NANOPARTICLES AND SUPERCONDUCTORS

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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 \(\xi\) distance over which the charge carriers generating Cooper pairs can still interact with each other. Cuprate superconductors display strong anisotropy therefore \(\xi\) depends on direction. The value of \(\xi\) 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 unwonted 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 YBa$_2$Cu$_3$O$_y$ 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 filed interacting with superconductor. a) superconducting state, b) mixed state, c) nonsuperconducting state.](image-url)
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 stable 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.

**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 oxidic compounds 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 Al₂O₃, SnO₂, CeO₂, C, MgO, ZrO₂, NiO, Pd, Pt, In₂O₃, BeO, CuO, SiC, WO₃ 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 In₂O₃ and CeO₂ 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 CeO₂ nanoparticles because of their availability. In the case of In₂O₃ fine milled powders were only mixed.

![Figure 2](image1.png)

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

![Figure 3](image2.png)

**Figure 3.** Difference between phase diagrams of ZrO₂-2223 and CeO₂-2223 is obvious.
Subsequently powder was pressed into pellets and sintered at 840 °C for one week on air. Samples contain 50 wt.% of In2O3 and 50 wt.% of first sintered portion in the case of In2O3 and 10 % and 50 % of CeO2 in case of CeO2 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 CeO2 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 #0-0 powder diffractometer with parafocusing Bragg-Brentano geometry using CuKα radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). Sample with 50 % CeO2 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, In2O3 and CeO2. BeO was deleted because of high toxicity and carcinogenicity of beryllium and its compounds especially in the form of nanoparticles. CeO2 and In2O3 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 ZrO2 (Figure 3). Next logical step is an experiment. In2O3 has been proved unstable in experimental conditions. Figure 4 displays zoomed XRD patterns of sintered mixture of 50 % In2O3 and 50 % of firstly sintered BiSCCO. In lower part of the picture is the most intensive peak from In2O3 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 In2O3 has not survived.

Opposite In2O3, CeO2 seems to be stable in Bi(Pb) CaCuO superconductor matrix. XRD pattern (Figure 5) shows presence of all CeO2 peaks. From XRD pattern also appeared that presence of such large amount of CeO2 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 CeO2 by CaO. Ce0.9Ca0.1O1.9 phase has nearly the same XRD pattern as CeO2 so it is impossible to diversify each other. But saturation of CeO2 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 CeO2 can possibly take place even at lower temperatures. For resolution sample was milled and

Figure 4. XRD patterns of sintered mixture of bulk In2O3 and BiSCCO (marked as S). Main peaks of In2O3 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 Ce$_{0.9}$Ca$_{0.1}$O$_{1.9}$. More likely present Ca forms phase with Bi, for example Bi$_{11.6}$Ca$_{4.2}$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 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.% 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$_2$O$_3$ and CeO$_2$ picked as inert materials to Bi(Pb)SrCaCuO superconductor based on thermodynamics calculations made by FactSage program. In$_2$O$_3$ 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].

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References