

High-temperature Superconducting Nanocomposites and their Stability

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Abstract — We synthesized composites based on high-temperature superconducting ceramics $\text{YBa}_2\text{Cu}_3\text{O}_{6.91}$ (Y123) with polymer additives poly(ethylene glycol) dimethacrylate (poly(EGDMA)). We studied the effect of additives in the obtained nanocomposites on processes of their degradation under the action of steam and water at various temperatures as well as changing phase composition and electro-physical characteristics of organic high-temperature superconducting composites. It is shown that application of organic polymer increases Y123 ceramics stability and does not effect considerably on their temperature of transition to the superconducting state.

Keywords — HTSC; composites; degradation; resistive properties.

I. INTRODUCTION

High-temperature superconducting (HTSC) cuprates are interesting and promising materials for both fundamental and applied investigations when developing electrical motors, energy storage systems, superpower magnets, microwave components, etc. [1]. Wide practical application of HTSC cuprates is restrained by degradation of superconducting ceramic that leads to reduction (or sometimes even to loss) of their superconducting properties. That is why stabilization of their electro-physical characteristics and improvement of structural homogeneity by doping with inorganic as well as organic impurities is an actual problem [2-5].

It was shown in [2-5] that introduction of another phase into superconducting ceramic may result in a slight reduction of temperature of its transition to the superconducting state but can also essentially improve its chemical stability and mechanical properties. In particular, dopants promote formation of efficient pinning centers, which has a positive impact on the current-carrying ability of superconducting oxides. It is known from literature sources about the effect of additives of silver [6], calcium [7], boron [8], Al_2O_3 [9], Nb_2O_5 [10] and ZrO_2 [2, 9] on the properties of superconducting composition Y123.

The investigations of degradation of HTSC cuprates Y123 [11] in electrolyte solutions showed that acids not only suppress superconductivity, but also completely destroy

ceramic. The effect of alkalis on HTSC ceramic proceeds somewhat slower. Under the action of electrolyte solutions, the rate of HTSC phase destruction varies in the following sequence: $\text{HCl} > \text{HNO}_3 > \text{CH}_3\text{COOH} > \text{H}_2\text{SO}_4 \gg \text{NaOH}$.

Loss of the superconducting properties of Y123 in the above solutions is related to dissolution and transition of individual ions (or all components of HTSC materials) into liquid phase.

It is known that superconducting ceramic / polymer composites have excellent mechanical properties, greater flexibility in processing and processing compared to ceramics [4-5, 12-13].

At the same time, moisture is the most important atmospheric factor influencing stability of superconducting ceramic at application of products made of HTSC materials.

Therefore, the aim of our work was investigation of the effect of organic additive poly(EGDMA) - on stability of the HTSC Y123 ceramics under action of steam and humid environment.

II. MATERIALS AND METHODS

The initial substances for synthesis of superconducting ceramic were Y_2O_3 (99.0%, High Purity Chemicals), BaCO_3 (99.0%, High Purity Chemicals) and CuO (99.0%, High Purity Chemicals).

The $\text{YBa}_2\text{Cu}_3\text{O}_{6.91}$ (Y123) ceramic was synthesized by the sol-gel method. The initial components oxides (yttrium and copper) and barium carbonate were dissolved into concentrated nitric acids. The stoichiometric ratio of the $\text{Y}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ solutions were mixed together at room temperature for 15 min, after that the solution of ammonium citrate was added to pH ~ 6-7. Formation of the gel took place in a water bath for 2 hours. Slow evaporation of mixture during 2 h at 100–110⁰ C led to transformation into a transparent gel. After drying in an oven at 200°C, powder was obtained. Dried mass was calcinated using step-by-step heating up to temperature 920°C for 24 hours with intermediate grinding. After this, the samples were pressed into pellets (diameter of 15 mm and thickness of 1-2 mm). The superconducting phase was formed at burning in an oxygen flow at 900-920°C for 24 hours. Then the samples were slowly

cooled in an oxygen flow with rate of 1-2 deg/min and isothermal storage at 400°C for 6 hours. Scheme of synthesis process of pure Y123 sample is presented in Fig. 1.

