Physical-Mechanical Properties of ErBaCuO Superconductors Doped With Gold And Gallium

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Abstract. Physical-mechanical properties of non-doped ErBCO high temperature superconductor ceramics and doped with Ga and Au has been investigated using the complex method of low frequency internal friction and shear modulus measurements in the temperature range 20-700°C. Near 200°C internal friction relaxation maximum and shear modulus defect were found. It is established that the relaxation process is caused by movement of twin boundary, interacted with the oxygen atoms. It was established that activation energy of the relaxation processes is equal to $\sim 0.9\text{eV}$ and the frequency factor to $10^{12}\text{sec}^{-1}$. Doping by gold and gallium significantly increase internal friction temperature spectrum and thermal stability, activation characteristics of relaxation processes, and values of shear modulus and dislocation elastic limit.

1. Introduction

For investigation of the phase state, phase transformation and the physical-mechanical properties of superconducting ceramics the structurally-sensitive method of internal friction (IF) can be used successfully. The anomalous of IF and shear modulus connected with motion of active oxygen atoms in the structure of ceramics, with phase inhomogeneities in the ceramics and with phase transformation in it are revealed by method of IF in the 1-2-3 high temperature superconductor ceramics (HTCS) [1-3]. It’s observed considerable reduction of the value of Young’s module higher $T_c$ caused by the interaction between sound and silt mode of fluctuation of cooper atoms [4].

It is shown [5,6] that energetic conditions of the defects motion can be changed by metal doping, substitutational elements of the lanthanum group or copper mainly in the Cu-O planes. Sharp decrease of shear modulus are revealed in the first case [7]. Variations of the energetic characteristics of the phase transformations and the relaxation and the hysteretic processes were revealed in the second case[8,9].

Characteristics of IF relaxation processes and hysteretic type dispersion of oscillation energy in non-doped HTSC structures connected with twins are discussed in the papers [10-13]. Despite the neumerous work devoted to the study of the properties of YBaCuO HTCS practically haven’t been investigated influence of doping on the structural sensitive IF properties of these materials. Purpose of this work is investigation of the physical-mechanical properties of YBaCuO type ceramics doped with Au and Ga.

2. Experimental Details

The purpose of the present work is to study relaxation and hysteretic type IF and shear modulus of YBCO type ceramics doped by gold and gallium in the range of high temperature (above room
temperature). Measurement of the temperature and amplitude dependence internal friction and shear modulus were carried out at ~ 1Hz frequencies of free torsional oscillations. Measurement were performed in the temperature range 20-700°C and relative values of deformation during oscillations in the range $5 \cdot 10^{-5} \div 5 \cdot 10^{-3}$.

In order to reveal the defects and to study their transformation, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) investigations of the large-grained crystalline $\text{Er}_2\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ superconducting ceramics produced by standard methods [1] were carried out. The SEM observations were conducted directly on the fractures of the bulk samples.

3. Result and Discussion

In Figure 1a, the SEM image of the fracture formed by the refracted and secondary electron beam is shown. As is seen, the crystallites preferably have a shape of the elongated parallelepiped. Mainly, the intercrystallite fractures were observed, however in bigger crystallites a transcryallite fracture was observed as well. In the latter case, a peculiar contrast characteristic of the polysynthetic twins was clearly observed (Figure 1.b). The stacks of the twins are disposed as parallel packets across the crystallites and are enveloped by a shell that caused the contrast characteristic to an amorphous (or at least very disperse crystalline) state. That is why the twins oriented in such a way that the intercrystal fractures are exposed cannot be observed without specific treatment of the sample; for example via bombardment of the surface by the accelerated Ar+ ions (Figure1.c).

The TEM investigations of the samples, thinned by the method of ion bombardment (-1000Å)[14], showed that, practically in each grain of the superconductive orthorhombic phase, a large number of twins and staking faults is observed on the $\{110\}$ crystallographic planes. In the large grains, mostly both twinning systems (110) and (1 $\overline{1}$ 0) or stacking faults as thin twins are observed. Such a case is shown in Figure 1d, where the typical strip-like contrast caused by the stacking faults with the bounding dislocation is seen.

