

NANOPARTICLES AND SUPERCONDUCTORS

VILÉM BARTUŇEK, OLGA SMRČKOVÁ

*Institute of Chemical Technology Prague, Department of Inorganic Chemistry
Technická 5, 166 28 Prague, Czech Republic*

E-mail: vilem.bartunek@vscht.cz

Submitted February 16, 2010; accepted April 07, 2010

Keywords: Superconductor, Pinning centres, Nanoparticles

Limiting parameters for cuprate Bi(Pb)SrCaCuO and YBaCuO superconductors are critical current density, critical external magnetic field and critical temperature. Since technology of cooling of superconductors by liquid nitrogen is well mastered, crucial limiting parameter is critical current density (with critical field linked). For II. type superconductors (including cuprates) mixed state where magnetic field penetrates to the mass of superconductor exists. Magnetic flux penetrates in form of moving vortices. Vortices could be pinned on pieces of nonsuperconducting phase and such process increases critical current density of superconductor. Possible pinning centres are nanoparticles in sizes to 10 nm but problem is chemical stability in material. In this work system of choosing of suitable materials has been developed. Firstly selected materials were tested to stability via thermodynamics calculations by using program FactSage. Two materials survived test and were tested experimentally. In₂O₃ was not inert to Bi(Pb)SrCaCuO superconductor but CeO₂ (in form of nanoparticles about 3 nm in diameter) was. Therefore CeO₂ seems to be good material for both purpose of research and for possible industrial use.

INTRODUCTION

Phenomenon of superconductivity is about one hundred years known. Superconducting material shows electric resistance near zero and it is able to transport an electric current without losses. These materials are divided into low and high temperature superconductors. The high temperature superconductors work beyond the boiling temperature of the liquid nitrogen. Factors limiting superconducting state of all superconductors are critical temperature (T_c), critical current density (j_c) and critical intensity of outer magnetic field (H_c). Among the high temperature superconductors the widest focus is on the cuprate superconductors divided into two groups: YBCO (YBaCuO) and BiSCCO (Bi(Pb)SrCaCuO). These two types of high temperature superconductors are widely used in applications [1, 2]. The examples are I. generation (BiSCCO tube in technique made tapes) and II. generation (YBCCO coated tapes) superconducting wires [1-3]. Main limiting factors for both are i_c – critical current of the wire (77 K, linked with H_c), mechanical properties and of course cost. Wires of both generations have advantages and disadvantages but both display i_c in the order of hundreds Amperes. j_c of YBCCO coated wires is of course significantly higher (about thousand times) than j_c of BiSCCO wires because of lower thickness of superconducting core. So it could be very interesting to improve j_c of BiSCCO superconducting material.

YBCCO and BiSCCO are second type superconducting materials. It means between regular superconducting state and non-superconducting state is mixed state (Figure 1). In mixed state magnetic field penetrate into mass of superconductor matrix in form of vortices of magnetic flux. The core of vortices is in non-superconducting state. All vortices in superconductors are subjected to Lorentz force because carry a magnetic moment and therefore move through crystal. During moving through crystal vortices interact with supercurrent carriers and causing their interaction with crystal lattice. It leads to dissipation of their energy and electric resistance appears [4]. It means ideal superconducting crystal will show electric resistance in mixed state. To each vortex we could assign core energy higher then energy of surrounding superconductive matrix. If matrix reaches some place in material which exhibits no superconductivity, for example lattice defect, it will lead to decreasing of overall energy of system and vortex will be pinned in such place [5]. Crucial for pinning force is energy gradient. So for too large or too small nonsuperconducting place the gradient is too small and such place will not be good pinning centre. Key dimension is diameter of vortex core equal to coherence length (ξ) distance over which the charge carriers generating Cooper pairs can still interact with each other. Cuprate superconductors display strong anisotropy therefore ξ depends on direction. The value of ξ is commonly less then 10 nm in high temperature

superconductors. So the best pinning centres for BiSCCO and YBCO superconductors are nanosized pinning centres.