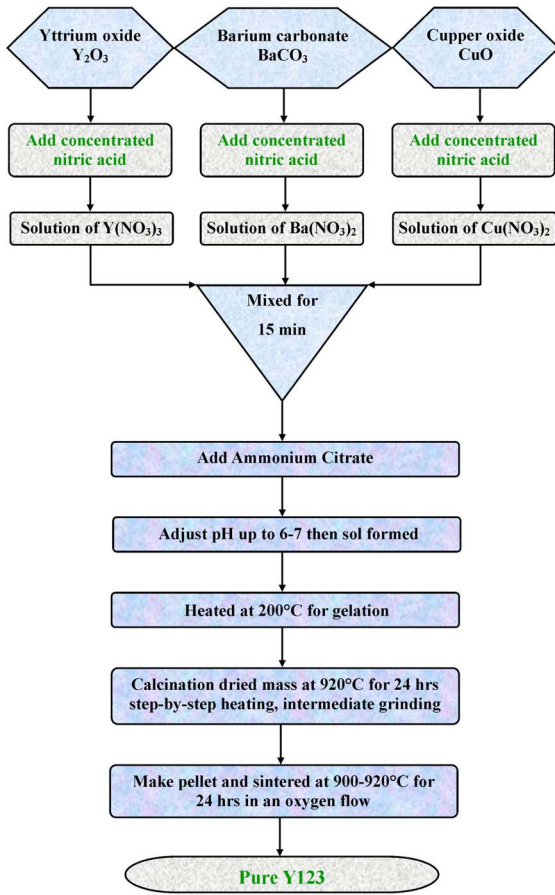


Fig. 1. Scheme of synthesis process of pure Y123 sample.

After performing a number of experiments, we found poly(EGDMA) - an organic polymer that does not interact with the superconducting phase. Therefore, to synthesize polymer-ceramic nanocomposites, we used EGDMA monomer (of purum grade) and benzoyl peroxide initiator (of purissimum grade), as well as the HTSC Y123 ceramics in the form of a powder or pelleted samples.

The 0-3 polymer-ceramic nanocomposites were obtained by impregnation with a benzoyl peroxide initiator solution in the EGDMA monomer of highly dispersed superconductor powder. The mixtures were pelleted and subjected to thermal polymerization at 80°C for 1 hour. The 3-3 polymer-ceramic composites were obtained by impregnation of superconducting ceramic with liquid monomer and its polymerization in pores of a compact sample according to the procedure [14-15]

The process of blend decomposition at synthesizing HTSC compounds and investigation of nanocomposite ceramic degradation were controlled using X-Ray radiography and IR spectroscopy. The phase composition of the samples and unit cell parameters were determined using x-ray diffraction (XRD) with a diffractometer DRON-3 ($\text{CuK}\alpha$ radiation, wavelength of 1.54178 Å) equipped with a Ni filter.

We studied degradation of compact samples (pellets 1-2 mm thick and 15 mm in diameter) exposed to steam and water.

The IR absorption spectra of pelleted thermolysis products with KBr were registered in the 400-4000 cm^{-1} range using a spectrophotometer Spectrum BX FT-IR (Perkin Elmer). The resistive properties of the obtained samples were measured in the 300-78 K temperature range by the standard four-contact method with an ACTC device using indium-gallium eutectic. Doubly distilled water (State Standard of Ukraine ISO 3696:2003) was used when studying degradation processes.

III. RESULTS AND DISCUSSION

The XRD powder patterns of the nanocomposite and pure Y123 compounds are shown in Fig. 2. The pure Y123 sample is crystallized in single phase with orthorhombic structure o-Y123 (see Fig. 2a), belonging to the space group $Pmmm$. These results are agreed with the standard cards of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (JCPDS card 39-1434).

The calculated unit cell lattice parameters of pure Y123 are $a = 0.3827(1)$ nm, $b = 0.3881(2)$ nm, $c = 1.1684(2)$ nm. These crystallographic parameters are correspondent with the published previously [16].

In the case of the nanocomposite Y123, the result indicated that the Y123 ceramic phase was retained (Fig 2b). Thus, the polymer did not destroy the superconducting phase.

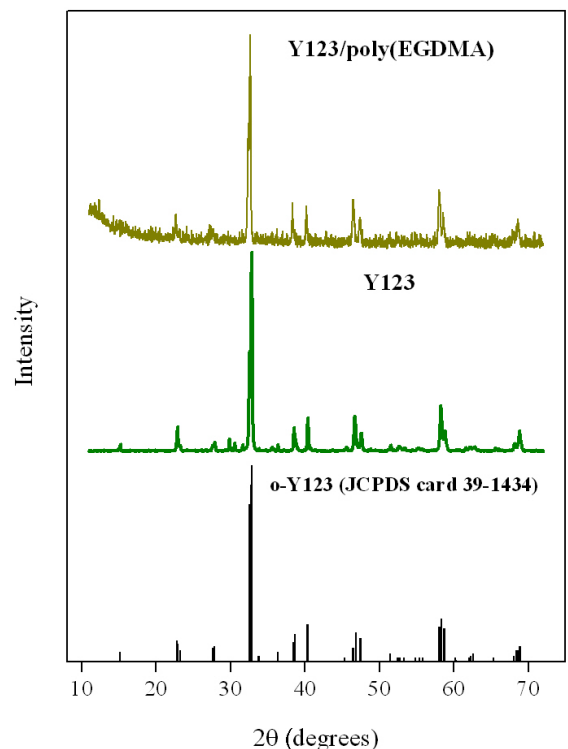


Fig. 2. XRD patterns for pure Y123 and Y123/poly(EGDMA) nanocomposite.

