

Sol–gel synthesis and characterization of superconducting REBa₂Cu₄O₈ (RE = Y, Eu, Gd, Yb and Lu) oxides

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In this study superconducting REBa₂Cu₄O₈ (RE = Y, Eu, Gd, Yb and Lu) cuprates have been synthesized by an aqueous sol–gel method. The superconducting YBa₂Cu₄O₈ (Y-124), EuBa₂Cu₄O₈ (Eu-124), GdBa₂Cu₄O₈ (Gd-124), YbBa₂Cu₄O₈ (Yb-124) and LuBa₂Cu₄O₈ (Lu-124) compounds have been characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), resistivity and magnetic susceptibility measurements. The X-ray diffraction patterns showed that single phase compounds formed in all the cases. The results of resistivity measurements for the REBa₂Cu₄O₈ samples showed that the onset critical temperature of superconductivity is in a good correlation with changes in the orthorhombicity of the RE-124 unit cell and ionic radius of lanthanide ion. However, no correlation between the T_c(onset) of RE-124 superconducting oxides and the superconducting volume fraction was observed.

Key words: REBCO, RE-124, lanthanides, sol–gel preparation, superconducting properties

INTRODUCTION

YBa₂Cu₄O₈ (Y-124), a superconducting compound, is a member of the homologous series of compounds of the general formula Y₂Ba₄Cu_{6+n}O_{14+n} (n = 0, 1, 2) [1–4]. It exhibits a superconducting transition temperature (T_c) at around 79–80 K. The Y-124 phase is thermodynamically stable, isostructural and stoichiometric. All these features make the Y-124 phase very interesting from a theoretical point of view as a model system for testing the general trends of high-temperature superconductors and also in a view of possible applications [5–9].

Recently, the dependence of the magnetic irreversibility field (H_{irr}) on the ionic radius of a rare earth element for REBa₂Cu₄O_{7-δ} (R = Y, Eu, Gd, Yb, Lu) phase has been studied [10]. In this study the authors reported that with a decrease in the ionic radius of the rare earth element, the characteristics of magnetic irreversibility field were clearly enhanced in a monotonic way. Moreover, it was considered that the isovalent rare earth element substitution induced a more homogeneous hole-density distribution along *c* axis, resulting in better H_{irr} characteristics [11, 12]. Although many studies have reported on the correlation between the radius of a rare earth ion and the superconducting transition temperature of YBa₂Cu₄O₈, the dependence of the superconducting volume on the ionic radius of rare earth elements has not been established. However, for such investigations single-phase cationic–stoichiometric samples of extreme phase purity and homogeneity are required [13–17].

In the last decade, the use of high purity oxides for electronic, optical and catalytic applications has gained an increasing importance. In this context, the sol–gel technique [18–20]

has been used for many years. In this study we report the sol–gel synthesis and systematic characterization of the rare-earth substituted superconducting Y(RE)Ba₂RCu₄O₈ (R = Eu, Gd, Yb, and Lu) oxides.

EXPERIMENTAL

A series of acetate–tartrate gel precursor samples for the preparation of the superconducting REBa₂RCu₄O₈ (RE = Y, Eu, Gd, Yb, and Lu) oxides were synthesized by an aqueous sol–gel processing route [21]. Stoichiometric amounts of analytical grade Y₂O₃ or Eu₂O₃ or Gd₂O₃ or Yb₂O₃ or Lu₂O₃, Ba(CH₃COO)₂, and Cu(CH₃COO)₂·H₂O were used as starting materials. First, in the sol–gel process an appropriate amount of RE₂O₃ was dissolved in 200 ml of 0.2 M CH₃COOH. After stirring for 10–15 h at 60–65 °C clear solutions were obtained. Next, barium acetate (Ba(CH₃COO)₂), copper acetate (Cu(CH₃COO)₂·H₂O) and tartaric acid (C₄H₆O₆), all dissolved in small amounts of distilled water, were added to the metal acetate solution with adequate intermediate stirring. Finally, after concentrating for 8–10 h at 65–70 °C in an open beaker the acetate–tartrate solutions turned into blue transparent gels. The obtained RE–Ba–Cu–O gels were dried in air at 80–100 °C. The precursor gel powder was calcined for 10 h at 700 °C in flowing oxygen, reground in an agate mortar, again heated for 10 h at 780 °C, reground intermediately and annealed for 20 h at 780 °C in a flowing oxygen atmosphere at ambient pressure.