Pinning centres could be divided to the point, columnar and splayed (nonparallel) columnar. From theory and experiments result point defect has major role in temperatures below $0.5 T_c$ so for practical use in liquid nitrogen temperatures are nearly useless in current materials [6]. Opposite columnar pinning centres look promising [7] especially for high anisotropy materials as BiSCCO [8]. Several methods how create nanosized pinning centres in BiSCCO and YBCO superconductors have been used. One of the methods is using various irradiations to create melted traces in material. So columnar pinning centres could be created by heavy ion irradiation [9], neutron irradiation [10] and proton irradiation [11] and point defects by electron irradiation [12]. Splayed columnar defect could be prepared by addition of small amount of ^{235}U and subsequent irradiation by thermal neutrons [13]. Although these methods have had some success some problems seem to prevent its use on industrial scale. For example low thermal stability of defects [14], possible residual radioactivity, cost and so on. Another method of improving properties of high-temperature superconductors is doping superconductors by certain compounds or elements to give small amount of inclusions or secondary phases placed randomly or oriented in the mass of matrix. So created pinning centres are called chemical pinning centres [15]. Lots of compounds has been tried [16]. Main problem in this case is that shape, size and distribution is often far from optimal. More this works only with low amounts of additions, with higher amounts formation of superconducting phase is prevented. In some view one can say that small amount of nearly everything can improve critical current density and large portion will destroy the superconductivity.

Better way is including inert or nearly inert nanoparticles into superconducting matrix. Problem is number of elements of superconducting phases which may create unwanted phases by reactions with nanoparticles in conditions of high temperatures and long reaction times of processing. YBCO is in better position because it contains only four elements in contrast to BiSCCO

containing fifth elements and for more it is usually doped by PbO (or PbO_2) for better processing (so called Bi(Pb)SrCaCuO superconductor). Another complication is different chemical and physical behaviour of nanoparticles in comparison with bulk. In the case of YBCO some successes have been achieved by pulsed-laser deposition of BaZrO_3 -doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ films [17, 18]. Created nanoparticles of BaZrO_3 were columnar pinning centers required shapes, orientation and sizes. BiSCCO superconductors can contain two high temperature superconducting phases $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223 phase) and $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ (2212 phase). 2223 phase have critical temperature about 110 K and 2212 phase about 80 K [19]. 2223 phase has better superconducting properties but 2212 phase is more stable and is created at lower temperature [20]. Presence of PbO is needed to optimal process of formation 2223 phase. Carbon nanotubes have been used with some success to improve j_c of BiSCCO 2212 superconductors [21, 22]. Nanoparticles were firstly annealed in argon atmosphere with superconductor's precursor and subsequently annealed in oxygen atmosphere to form 2212 phase below 800°C . Problem is reactivity of carbon with present metal oxides and possible reaction with diffused oxygen in current annealing in oxygen atmosphere. It is very likely that at least some carbon react with oxygen to CO_2 . Defects created during formation and escaping of the gas should be partially responsible for increased critical current density [21]. The best to current date seems to be using MgO nanoparticles especially in the form of nanorods. Doping significantly increased the value of critical current at all temperatures and works with both 2212 and 2223 phases [24, 25]. But problem of this method is probably chemical interaction MgO with PbO. Therefore use of MgO is probably limited (Figure 2).

In this article we propose possible way how to determine suitable materials for nanoparticles pinning centers for BiSCCO superconductors containing Pb-2223 phase for both research and possible industrial applications. These materials have to have these properties:

1. Chemical stability in Bi(Pb)SrCaCuO at least at 840°C .

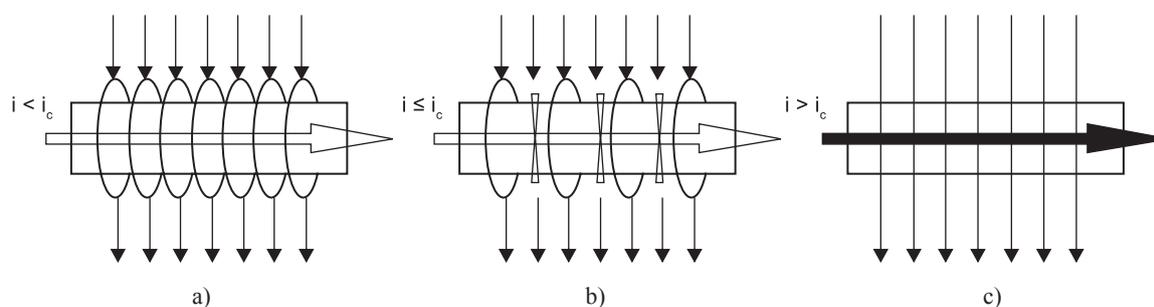


Figure 1. Schematic drawings of behaviour of magnetic field interacting with superconductor. a) superconducting state, b) mixed state, c) nonsuperconducting state.

