

## High temperature superconductors for power cables

C. Dineen, W.G. Freeman, S.R. Hall, M.R. Harrison, D.M. Jacobson and S.J. Zammatio  
GEC-Marconi Ltd., Hirst Research Centre, East Lane, Wembley, Middlesex HA9 7PP, England

J.C. Bobo, G. Duperray, P. Millet, A. Petitbon and A. Wicker  
Alcatel Alsthom Recherche, Division Energetique et Materiaux, Route de Nozay, F-91460 Marcoussis, France

E. Klemt<sup>1</sup>, K.B. Muller<sup>2</sup> and H. Reiss<sup>1</sup>

<sup>1</sup>ABB AG, Konzernforschungszentrum (CRH), Postfach 101332, D-6900 Heidelberg, Germany;

<sup>2</sup>ABB Kabel und Draht GmbH, Postfach 101855, D-6800 Mannheim 1, Germany

H. Assmann, G. Bogner and H.W. Neumuller

Siemens AG, Corporate R & D, Physical Science and Engineering, ZFE ME-TPH2, Paul Gossen Strasse 100, Postfach 3220, D-8520 Erlangen, Germany

P. Caracino, L. Gherardi and P. Metra

Pirelli Cavi Spa, Group Research Centre, Divisione Italia, Viale Sarca 202, I-20120 Milano, Italy

S.P. Ashworth<sup>1</sup>, T.P. Beales<sup>1</sup>, S.E. Hughes<sup>1</sup>, J.M. Parberry<sup>2</sup> and J.S. McCormack<sup>2</sup>

<sup>1</sup>BICC Cables Ltd., Energy Cables Division, Church Manorway, Erith, Kent DA8 1HS, England

<sup>2</sup>BICC Plc, Quantum House, Maylands Avenue, Hemel Hempstead, Herts HP2 4SJ, England

### Abstract

Six major European electrical companies have been collaborating together in a precompetitive BRITE/EURAM research project targeting the application of high  $T_c$  superconductors in power cables and other high-current applications. The main objectives that have been addressed are: (1) identifying new superconducting phases with superior properties for the intended applications, including improved flux pinning at liquid nitrogen temperature; and (2) devising and improving techniques for fabricating experimental conductors with a high degree of texturing. The results obtained to date include the discovery of a new (Pb,Cd)-1212 superconducting phase and the fabrication and assessment of experimental conductors incorporating YBCO and BSCCO phases. Some of these samples provide encouragement for high-current applications.

### 1. Economics of superconducting power cables

The use of high  $T_c$  superconductors in power cables and other high-current applications requires that superconducting tapes are available in long lengths carrying hundreds of Amps at liquid nitrogen temperature. The aim of this BRITE/EURAM research project [1] was to explore the various combinations of materials and processing methods in order to determine the most promising method of producing these tapes. Since none of the existing materials appeared to be completely satisfactory for this purpose, a search for new superconducting phases with superior properties was also initiated. This paper concentrates on the result of this search, a new (Pb,Cd)-1212 material with a  $T_c$  of 92K.

To aid this experimental study, a parallel techno-economic study of power cables and other high-current applications was performed as a JOULE research project [2]. The cable consists of three phase-conductors enclosed by a vacuum-insulated steel outer vessel. Within each phase-conductor, a steel support defines an internal duct carrying liquid nitrogen under pressure and a series of

copper tapes are wound on this support to provide cryogenic stabilisation of the superconducting tape forming the inner conductor. The dielectric materials are similar to those used in conventional cables. Additional layers of superconducting and copper tapes form the outer conductor and the phase-conductor is enclosed in a pressure case. The liquid nitrogen is returned to the refrigeration stations in the space between the phase-conductors and the steel outer vessel. The study focussed on the capital cost of the cable and cooling system, the installation cost and the capitalised cost of the transmission losses.

For the purposes of costing the materials, it was assumed that the superconducting tape was produced by the powder-in-tube (PIT) processing of BSCCO in silver. The working voltage was fixed at 220kV requiring a current of 2625  $A_{RMS}$  for a 1GVA cable. The parameters of the cable were varied and it was shown that a  $J_c$  greater than  $2 \times 10^5 A/cm^2$  in a self magnetic field of 0.2T is needed for the optimised superconducting cable with an outer diameter of 192mm to be economically viable compared to a conventional copper 1GVA cable.

