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SYNTHESIS AND THERMAL PROPERTIES OF SUPERCONDUCTING MIXED COPPER OXIDES

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ABSTRACT

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 = 13.7K [1] and the Ba-Bi-Pb-O system with T_c = 13 K [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 [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 [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) [6] as well as the Bi-Sr-Cu-O system [7], the Bi-Ca-Sr-Cu-O system [8,9] and the Tl-Ca-Ba-Cu-O system [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 [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 the synthesis and the characterization of the thermal 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. 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.

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These 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 their formation as well as during their thermal treatment. Thus, 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. Therefore, temperature dependent structural characterizations by means of X-ray diffraction or neutron diffraction in the temperature range from liquid helium up to 1200K are 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 physical properties.

This means, that the above mentioned findings are correlated with the measurements of the temperature dependent changes of the physical properties, above all of the transition into the superconducting state in the range between 4K and room temperature.

In summary, the reproducible preparation using suitable precursor materials, the well controlled compositional and strucural alteration as well as the detailed characterization of the temperature dependence of chemical, thermodynamic and physical properties of these stirring ceramic superconductors not only afford a best possible performance but also widen the spectrum of applications of thermoanalytical techniques.

REFERENCES

1. D.C. Johnston et al., Mat. 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. J. Müller, Rep. Prog. Phys. 43 (1980) 663.
5. M.R. Beasley and T.H. Geballe, Phys. Today 36 (1984) 60.
6. C. Michel et al., Z. Phys. B 68 (1987) 421.
7. M.K. Wu et al., Phys. Rev. Lett. 58 (1987) 908.
8. H. Maeda et al., Jpn. J Appl. Phys. 27 (1988) L209.
9. H.G. von Schnering et al., to be published.
10. Z.Z. Sheng and A.M. Hermann, Nature 332 (1988) 55.