2. Physical stability (mainly sufficiently high melting point with consideration that melting points of nanoparticles are much lower).
3. Acceptable toxicity.
4. Possibility to create stabile nanoparticles of various shapes and sizes. If nanoparticles are stabilized by some surface stabilization agents, these agents have not to react with superconducting matrix significantly or decompose to significant amount of products mainly gases.
5. Reasonable availability and cost of material and methods of manufacturing of nanoparticles.

From above resulting materials have to be mainly simple compounds or elements, because predicting of behavior of compounds containing more elements is difficult and probability of forming phases with elements from superconductor increasing.

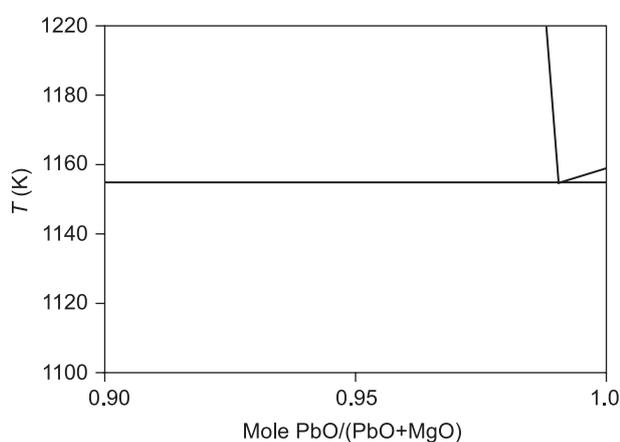
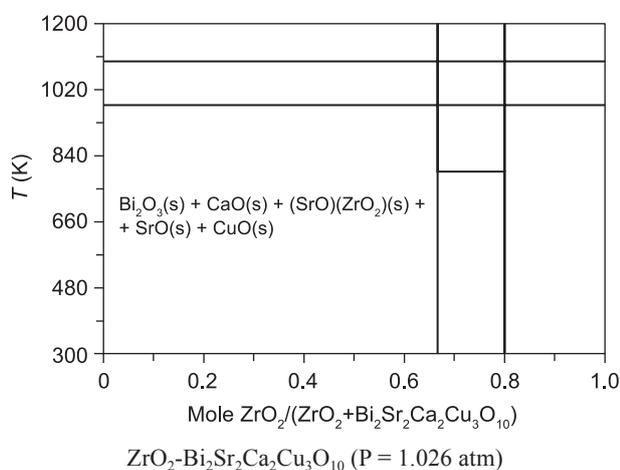


Figure 2. Calculated phase diagram shows possible dissolving of MgO in surrounding liquid PbO. For nano-MgO process could be even more rapid.



EXPERIMENTAL

Three steps for determination of suitability of material for adding to Bi(Pb)SrCaCuO have been used. First step was forecasting of materials by literature review and selecting of inert elements, simple oxides or simple oxides of elements with unusual valence electron configuration. Temperature of melting was taken to consideration (so were deleted for example Au or Ag). In this step for example Al_2O_3 , SnO_2 , CeO_2 , C, MgO, ZrO_2 , NiO, Pd, Pt, In_2O_3 , BeO, CuO, SiC, WO_3 and much more were selected.

During the second step chemical stability of selected candidates in 2223 phase and PbO has been estimated by thermodynamic calculation. FactSage[®] verse 5.5 software, database computing systems in chemical thermodynamics has been used. Such estimation is of course simple and depends on records in databases. So ideal 2223 phase were inserted and program due to lack of presence of 2223 phase in databases computing with it like with mixture of oxides but with proper composition. As a result it is not confirming of stability of selected candidate but confirming of instability. Despite of this most of candidates were deleted in this step.