The average sizes of the crystallites [coherent scattering regions (CSR)] were calculated from the obtained powder patterns using the Scherrer equation [17]:

$$D = K\lambda/\beta \cos\theta,$$

where D is the diameter of the scattering crystallites (nm); λ , the X-Ray wavelength ($\lambda_{Cu} = 0.15406$ nm); K , a constant depending on the method by which the line width and crystal shape was determined (in this instance $K = 0.9$); β , the peak width at half-height of the reflection maximum (deg); and θ , the diffraction angle (deg).

The true integrated peak width was calculated using the Warren formula:

$$\beta^2 = \beta_{exp}^2 - \beta_{tr}^2,$$

where β_{exp} is the full peak width at half-height of the maximum (FWHM) (deg) and β_{tr} , the broadening of the diffraction line determined by the instrument or instrumental broadening (deg) obtained from the diffraction pattern of a standard. The crystalline Si (JCPDS card 89-2955) was used as the standard.

The calculated crystallite size of the pure Y123 is above 100 nm, whereas, for composite Y123 is ~90 nm. The formation of Y123 nanocomposites is confirmed.

Group of composites based on Y123 superconducting ceramic and polymers may be singled out of the polymer-ceramic composite materials. They are so-called 0-3 and 3-3 composites. In the 0-3 nanocomposites individual granules of superconducting ceramic are in a polymer matrix. In the 3-3 nanocomposites both superconducting ceramic and polymer form 3D structures. Figure 3 illustrated of the schematic representations of polymer nanocomposites with 0-3 (A) and 3-3 (B) connectivity.

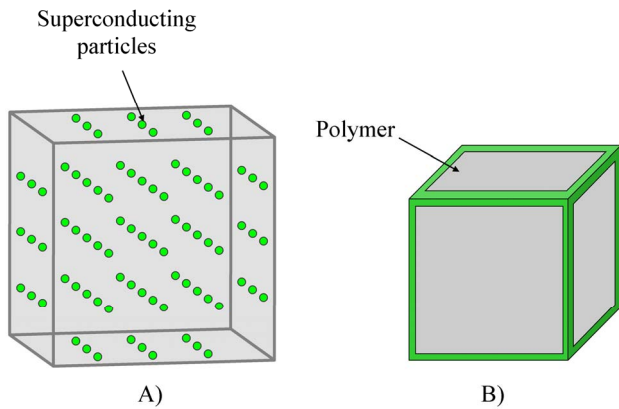


Fig. 3. Schematic representations of polymer nanocomposites with 0-3 (A) and 3-3 (B) connectivity.

Organic nanocomposites based on the Y123 superconducting ceramic were obtained after impregnation and polymerization. They were tested for stability to action of steam at elevated temperatures by controlling changes of magnetic and electrical properties and phase composition of samples before and after action of steam at 24°C for 5 days.

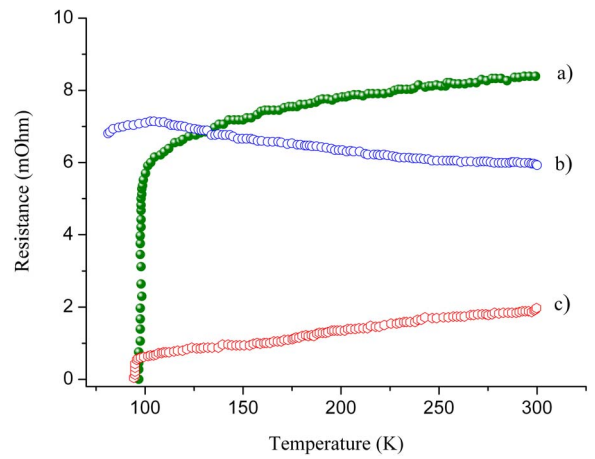


Fig. 4. Temperature dependence of electrical resistance for 3-3 composite based on Y123 (a) and 3-3 composite based on the Y123 ceramic after (b) and before (c) steaming at 100°C for 30 min.