## 2. Fabrication of superconducting tapes

In order to achieve this value of  $J_C$ , the polycrystalline superconducting material must be highly textured with clean grain boundaries and there must be sufficient flux pinning at 77K [3]. All of the known high  $T_C$  materials have a layered structure consisting of alternating superconducting slabs containing  $\text{CuO}_2$  layers and non-superconducting dopant slabs. The dopant slabs break up the flux cylinders into a series of flux pancakes and it is now widely accepted that materials where the dopant slab contains a single layer of ions (eg YBCO) have much stronger flux pinning at 77K than materials where the dopant slab contains a double layer of ions (eg BSCCO) [4].

The PIT processing of BSCCO currently appears to be the most promising route for the production of long lengths of conductor tape. The comparatively low formation and melting temperatures of BSCCO (less than 900°C) are compatible with the use of silver substrates and the mica-like nature of BSCCO permits texturing by both melt and mechanical methods. Uniaxial alignment of the grains is apparently sufficient to achieve a high  $J_C$  and values up to  $2 \times 10^4 \text{ A/cm}^2$  at 77K were achieved within this project for short lengths of tape. However, the weak flux pinning in BSCCO at 77K means that moderate magnetic fields of the order 0.5T applied perpendicularly to the  $\text{CuO}_2$  layers considerably reduce the  $J_C$  value. This is not a serious limitation for power cables but other high-current applications require that the  $J_C$  value is maintained in much higher magnetic fields.

Whilst YBCO shows strong flux pinning at 77K, it seems that biaxial alignment of the grains of this material is required to achieve a high  $J_C$  value and this is very difficult to realise in polycrystalline films on polycrystalline substrates such as zirconia and nickel-based alloys. The variable oxygen content of this material coupled with the high formation and melting temperatures also pose severe problems. CVD deposition of thin YBCO films and laser melt-texturing of thicker YBCO films formed by plasma spraying have both been examined within this project as potential methods of achieving the required texture. The best results were obtained with CVD films on polycrystalline zirconia which achieved  $J_C$  values up to  $6 \times 10^3 \text{ A/cm}^2$  at 77K.

## 3. The (Pb,Cd)-1212 phase

We simultaneously embarked on a search for new superconducting materials which might overcome these processing problems. Thallium-based 1212 phases have good superconducting properties but the high volatility and toxicity of thallium oxide makes it difficult to process these materials into practical superconducting tapes. Instead, we focussed on lead-based 1212 materials such as  $(\text{Pb}_{1-y}\text{Cu}_y)\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_7$  or (Pb,Cu)-1212. These

materials are comparatively difficult to prepare, however, and only exhibit superconductivity when calcium-containing compositions with  $x > 0.3$  are synthesised in high-pressure oxygen and either quenched to ambient temperature or annealed in inert atmosphere to control the oxygen content [5-8].

We produced an improvement on the (Pb,Cu)-1212 materials by substituting cadmium for the copper in the (Pb,Cu) rock-salt layer to form the (Pb,Cd)-1212 phase shown in Figure 1 [9,10]. This substitution was suggested by considering the possible arrangements of ions in the lead-containing dopant layer. From a structural point of view, lead prefers a rocksalt-structure environment whereas copper prefers a perovskite-structure environment. The resulting random arrangement of the oxygen ions would tend to trap holes within the lead-containing dopant layer and prevent their transfer into the  $\text{CuO}_2$  layers which carry the superconducting current. We argued that a possible solution to this problem might be to replace the copper in the dopant layer by cadmium since cadmium has a fixed valence state and would prefer the rocksalt-structure environment. Both of these factors would help to stabilise the oxygen content of the material.