Subsequently experimental confirmation of stability of selected candidates In_2O_3 and CeO_2 started. Samples were prepared by double calcination of raw precursors. After milling of calcined samples pellets were pressed. Samples were sintered at 840°C for one week. Prepared samples contained mainly 2212 phase and lower amount of 2223 phase. Next, samples were milled and added to ethanol dispersion system (obtained by treating nanoparticles in ethanol by ultrasound for 10 minutes) and treated in ultrasound for a few minutes. Ethanol was evaporated in evaporator. It was done only with CeO_2 nanoparticles because of their availability. In the case of In_2O_3 fine milled powders were only mixed.

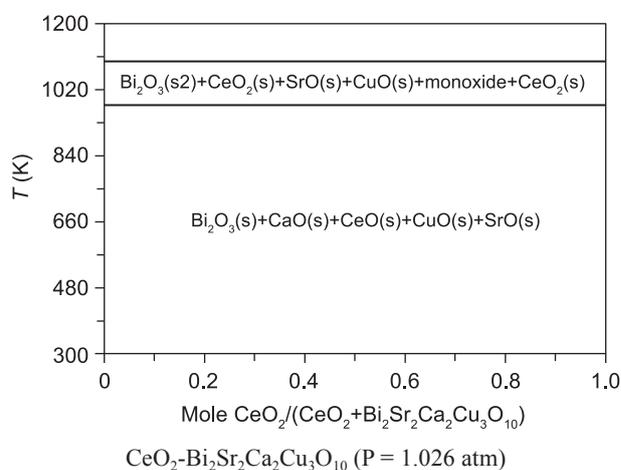


Figure 3. Difference between phase diagrams of ZrO_2 -2223 and CeO_2 -2223 is obvious.

Subsequently powder was pressed into pellets and sintered at 840 °C for one week on air. Samples contain 50 wt.% of In_2O_3 and 50 wt.% of first sintered portion in the case of In_2O_3 and 10 % and 50 % of CeO_2 in case of CeO_2 nanoparticles were prepared. Seed mediated preparation of cerium oxide nanoparticles was used [22]. Over-supply of ammonia solution (20 wt.%) was dropwise added into cerium(IV) sulphate solution (0.4 mol/l) at room temperature and continuous stirring. Yellow fine precipitate appeared. Precipitate was multiply carefully washed with distilled water and dried on air at 80°C. X'Pert HihgScore Plus program was used for processing data from XRD and calculating of nanoparticles sizes was made by using Scherrer formula. Average diameter of CeO_2 nanoparticles was determined around 3 nm. All prepared samples were characterized by XRD measurements. X-ray powder diffraction data were collected at room temperature by X'Pert PRO θ - θ powder diffractometer with parafocusing Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$). Sample with 50 % CeO_2 was milled to the fine powder and treated by diluted HCl (about 20 vol.%). Non-dissolved solid was washed in distilled water, dried and analyzed by XRD and XRF (X-Ray Fluorescence). ARL 9400 XP sequential WD-XRF spectrometer was used to perform XRF analysis.

RESULTS AND DISCUSSION

From processing with FactSage two groups of candidates emerged. First were three oxides: BeO, In_2O_3 and CeO_2 . BeO was deleted because of high toxicity and carcinogenicity of beryllium and its compounds especially in the form of nanoparticles. CeO_2 and In_2O_3 were examined experimentally. Second were two noble metals Pt and Pd which seems to be both chemical and physical stable in specified conditions.

Processing data with FactSage have limits of course and serves for elimination of materials creating compounds with BiSCCO, for example ZrO_2 (Figure 3). Next logical step is an experiment. In_2O_3 has been proved unstable in experimental conditions. Figure 4 displays zoomed XRD patterns of sintered mixture of 50 % In_2O_3 and 50 % of firstly sintered BiSCCO. In lower part of the picture is the most intensive peak from In_2O_3 pattern. This peak is clearly not present in the upper pattern displaying composition after sinteration. Similar is valid for other intensive peaks in patterns. Composition of new phase or phases contains Indium has not been characterized from X'Pert HihgScore Plus database. It is possible that some new compounds were created. But important output is that In_2O_3 has not survived.

