and G.L. Olcese, Thermochim. Acta, 133 (1988) 17.

72 M. Kikuchi, Y. Syono, A. Tokiwa, K. Oh-ishi, H. Arai, K. Hiraga, N. Kobayashi, T. Sasaoka and Y. Muto, Jpn. J. Appl. Phys., 26 (1987) L1066.

73 V.R. Chechetkin and A.S. Sigov, Phys. Rep., 176 (1989) 1.

74 E.G. Derouane, Z. Gabelica, J.-L. Brédas, J.-M. André, Ph. Lambin, A.A. Lucas and J.-P. Vigneron, Solid State Commun., 64 (1987) 1061.

75 Z. Gabelica, E.G. Derouane, J.P. Vigneron, Ph. Lambin, M. Renier, A.A. Lucas, G. Deconninck, F. Bodart and G. Demortier, Solid State Commun., 64 (1987) 1221.

76 S.R. Dharwadkar, V.S. Jakkal, J.V. Yakhmi, I.K. Gopalakrishnan and R.M. Iyer, Solid State Commun., 64 (1987) 1429.

77 J. Klamut, R. Horyn and K. Lukaszewicz, Bull. Pol. Acad. Sci., 36 (1988) 91.

78 E.M. Vogel, G.W. Hull and J.M. Tarascon, Mater. Lett., 6 (1988) 269.

79 T.W. Button, P.J. Ward, B. Rand, J.H. Sharp, P.F. Messer and E.A. Harris, Br. Ceram. Proc., 40 (1988) 93.

80 H. Strauven, J.P. Locquet, O.B. Verbeke and Y. Bruynseraede, Solid State Commun., 65 (1988) 293.

81 Y.T. Pavlyukhin, A.I. Rykov and N.G. Khainovskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 5 (1988) 101.

82 Y.T. Pavlyukhin, N.G. Khainovskii and A.I. Rykov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 5 (1988) 114.

83 Y.T. Pavlyukhin, N.G. Khainovskii and A.I. Rykov, Pramana, 31 (1988) L433.

84 G. Krabbes, G. Auerswald, A. Bartl, H. Eschrig, B. Lippold, M. Ritschel, H. Vinzelberg, E. Wolf and U. Wiesner, Cryst. Res. Technol., 23 (1988) 1161.

85 V. Balek and J. Šesták, Thermochim. Acta, 133 (1988) 23.

86 E. Kaisersberger, J. Janoschek and W. Haedrich, Thermochim. Acta, 133 (1988) 43.

87 Y. Shimakawa, J. Tabuchi, A. Ochi, K. Utsumi and M. Yonezawa, Nippon Seramikkusu Kyokai Gakuyutsu Ronbunshi, 96 (1988) 497.

88 T. Fujiwara, H. Nakata, T. Kumamaru, Y. Maeno, Y. Aoki and T. Fujita, Chem. Lett., 9 (1988) 1527.

89 H.M. O'Bryan and P.K. Gallagher, Solid State Ionics, 32 (1989) 1143.

90 S. Jantsch, J. Ihringer, J.K. Maichle, W. Prandl, S. Kemmler-Sack, R. Kiemel, S. Lösch, W. Schäfer and M. Schlichenmaier, J. Less-Common. Met., 150 (1989) 167.