The X-ray powder diffraction (XRD) studies were performed on a STOE diffractometer operating with CuKα₁ radiation. The lattice parameters of the synthesized samples were obtained from the diffraction spectra by fitting the peaks of the identified reflections using a least-squares procedure [22]. A scanning electron microscope (SEM) DSM 962 was used to study the

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morphology and microstructure of the ceramic samples. The superconducting properties were obtained by resistivity measurements using a standard four-point technique. T_C values of the superconducting compounds were also obtained from magnetic susceptibility measurements performed in gelatine capsules with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region between 5 and 120 K. From the obtained data on magnetic susceptibility, the volume of the diamagnetic fraction of RE-124 superconducting phases was calculated [23].

RESULTS AND DISCUSSION

In Fig. 1 the XRD patterns of the $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting oxides are presented. The X-ray diffraction patterns of all five samples show that single phase RE-124 compounds have formed. As seen, all single lines may be indexed and no unindexed lines can be observed. The lattice parameters of the synthesized RE-124 samples were obtained from the diffraction spectra by fitting the peaks of the identified reflections. In Table 1 we have given the lattice parameters (a , b , c), cell volume (V) and orthorhombicity, defined as $2(b-a)/(a+b)$, of the $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting cuprates. All the samples are crystallized in the orthorhombic phase, indicating that the systems do not tend towards tetragonality by changing lanthanide ion for yttrium. The determined orthorhombic lattice parameters for the Y-124 cuprate are in good agreement with those reported previously [24–26]. As seen from Table 1, the c axis slightly increases by changing Eu and Gd for Y, and decreases by introducing Yb and Lu. This is in good agreement with the effective (octahedral occupation) ionic radii considerations ($r(\text{Y}^{3+}) = 0.90 \text{ \AA}$, $r(\text{Eu}^{3+}) = 0.95 \text{ \AA}$, $r(\text{Gd}^{3+}) = 0.94 \text{ \AA}$, $r(\text{Yb}^{3+}) = 0.87 \text{ \AA}$, and $r(\text{Lu}^{3+}) = 0.86 \text{ \AA}$). In consequence, there is a small increase in the cell volume as the occupation of yttrium crystallographic position passes from the lower to the upper value of the ionic radius. Contrary, the results in Table 1 also show that the orthorhombicity decreases with increasing ionic radius of RE^{3+} . Fig. 2 shows an almost linear correlation between the orthorhombicity of unit cell of RE-124 and ionic radius of RE^{3+} .

The textural properties of the superconducting powders were investigated by SEM, from which the grain size and typical morphologies were obtained. Scanning electron micrographs