Opposite In_2O_3 , CeO_2 seems to be stable in Bi(Pb) CaCuO superconductor matrix. XRD pattern (Figure 5) shows presence of all CeO_2 peaks. From XRD pattern also appeared that presence of such large amount of CeO_2 prevent forming of 2223 phase and even causing decomposition of 2212 phase to the mixture of non specified oxides. Preventing of forming 2223 phase seems clear because 2223 needs Pb containing liquid for transporting reactions at 840 °C and presence of such amount of ultrafine nanoparticles prevent efficient function of liquid. Cause of decomposition of 2212 is unclear. Two possible processes have been taken into account. First is possible shifting of chemical balances of complex chemical reactions caused by presence of large volume of fine uniformly distributed nanoparticles. Second possible process should be saturation of CeO_2 by CaO. $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9}$ phase has nearly the same XRD pattern as CeO_2 so it is impossible to diversify each other. But saturation of CeO_2 by CaO usually take place at much higher temperatures (above 1400°C) [23]. Of course one week is long time and some diffusion of CaO to the CeO_2 can possibly take place even at lower temperatures. For resolution sample was milled and

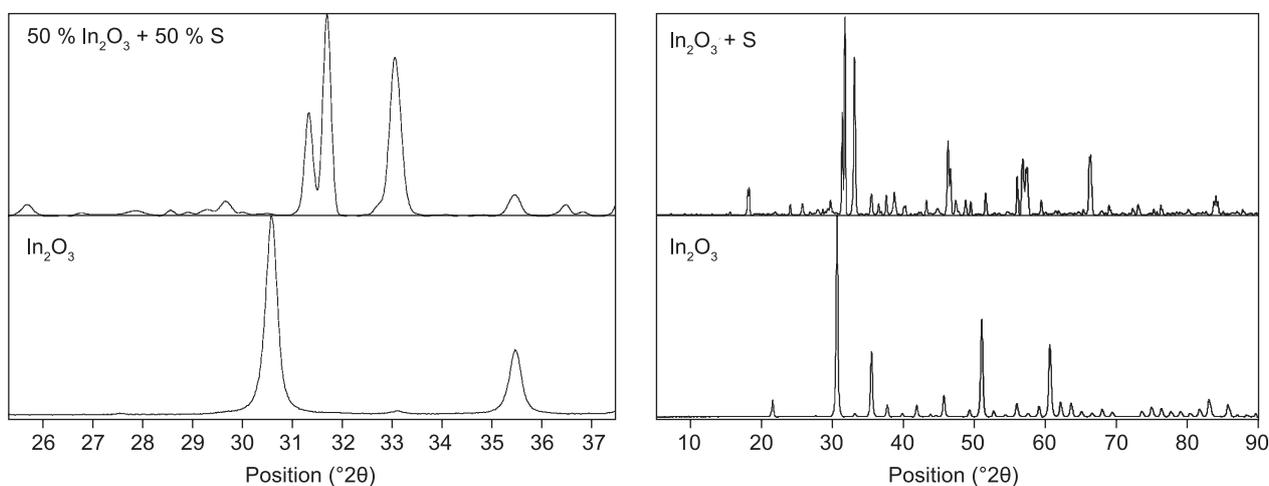


Figure 4. XRD patterns of sintered mixture of bulk In_2O_3 and BiSCCO (marked as S). Main peaks of In_2O_3 disappeared after heat treatment at 840°C for one week.

powder was treated in 20 vol.% HCl for 5 minutes at ambient temperature. Obtained non dissolved solid was washed with distilled water and dried. XRD and XRF analyzes were made. XRD pattern respond to nearly clear CeO_2 . Content resulting from XRF was 95.7 wt.% Ce, 0.75 wt.% Ca, 2.7 wt.% Bi and 0.6 wt.% oxidic sulfur (CeO_2 nanoparticles are stabilized by sulfate [22]). From XRF results insufficient amount of Ca to form compound like $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9}$. More likely present Ca forms phase with Bi, for example $\text{Bi}_{11.6}\text{Ca}_{4.2}\text{O}_{1.6}$ with very similar diffraction pattern to CeO_2 . So if any CaO reacts with CeO_2 that it reacts in insignificant measure, surely for small amounts of CeO_2 .