![Figure 1. The structure of YBCO superconducting ceramics bulk samples) SEM image of the fracture; b) trans-cryalline fracture; magnified SEM image of areas B; c) the same area for area A, after bombardment by the $\text{Ar}^+$ ions; d) TEM image of the sample thinned by the $\text{Ar}^+$ ion bombardment](image_url)
In Figure 2 are observed two maxima of high intensity-relaxation \( \sim 180^\circ C \) and non relaxation \( \sim 600^\circ C \) in the internal friction temperature spectra for non-doped ErBaCuO superconducting ceramic. At the 420 and 500\(^\circ\) C temperature, there are wide maxima of high intensity. Relaxation maximum at 180\(^\circ\) C temperature is characterized by 0.9 eV activation energy and \( 1 \cdot 10^{13} \) sec\(^{-1}\) frequency factor.

The temperature spectrum of IF of specimen doped with Au is characterized by changing intensity of maximum at 220\(^\circ\) C, weak intensities of maxima at 420 and 500\(^\circ\) C, high intensity of maximum at 630\(^\circ\) C and also sharp increase of the IF background in the high temperature interval. Their slope are identical with the slope of non-doped specimens. During the experiment were carried out thermal treatment, which doesn’t influence on the intensity of internal friction spectrum. Also the repeated measurement doesn’t influence on IF temperature dependence. These properties are different from the properties of non-doped specimens. Relaxation maximum at 200\(^\circ\) C is characterized comparatively high activation characteristics: activation energy 1.0 eV and frequency factor \( \sim 2 \cdot 10^{13} \) sec\(^{-1}\). Defect of shear modulus are observed at the temperature 200\(^\circ\) C and 600\(^\circ\) C in the specimens doped by gold.
The temperature spectrum of IF of specimen doped with 0.05% Ga is characterized by changing intensity of maximum at 200°C, weak intensities of maxima at 420 and 500°C, high intensity of maximum at 620°C and also sharp increase of the internal friction background in the high temperature interval. Their slope is identical with in slope of high temperature IF background of undoped and Au-doped specimens.

Relaxation maximum at 200°C is characterized comparatively high activation characteristics—activation energy 1.1 eV and frequency factor \( \sim 5 \times 10^{13} \text{ sec}^{-1} \). The intensities of the relaxation maxima decrease with the increase of Ga concentration from 0.1 to 0.15 %, but its temperature and activation characteristics are the same. Practical Ga concentration doesn’t influence on IF in the temperature range 350-650°C. The shear modulus sharply decrease at 220, 500 and 600°C temperatures in Ga-doped specimens. The biggest decrease of shear modulus is observed in the specimens with 0.15%Ga. The repeated measurement doesn’t influence on IF temperature dependence. The shear modulus is reduced by the cycle deformation. Some physical-mechanical characteristics of investigated samples are presented in the Table 1. As it is evident from the Table 1 in comparison with non doped HTSC doping by gold and gallium causes significant increasing values of dislocation elastic limit.

| Specimens | Temperature of measurement \((T, ^\circ \text{C})\) | Activation energy of maxima, (eV) | Frequency factor, \((\text{sec}^{-1})\) | Shear modulus at the room temperature, \((\text{n/m}^2\times10^9)\) | Elastic limit at the room temperature, \((\text{n/m}^2\times10^9)\) |
|-----------|---------------------------------|-------------------------------|-----------------|---------------------------------|---------------------------------|
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\) | 180 | 0.9 | \(1\times10^{13}\) | 1.02 | 4.9 |
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\):Au(0.05%) | 200 | 1.0 | \(2\times10^{13}\) | 1.05 | 5.25 |
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\):Ga(0.05%) | 200 | 1.1 | \(5\times10^{13}\) | 1.15 | 6.9 |
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\):Ga(0.1%) | 210 | 1.2 | \(5\times10^{13}\) | 1.2 | 7.45 |
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\):Ga(0.15%) | 220 | 1.2 | \(5\times10^{13}\) | 1.3 | 8.6 |
| ErBa\(_2\)Cu\(_3\)O\(_7\)\(_x\):Ga(0.15%) | 200 | 0.9 | \(1\times10^{13}\) | 0.95 | 4.3 |
| YBa\(_2\)Cu\(_3\)O\(_7\)\(_x\) |                               |                               |                 |                                |                                |

Study of the IF and shear modulus amplitude dependence show superposition of three different processes. First is in the low range \((\varepsilon<1\times10^{-4})\) in which, IF slightly increase, but the value of shear modulus is practical, the same. In the middle range \((1\times10^{-4}÷5\times10^{-4})\) the maximum of IF and decrease of shear modulus are observed. In high temperature range \((\varepsilon<1\times10^{-4})\) the both characteristics are sharply changed: IF increases exponentially and shear modulus decreases.