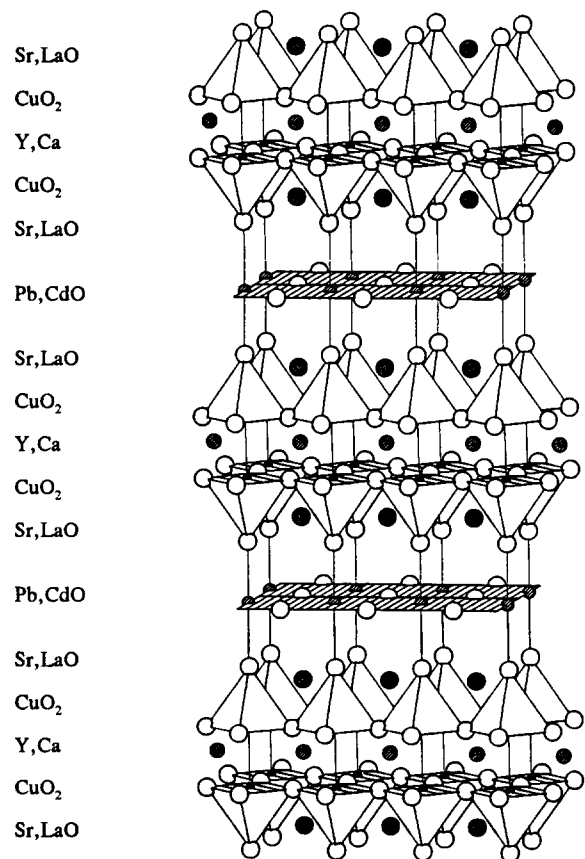


Figure 1. The (Pb,Cd)-1212 phase

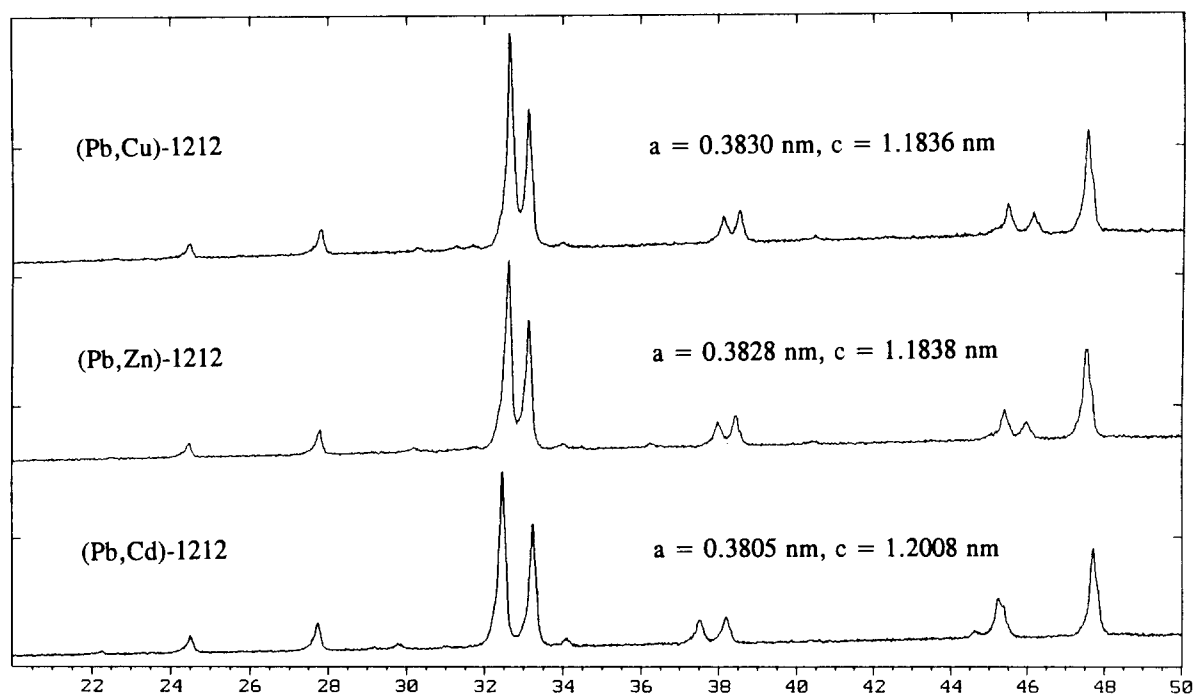


Figure 2. X-ray powder diffraction patterns of  $(\text{Pb}_{0.5}\text{M}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$  ( $\text{M} = \text{Cd}, \text{Zn}, \text{Cu}$ )

All of the samples were prepared using a Zymark robot. This system produces an intimate mixture of the constituent cations by combining approximately 0.1M aqueous solutions containing an EDTA complex of the metal ion. The water is evaporated from the mixed cation solution to leave a viscous gel which is calcined in air at 500°C to produce a fine-grained powder composed of oxides and carbonates. This mixture is then ground and re-calcined in air at the desired reaction temperature in a zirconia crucible. The reacted powder is finally allowed to cool to room temperature at the natural rate of the furnace (approximately 10°C per minute). The phases present in the calcined powders were determined with a Siemens D5000 diffractometer using  $\text{CuK}\alpha$  radiation and superconductivity was detected with a Quantum Design MPMS SQUID magnetometer using a magnetic field of 100G.