Sample with 10 % of CeO_2 and 90 % BiSCCO was prepared by the same way as sample with 50 % CeO_2 . In this concentration 2212 phase didn't decompose but 2223 phase didn't appear in larger volume in contrast

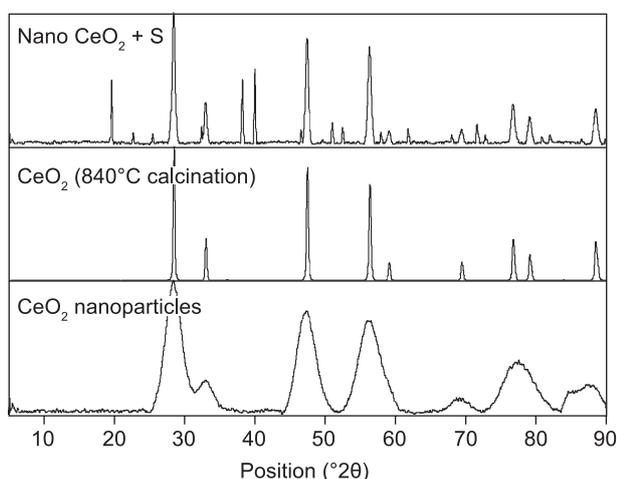


Figure 5. Comparison of XRD patterns of nano CeO_2 , CeO_2 calcined at 840°C (about one day) and sintered mixture of once sintered BiSCCO (marked as S) and nano CeO_2 (CeO_2 peaks are present in all patterns).

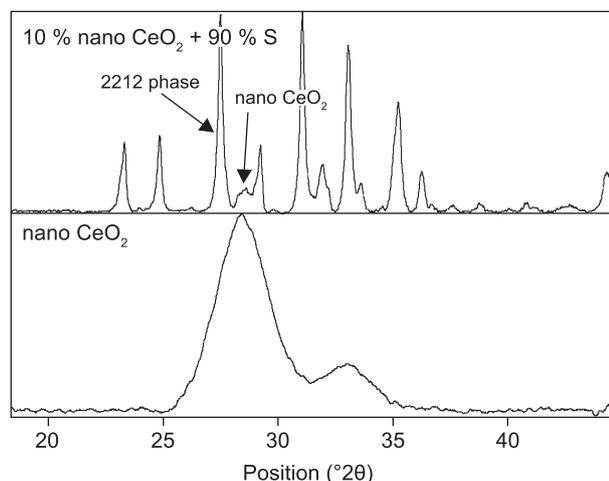


Figure 6. XRD pattern of BiSCCO containing 2212 phase and CeO_2 nanoparticles.

with standard without CeO_2 addition where 2223 was main phase in sample. On Figure 6 the most intensive peak of CeO_2 nanoparticles could be identified. From half width of peak diameters of nanoparticles were roughly estimated about 13 nm by Scherrer formula. If nanoparticles of such sizes are surviving for 10 wt.% of CeO_2 very likely survive nearly in their original size for amounts less than 1 wt.% which will be used for creation of pinning centers.

CONCLUSION

System of choosing of materials for nanoparticle pinning centres has been developed. Firstly, candidates are tested by thermodynamics calculations and subsequently tested via experimental procedure. In_2O_3 and CeO_2 picked as inert materials to Bi(Pb)SrCaCuO superconductor based on thermodynamics calculations made by FactSage program. In_2O_3 were recognized experimentally as reactive with BiSCCO and so must be claimed as unsuitable material for inert pinning centres to BiSCCO. CeO_2 were tested in form of nanoparticles about 3 nm in diameter. It has been discovered CeO_2 survive BiSCCO preparation process and seems to be inert to Bi(Pb)SrCaCuO matrix. Only possible detected reaction of CeO_2 is with Ca and only on a very low scale. Even with possibility of full saturation of CeO_2 by Ca there is only very little volume change of material [24] and decrease of Ca could be compensated. But only about 1 % or less of CeO_2 is probably enough for doping of BiSCCO by CeO_2 to sufficient density of pinning centres. Therefore CeO_2 has been considered as suitable material. Moreover it is cheap, nontoxic and nanoparticles could be prepared by simple way [25-27].

Acknowledgment

This work was financially supported by MSMT CR as project No. 6046137302.