Measurement at the fixed temperatures show increase intensity of IF maxima and increase of IF background at high values of oscillations amplitude. It is established, that critical values of oscillations amplitude decreases, with the increase of measurement temperature. The respective changes are represented as the dependence of shear modulus on the amplitude of oscillations, in the amplitude range \(1\times10^{-4}÷5\times10^{-4}\).

In the dislocation string model of Granato-Luke, for undoped specimens, the interaction energy of dislocation with point defects is 0.29eV. After the heating up to the 600°C, its value decrease to 0.32eV. Further annealing, at 400°C for 0.5h, it restores its value to 0.37eV.
It is established, that above 400°C temperature the dependence of IF on the amplitude of oscillation changes. In particular, IF maxima are disappear and value of critical amplitude decrease at which exponential background sharply increase, and simultaneously slope of exponential background decreases. Values of shear modulus and critical amplitude of oscillations increase and intensity of maxima and slope of exponential background decrease for 10-15%, with the doping with Au. For the Au-doped specimens dislocation point defects interaction energy has comparatively high value \( \sim 0.45\text{eV} \). Intensity of maxima and slope of exponential background decrease, with the doping with Ga.

These changes are represented in the specimens, with high concentration of Ga. It is shown, that with the increase of a concentration from 0.05-0.15%. Dislocation point defects interaction energy of increase up to 1.2eV. On the base of determination of frequencies of standard and experimental YBaCuO ceramics specimens of identical size is estimated absolute value of shear modulus. It is shown that with doping values of shear modulus and elastic limit increase.

According to the results of study of real structure of high temperature superconducting ceramics and analysis of relaxation processes parameters. It is proposed that high intensity IF relaxation maximum near 180-200°C caused by twinning dislocation motion at with takes place redistribution of oxygen atoms from \((0,\frac{1}{2},0)\) to \((\frac{1}{2},0,0)\) position.

**Figure 3** Amplitude dependence of internal friction\((Q^{-1})\) and shear modulus \((f^2/f_0^2)\),

- \(Q^{-1}(\varepsilon)\) and \(f^2/f_0^2(\varepsilon)\), 20°C
- \(Q^{-1}(\varepsilon)\) and \(f^2/f_0^2(\varepsilon)\), 60°C
- \(Q^{-1}(\varepsilon)\) and \(f^2/f_0^2(\varepsilon)\), 100°C
- \(Q^{-1}(\varepsilon)\) and \(f^2/f_0^2(\varepsilon)\), 150°C

At temperatures near 600°C, where polymorphic orthorhombic-tetragonal phase transformation take place, exist non-relaxation IF maximum. It can be considered, that maximum is caused by phase transformation. In doped specimens, decrease of IF maxima temperature, may be connected with
internal strain, those are created surrounding doping atoms. Mobility of dislocation origins defects can
decrease, after doping with Au and especially with Ga.

4. Conclusion

Presence of high intensity, obvious amplitude dependences of temperature, the form and intensity of maximum IF at the 180-200°C, and changes its activation characteristics due to doping give foundation, to suppose that origin of these peaks is connected with defects of dislocation origins. Considering the tendency of structure 1-2-3 type ceramic to twinning it is possible to suppose, that relaxation IF and defect of the shear modulus in the area of 180-200°C are caused by motion of the polysynthetic twin grain boundaries which interacted with the oxygen atoms. In the proposed model, increasing of activation energy of relaxation process as result of doping by gallium, is explained by blocking twining dislocation by gallium atoms. It also leads to the increasing of absolute value of the shear modulus and critical amplitude of deformation, and detachment of dislocation from pinning centers and dislocation elastic limit. Increase of the thermal stability of IF characteristics and shear modulus in the specimens doped by gold is connected to formation of the gold protective shell around of particles grains which effectively blocks diffusion of oxygen atoms from volume of particles grain to the grain boundaries direction. Retardation of full dislocation was observed in the doped ceramics. It was revealed in the increase of critical amplitude of deformation in the area of high values of amplitudes oscillation that correlates with increasing values of shear modulus and elastic limit.

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