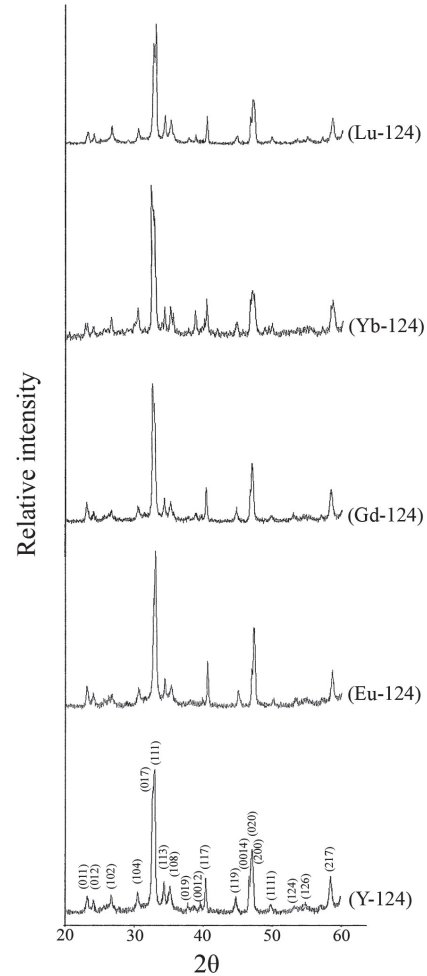


Fig. 1. X-ray diffraction patterns of $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting oxides prepared using the sol-gel technique

of the $\text{REBa}_2\text{Cu}_4\text{O}_8$ samples are shown in Fig. 3. As seen, almost identical microstructures were observed for all RE-124 samples. The obtained micrographs reveal a broad distribution of fine particles with sizes around 1–3 μm . Individual particles are micro-sized volumetric plate-like crystals and they are partially fused to form hard agglomerates.

Table 1. Lattice parameters and orthorhombicity of the superconducting $\text{REBa}_2\text{Cu}_4\text{O}_8$ cuprates

Sample	a , \AA	b , \AA	c , \AA	Volume V , \AA^3	Orthorhombicity
$\text{YBa}_2\text{Cu}_4\text{O}_8$	3.847	3.870	27.239	405.5	0.0060
$\text{EuBa}_2\text{Cu}_4\text{O}_8$	3.859	3.879	27.251	407.9	0.0052
$\text{GdBa}_2\text{Cu}_4\text{O}_8$	3.853	3.874	27.246	406.7	0.0054
$\text{YbBa}_2\text{Cu}_4\text{O}_8$	3.846	3.871	27.231	405.4	0.0065
$\text{LuBa}_2\text{Cu}_4\text{O}_8$	3.844	3.871	27.225	405.1	0.0070

Table 2. Mass susceptibilities, densities and estimated superconducting volume fractions

Sample	d , g/cm^3	100% calculated superconductivity, 10^3 emu/g	Mass susceptibility at 5 K, 10^3 emu/g	Superconducting volume fraction, %
$\text{YBa}_2\text{Cu}_4\text{O}_8$	6.12	13.0094	12.9963	99.9
$\text{EuBa}_2\text{Cu}_4\text{O}_8$	6.59	12.0816	12.0211	99.5
$\text{GdBa}_2\text{Cu}_4\text{O}_8$	6.65	11.9726	11.9403	99.7
$\text{YbBa}_2\text{Cu}_4\text{O}_8$	6.81	11.6913	11.6211	99.4
$\text{LuBa}_2\text{Cu}_4\text{O}_8$	6.83	11.6570	11.6336	99.8