References

1. Dou S. X., Liu H. K.: Supercond. Sci. Technol. 6, 297 (1993).
2. Li C. G., Yi Y. G.: Rare Metal Mat. Eng. 28, 193 (1999).
3. Riley G. N., Li Q., Fritzscheier L. G.: Curr. Opin. Solid State Mat. Sci. 4, 473 (1999).
4. Bardeen J., Stephen M. J.: Physical Review. 140, 1197 (1965).
5. Cooley L. D., Grishin A. M.: Phys. Rev. Lett. 74, 2788 (1995).
6. Terai T., Masegi T., Kusagaya K., Takahashi Y., Kishio K., Motohira N., Nakatani K.: Physica C. 185, 2383 (1991).
7. Horvat J.: Encyclopedia of Nanoscience and Nanotechnology, p. 207, 2004.

8. Kummeth P., Neumuller H. W., Ries G., Kraus M., Klaumunzer S., Saemannschenko G.: *J. Alloy. Compd.* 195, 403 (1993).
9. Wahl A., Hervieu M., Vantendeloo G., Hardy V., Provost J., Groult D., Simon C., Raveau B.: *Radiat. Eff. Defects Solids.* 133, 293 (1995).
10. Weber H. W., Wiesinger H. P., Kritscha W., Sauerzopf F. M., Crabtree G. W., Liu J. Z., Chang Y. C., Jiang P. Z.: *Critical Currents In Neutron-Irradiated YBCO And BiSCO Single-Crystals*, Adam Hilger Ltd, Bristol, 1991.
11. Safar H., Cho J. H., Fleshler S., Maley M. P., Willis J. O., Coulter J. Y., Ullmann J. L., Lisowski P. W., Riley G. N., Rupich M. W., Thompson J. R., Krusinbaum L.: *Applied Physics Letters.* 67, 130 (1995).
12. Giapintzakis J., Lee W. C., Rice J. P., Ginsberg D. M., Robertson I. M., Wheeler R., Kirk M. A., Ruault M. O.: *Phys. Rev. B.* 45, 10677 (1992).
13. Hart H. R., Luborsky F. E., Arendt R. H., Fleischer R. L., Tkaczyk J. E., Orsini D. A.: *IEEE Trans. Magn.* 27, 1375 (1991).
14. Thompson J. R., Paul D., Wang Z. L., Kroeger D. M., Christen D. K.: *Applied Physics Letters.* 67, 1007 (1995).
15. Weinstein R., Sawh R.-P.: *Physica C: Superconductivity* 383, 438 (2003).
16. Dou S. X., Wang X. L., Guo Y. C., Hu Q. Y., Mikheenko P., Horvat J., Ionescu M., Liu H. K.: *Supercond. Sci. Technol.* 10, A52 (1997).
17. Driscoll J. L., Foltyn S. R., in: *Laboratory U.O.C.L.A.N.* (Ed.), U.S. Pat. Appl. Publ., U.S., 2004.
18. Maiorov B., Bailly S. A., Zhou H., Ugurlu O., Kennison J. A., Dowden P. C., Holesinger T. G., Foltyn S.R., Civale L.: *Nat. Mater.* 8, 398 (2009).
19. Cava R. J.: *J. Am. Ceram. Soc.* 83, 5 (2000).
20. Majewski P.: *J. Mater. Res.* 15, 854 (2000).
21. Bartunek V., Smrckova O.: *Ceramics-Silikaty* 51, 213 (2007).
22. Xu J. X., Li G. S., Li L. P.: *Materials Research Bulletin.* 43, 990 (2008).
23. El Adham K., Hammou A.: *Solid State Ionics.* 9-10, 905 (1983).
24. Mogensen G., Mogensen M.: *Thermochimica Acta.* 214, 47 (1993).
25. Feng X. D., Sayle D. C., Wang Z. L., Paras M. S., Santora B., Sutorik A. C., Sayle T. X. T., Yang Y., Ding Y., Wang X. D., Her Y. S.: *Science.* 312, 1504 (2006).
26. Chen H. I., Chang H. Y.: *Ceramics International.* 31, 795 (2005).
27. Yang P. D., Lieber C. M.: *J. Mater. Res.* 12, 2981 (1997).