We prepared a series of samples with the nominal stoichiometry  $(\text{Pb}_{1-y}\text{M}_y)\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_7$  ( $\text{M} = \text{Cd}, \text{Zn}, \text{Cu}$ ). Phase-pure samples of the calcium-free compositions with  $y=0.5$  and  $x=0$  were formed at temperatures above 750°C with the optimum preparation temperature around 850°C. The powder diffraction patterns of these tetragonal symmetry samples are shown in Figure 2 and reveal that the c-axis length increases and the a-axis length shortens as we move from  $\text{M} = \text{Cu}$  to  $\text{Zn}$  to  $\text{Cd}$  in the  $(\text{Pb},\text{M})$  layer. The a-axis length is approximately twice the Cu-O bond length in the  $\text{CuO}_2$  layers and therefore reflects the degree of oxidation of the copper ions.

Magnetisation measurements showed that only the  $\text{M} = \text{Cd}$  samples were superconducting with the onset of weak diamagnetism occurring at 60K. The phase purity of the samples and the strength of the diamagnetism at 5K

decrease if the ratio of lead and cadmium ions in the  $(\text{Pb},\text{Cd})$  dopant layer is varied ( $0.25 \leq y \leq 0.75$ ) suggesting that the optimum mixture occurs at or near to the  $(\text{Pb}_{0.5}\text{Cd}_{0.5})$  composition. The phase purity of the samples also decreases as calcium ions are substituted for yttrium ions between the  $\text{CuO}_2$  layers ( $0.0 \leq x \leq 1.0$ ) although the 1212 phase remains the majority phase until  $x > 0.5$ . However, the superconducting properties of the  $(\text{Pb},\text{Cd})$ -1212 samples improve with the highest onset  $T_c$  of 92K occurring at  $x=0.3$  as shown in Figure 3.

The strength of the diamagnetism at 5K remains comparatively weak, however, and is equivalent to a few percent of an ideal superconductor. This can partly be explained by the small grain size of the material (0.2 $\mu\text{m}$ ) relative to the penetration depth and also by a possible decomposition reaction at the grain boundaries resulting in a material with very granular characteristics. The calcium-rich compositions may not be fully stable under these calcining conditions resulting in an inhomogeneous distribution of calcium ions throughout the sample.

Figure 4 shows the magnetisation curves for the  $(\text{Pb},\text{Cd})$ -1212,  $(\text{Pb},\text{Zn})$ -1212 and  $(\text{Pb},\text{Cu})$ -1212 samples with  $x=0.5$ . The  $(\text{Pb},\text{Cd})$ -1212 sample is superconducting with a slightly reduced onset  $T_c$  of 85K. The magnetisation curve of the  $(\text{Pb},\text{Zn})$ -1212 sample shows a weak transition around 50K but it is not certain whether this is a superconducting transition or not as a paramagnetic component dominates at lower temperatures. The partial substitution of zinc ions for copper ions in the  $\text{CuO}_2$  layers is very deleterious for superconductivity. The  $(\text{Pb},\text{Cu})$ -1212 sample is not superconducting above 5K when prepared in this manner.

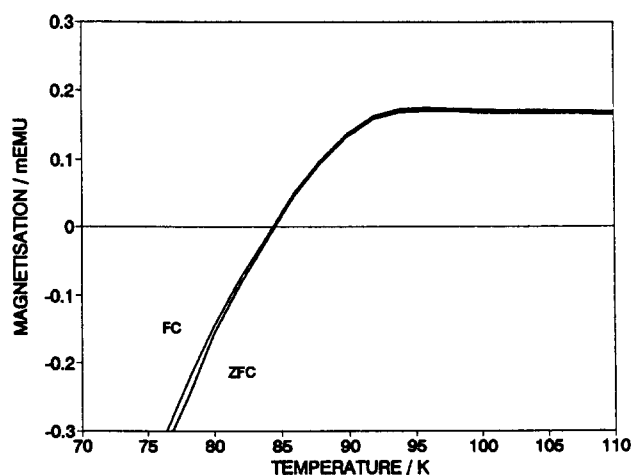
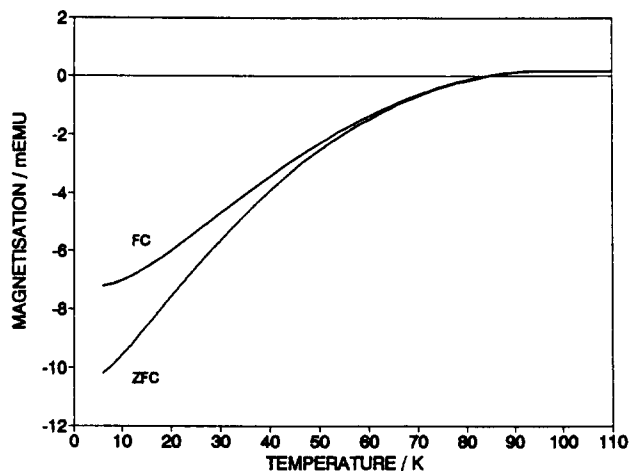