The electrical and magnetic properties of the 3-3 nanocomposites obtained by us practically were the same as those of the initial HTSC ceramic (Fig. 4a). The samples of nanocomposites demonstrated an abrupt superconducting transition at $T_s = 94$ K. This indicates that the bonds between individual granules of superconductor were not broken by action of the organic phase. Action of steam at 100°C for 30 min on the 3-3 nanocomposite Y-123 ceramic impairs the resistive characteristics of a sample, and there is a tendency for transition to the superconducting state at a temperature below the boiling point of liquid nitrogen (Fig. 4b, 4c).

The 0-3 nanocomposites demonstrated high resistance and somewhat lower paramagnetic signal due to poor contact between the ceramic grains. The $I-V$ curves of the 0-3 nanocomposites also evidenced that there is no ohmic contact (see Fig. 5). One can see that all these curves indicate that current is a nonlinear function of voltage. Generally the $I-V$ curve may be presented as $I = \text{const } U^n$ ($n = 1$ corresponds to Ohm's law). Both non-linearity factor n and resistance grow when the polymer fraction in nanocomposite increases. This fact evidences that contact between grains became poorer. These results are according to [14].

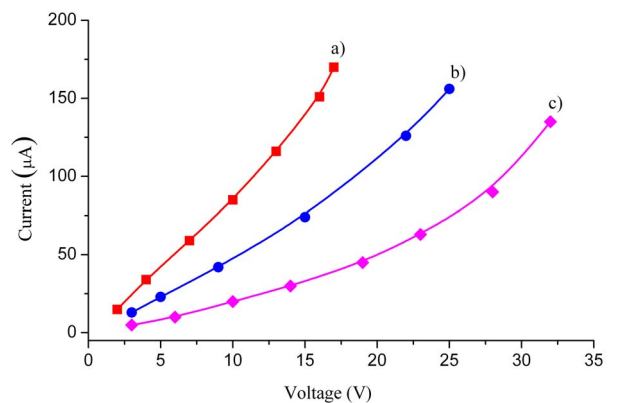


Fig. 5. Volt-ampere characteristics ($I = \text{const } U^n$) of Y123/poly(EGDMA) nanocomposite: a - 80% Y123, $n = 1.18$; b - 77% Y123, $n = 1.29$; c - 75% Y123, $n = 1.93$.

Stability of both 0-3 and 3-3 nanocomposites to degradation was much higher than that of the initial HTSC phases. After 5 days stay in steam at 24°C the initial HTSC yttrium ceramic had paramagnetic signal half as much as the initial one, while the intensity of paramagnetic signal of the 0-3 nanocomposite decreased by 5% and that of the 3-3 nanocomposite remained the same. Besides, it was determined that nanocomposite stability essentially depends on the quality of the initial HTSC ceramic.

Thus rate of destruction of the superconducting phase considerably decreases after ceramic sample impregnation with poly(EGDMA) because the polymer adds stabilization properties to the superconducting ceramic. By filling pores in ceramic, the polymer prevents for water penetration into the ceramic bulk. It should be noted that, by filling the spaces between grains, an organic matter does not reduce the superconducting properties and does not affect the ceramic structure. Impregnation of superconducting ceramic samples with an organic polymer increases their stability and does not effect considerably on their temperature of transition to the superconducting state.

Application of poly(EGDMA) for production of composite leads (in the cases of both the Y-123 HTSC ceramics) to stabilization of superconducting properties of the above compounds. So, one can say that HTSC organic composites are rather promising materials to be applied for technical purposes. In this case, the mechanical properties of the obtained 0-3 and 3-3 nanocomposites are much better than those of the initial ceramic.

This is due to the fact, that the introduction of organic polymer is made into already prepared HTSC ceramics. In this case, the superconducting phase structure is not destroyed.

An organic polymer fills the spaces (pores) between granules of the HTSC phase thus preventing penetration of water into the ceramic bulk. It should be noted that polymer and the HTSC phase must not interact with decreasing the amount of oxygen in the latter. A question as to whether or not an additive makes stabilizing effect depends on the features of interaction between the HTSC phase and dopant.

IV. CONCLUSIONS

We synthesized nanocomposites based on the HTSC pure Y123 ceramics and of Y123/poly(EGDMA).

Degradation under action of a humid environment and steam is investigated for polymer-ceramic nanocomposite materials of two types: the composites where individual granules of superconducting ceramic are in a polymer matrix (0-3 nanocomposites) and those where both superconducting and polymer phases form 3D structures of poly(EGDMA) with Y-123 (3-3 nanocomposites). Improvement of mechanical properties is observed for both types of polymer-nanocomposite materials. It is rather easy to give irregular shape to the materials as well as to provide high stability to action of a humid environment and hot steam. It is determined that the 3-3 nanocomposites completely retain their resistive and magnetic properties (contrary to the 0-3 nanocomposites).

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