91 G. Ottaviani, C. Nobili, F. Nava, M. Affronte and T. Manfredini, J. Less-Common. Met., 150 (1989) 177.

92 E. Saiz and J.S. Moya, Mater. Sci. Eng., A109 (1989) 329.

93 O.F. Delima, R.F. Jardim, S. Gama and I. Torriani, IEEE Trans. Magn., 25 (1989) 2171.

94 A. Reller, Pure Appl. Chem., 61 (1989) 1331.

95 Y. Zhao, T. Shi, S. Hu and L. Xie, Mater. Lett., 8 (1989) 83.

96 R. Schöllhorn, Angew. Chem., 100 (1988) 1446.

97 H.R. Oswald and A. Reller, Pure Appl. Chem., 61 (1989) 1323.

98 M.G. Ramsey and F.P. Netzer, Mater. Sci. Eng., B2 (1989) 269.

99 R. Schlögl, H. Eickenbusch, W. Paulus and R. Schöllhorn, Mater. Res. Bull., 24 (1989) 181.

100 K. Naukkarinen, K. Arlauskas, L. Grönberg, R. Laiho and J. Vanhatalo, J. Mater. Sci., 24 (1989) 1203.

101 R. Bormann and J. Nölting, Appl. Phys. Lett., 54 (1989) 2148.

102 P.K. Gallagher, G.S. Grader and H.M. O'Bryan, Mater. Res. Bull., 23 (1988) 1491.

103 H.G. Langer and R.A. Di Chiara, Thermochim. Acta, 133 (1988) 33.

104 J.E. Shelby, A. Bhargava, J.J. Simmins, N.L. Corah, P.H. McCluskey, C. Sheckler and R.L. Snyder, Mater. Lett., 5 (1987) 420.

105 A. Bhargava, M. Heuberger and R.L. Snyder, Mater. Lett., 5 (1987) 495.

106 D.N. Matthews, A. Bailey, T. Puzzer, G.J. Russell, J. Cochrane, R.A. Vaile, H.B. Sun and K.N.R. Taylor, Solid State Commun., 65 (1988) 347.

107 R. Schlögl, private communication.

108 R.L. Barns and R.A. Laudise, Appl. Phys. Lett., 51 (1987) 1373.

109 J. Dominec, L. Smircka, P. Vasek, S. Geurten, O. Smrckova, D. Sykorova and B. Hajek, Solid State Commun., 65 (1988) 373.

110 Z. Dexin, X. Mingshan, Z. Ziqing, Y. Shubin, Z. Huansui and S. Shuxia, Solid State Commun., 65 (1988) 339.

111 S. Jin, L. Liu, Z. Zhu and Y. Huang, Solid State Commun., 69 (1989) 179.

112 N.M. Hwang, G.W. Bahng, Y.K. Park, J.C. Park, H.G. Moon and D.N. Yoon, J. Mater. Sci. Lett., 8 (1989) 517.

113 P. Salvador, E. Fernandez-Sanchez, J.A. Garcia-Dominguez, J. Amador, C. Cascales and I. Rasines, Solid State Commun., 70 (1989) 71.

114 H.K. Liu, S.X. Dou, A.J. Bourdillon and C.C. Sorrell, Supercond. Sci. Technol., 1 (1988) 194.

115 H. Endo, J. Tsuchiya, N. Kijima, A. Sumiyama, M. Mizuno and Y. Oguri, Jpn. J. Appl. Phys., 27 (1988) L1906.

116 J.S. Park and H.G. Kim, J. Appl. Phys., 65 (1989) 877.

117 N.M. Hwang, G.W. Bahng, H.G. Moon and J.C. Park, Appl. Phys. Lett., 54 (1989) 1588.

118 R.P. Gupta, W.S. Khokle, J.P. Pachauri and C.C. Tripathi, Pramana, 32 (1989) L299.

119 R.S. Liu, Y.T. Huang, J.M. Jiang, P.T. Wu and C.T. Chang, Jpn. J. Appl. Phys., 28 (1989) L395.

120 S. Casagrande, Diploma Thesis, University of Zürich, 1989.

121 M. Kawasaki, S. Nagata, K. Takeuchi and H. Koinuma, Jpn. J. Appl. Phys., 27 (1988) L2227.

122 M. Gasgnier and M.-O. Ruault, Mater. Sci. Eng., B2 (1989) 287.

123 J.M.D. Coey, X.Z. Wang, K. Donnelly and J.F. Lawler, J. Less-Common. Met., 151 (1989) 195.

124 Y. Zhang, J. Liang, S. Xie, J. Huang, G. Rao, X. Cheng, H. Liu, D. Zheng and S. Qia, J. Phys. D, 21 (1988) 845.

125 T. Itoh and H. Uchikawa, Jpn. J. Appl. Phys., 28 (1989) L591.

126 H. Müller-Buschbaum, Angew. Chem., 101 (1989) 1503.

127 R.J. Cava, Sci. Am., 263 (1990) 24.