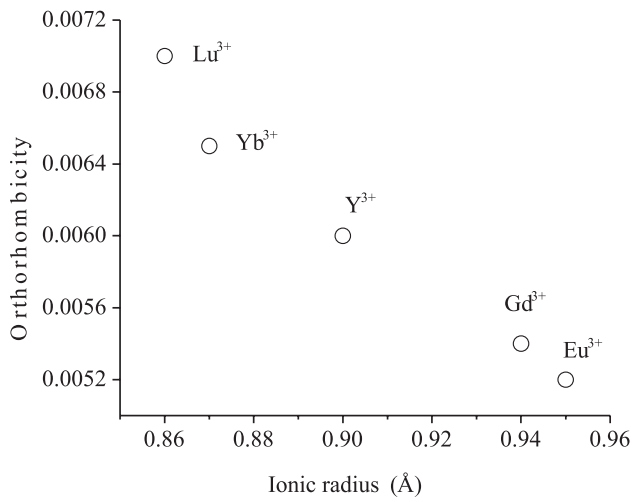


Fig. 2. Correlation between orthorhombicity and ionic radius

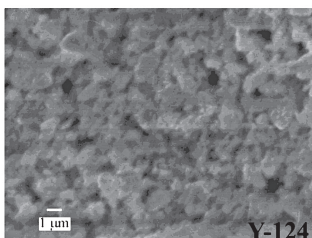
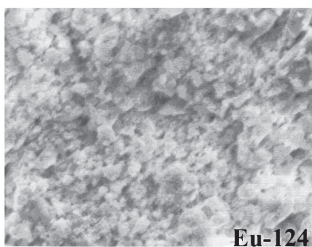
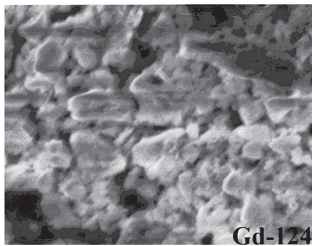
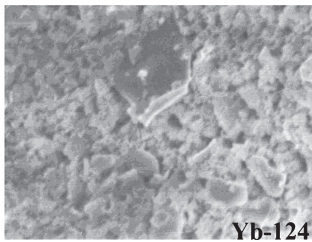
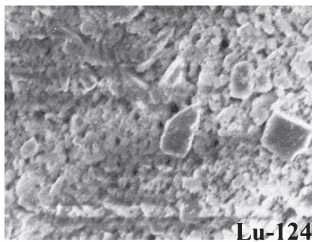


Fig. 3. Scanning electron micrographs of $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting oxides

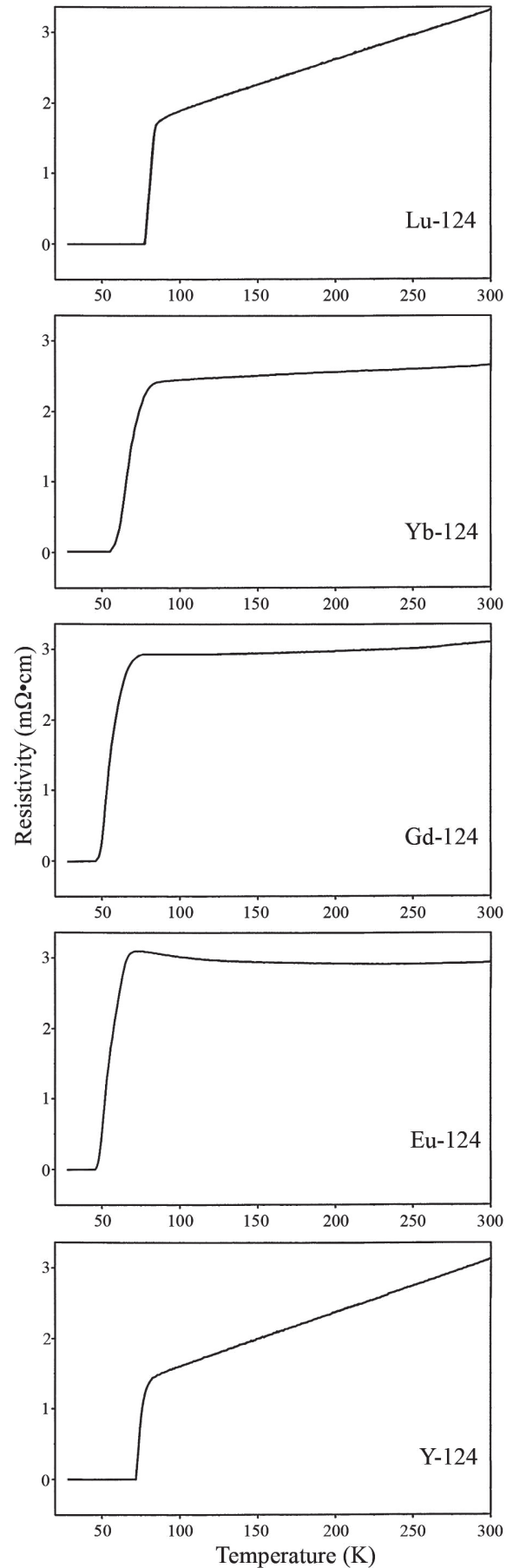


Fig. 4. Resistivity vs. temperature for the superconducting $\text{REBa}_2\text{Cu}_4\text{O}_8$ samples