Figure 3. ZFC and FC magnetisation curves in 100G for 1g of  $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.7}\text{Ca}_{0.3})\text{Cu}_2\text{O}_7$

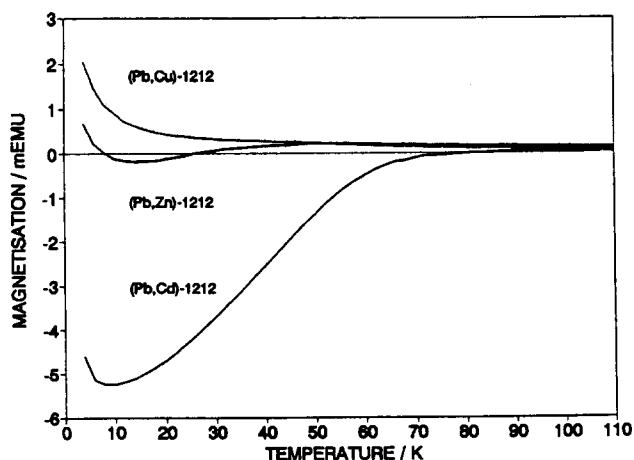


Figure 4. ZFC magnetisation curves in 100G for 1g of  $(\text{Pb}_{0.5}\text{M}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$  ( $\text{M}=\text{Cd}, \text{Zn}, \text{Cu}$ )

Liu *et al.* [11] and Qian *et al.* [12] have also investigated the superconducting properties of the (Pb,Cd)-1212 phase although their use of a conventional solid-state reaction method and higher preparation temperatures (around 975°C) appears to have limited the  $T_C$  to 70K. It has been suggested that elemental substitution of cadmium ions for calcium ions between the  $\text{CuO}_2$  layers occurs at high temperatures and that this may be deleterious for superconductivity.

In conclusion, we have prepared new high  $T_C$  materials containing a (Pb,Cd) rock-salt dopant layer and compared their properties with the corresponding (Pb,Zn) and (Pb,Cu) analogues. The observation of superconductivity in  $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$  shows that the (Pb,Cd) layers are able to spontaneously create charge carriers in the  $\text{CuO}_2$  layers presumably via Pb-O:Cu-O band overlap. This class of material is therefore very promising for future applications provided that the preparation problems can be overcome.

#### Acknowledgements

Support for this work is acknowledged from the BRITE/EURAM and JOULE Directorates of the Commission of the European Communities.

#### References

- 1 Summary report, BRITE/EURAM Project BREU-0095
- 2 Summary report, JOULE Project JOUE 0050-GB
- 3 M P Maley, *J. Appl. Phys.*, 70 (1991) 6189.
- 4 K E Gray and D H Kim, *Physica C*, 180 (1991) 139.
- 5 R S Liu, S F Hu, I Gameson, P P Edwards, A Maignan, T Rouillon, D Groult and B Raveau, *J. Solid State Chem.*, 93 (1991) 276.
- 6 T Maeda, K Sakuyama, S Koriyama, H Yamauchi and S Tanaka, *Phys. Rev. B*, 43 (1991) 7866.
- 7 X X Tang, D E Morris and A P B Sinha, *Phys. Rev. B*, 43 (1991) 7936.
- 8 H Zhang, G S Chen, S Q Feng, K Wu, X Zhu and Q R Feng, *Solid State Comm.*, 83 (1992) 601.
- 9 T P Beales, C Dineen, W G Freeman, D M Jacobson, S R Hall, M R Harrison and S J Zammattio, *Supercond. Sci. Tech.*, 5 (1992) 47.
- 10 T P Beales, W G Freeman, S R Hall, M R Harrison and J M Parberry, submitted to *Physica C*.
- 11 R S Liu, D Groult, A Maignan, S F Hu, D A Jefferson, B Raveau, C Michel, M Hervieu and P P Edwards, *Physica C*, 195 (1992) 35.
- 12 Y Qian, H Huang, K Tang, G Cao, Z Chen, G Zhou and N Wang, *Chinese Phys. Lett.*, 9 (1992) 552.