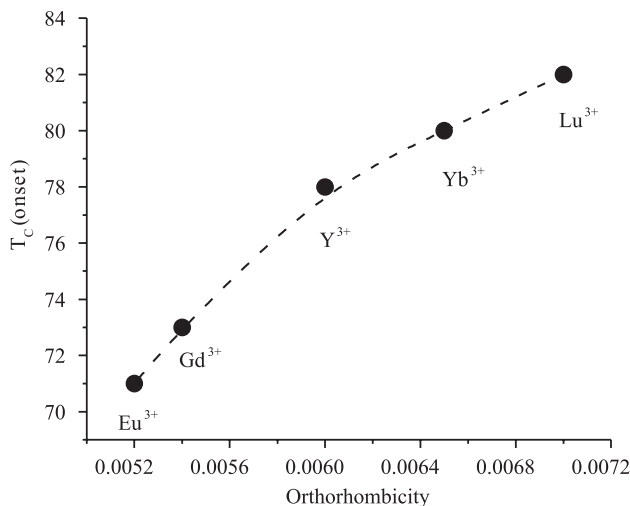


Fig. 5. T_c vs. orthorhombicity of $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting cuprates

Fig. 4 shows the resistivity versus temperature on as-prepared $\text{REBa}_2\text{Cu}_4\text{O}_8$ samples. As seen, all the specimens were found to be superconducting and having $T_c(\text{onset}) = 78$ K (for $\text{YBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 71$ K (for $\text{EuBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 73$ K (for $\text{GdBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 80$ K (for $\text{YbBa}_2\text{Cu}_4\text{O}_8$) and $T_c(\text{onset}) = 82$ K (for $\text{LuBa}_2\text{Cu}_4\text{O}_8$). The relationship between $T_c(\text{onset})$ and orthorhombicity is plotted in Fig. 5. It can be seen that T_c increases with the increasing orthorhombicity. Moreover, the $T_c(\text{onset})$ is correlated very well with the values of the ionic radius of lanthanide ion. As seen from Fig. 6, the T_c increases linearly with the decreasing ionic radius, probably, indicating the highest hole concentration to be in the $\text{LuBa}_2\text{Cu}_4\text{O}_8$ sample.

The same T_c values of superconducting RE-124 compounds were also obtained from the magnetic susceptibility measurements. From the obtained data on magnetic susceptibility, the volume of the diamagnetic fraction of RE-124 superconducting phases was calculated. According to Loureiro et al. [27], 100% superconductivity corresponds to $-1/4\pi d$, if the susceptibility is expressed in emu/g. The densities of the samples were calculated using a simple equation $d = 1.66 \text{ MZ/V}$ [28]. Considering the above-mentioned relations, the superconducting volume fractions of RE-124 compounds were calculated. The results are summarized in Table 2. However, having inspected the figures in Table 2, one can see that the $T_c(\text{onset})$ of RE-124 superconducting oxides does not correlate with the superconducting volume fraction. A random distribution of the results is seen, indicating that the $T_c(\text{onset})$ for the $\text{REBa}_2\text{Cu}_4\text{O}_8$ oxides is independent on the superconducting volume fraction. However, in order to draw such conclusion, two important points should be considered. Firstly, it would be pertinent to compare the obtained results of magnetic susceptibility measurements with the ones using demagnetization corrections. Secondly, the Loureiro's suggested expression is suitable for spherical particles. The SEM micrographs recorded for our RE-124 solids, however, clearly revealed the formation of plate-like crystallites.

CONCLUSIONS

In this study, the sol-gel synthesis and systematic characterization of the rare-earth substituted superconducting

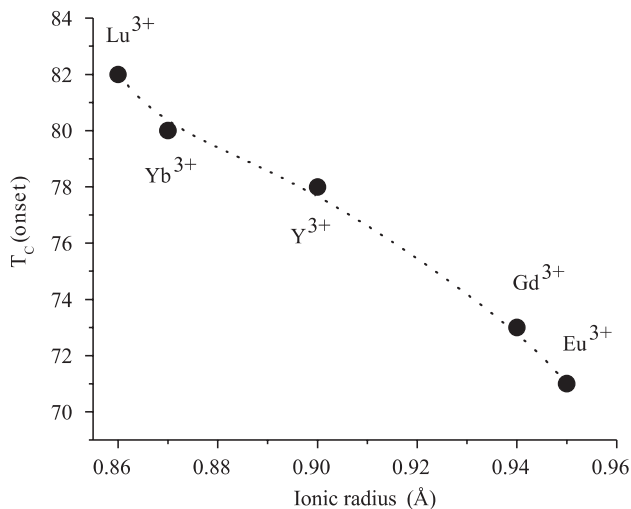


Fig. 6. T_c vs. ionic radius of RE^{3+} ion of $\text{REBa}_2\text{Cu}_4\text{O}_8$ superconducting cuprates

$\text{Y}(\text{RE})\text{Ba}_2\text{RCu}_2\text{O}_8$ ($\text{R} = \text{Eu}, \text{Gd}, \text{Yb}, \text{and Lu}$) oxides have been reported. The X-ray diffraction patterns of all five samples showed that the sol-gel synthesis route gave single phase RE-124 compounds. The determined orthorhombic lattice parameters for the RE-124 superconducting cuprates were in good agreement with those reported previously. The SEM micrographs of RE-124 superconductors showed the formation of plate-like particles with sizes around 1–3 μm . All the specimens were found to be superconducting having $T_c(\text{onset}) = 78$ K (for $\text{YBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 71$ K (for $\text{EuBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 73$ K (for $\text{GdBa}_2\text{Cu}_4\text{O}_8$), $T_c(\text{onset}) = 80$ K (for $\text{YbBa}_2\text{Cu}_4\text{O}_8$) and $T_c(\text{onset}) = 82$ K (for $\text{LuBa}_2\text{Cu}_4\text{O}_8$). The results of resistivity measurements for the $\text{REBa}_2\text{Cu}_4\text{O}_8$ samples showed that the onset critical temperature of superconductivity was in good correlation with orthorhombicity of the RE-124 unit cell and ionic radius of lanthanide ion. However, no correlation between the $T_c(\text{onset})$ and the superconducting volume fraction was observed.

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REBa₂Cu₄O₈ (RE = Y, Eu, Gd, Yb, Lu) SUPERLAIDININKŲ SINTEZĖ ZOLIŲ-GELIŲ METODU IR APIBŪDINIMAS

Santrauka

Šiame darbe zolių-gelių metodu susintetinti vienfaziai REBa₂Cu₄O₈ (RE=Y, Eu, Gd, Yb, Lu) superlaidininkai. Gauti junginiai apibūdinti Rentgeno spindulių difrakcinės analizės bei skleidžiamosios elektroninės mikroskopijos metodais. Nustatyta, kad YBa₂Cu₄O₈ (Y-124) oksido krizinė superlaidumo temperatūra (T_c) yra lygi 78 K, EuBa₂Cu₄O₈ (Eu-124) – 71 K, GdBa₂Cu₄O₈ (Gd-124) – 73 K, YbBa₂Cu₄O₈ (Yb-124) – 80 K ir LuBa₂Cu₄O₈ (Lu-124) – 82 K. Padaryta išvada, kad REBa₂Cu₄O₈ junginių T_c beveik tiesiškai priklauso nuo RE-124 fazių kristalinių gardelių ortorombiškumo bei lantanoidų joninių spindulių. Matuojant tiriamųjų junginių magnetinį jautrį, nenustatyta tiesioginės priklausomybės tarp T_c ir REBa₂Cu₄O₈ superlaidininkų superlaidžios frakcijos tūrio.