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Mössbauer study of the Eu substitution in (Tl,Pb)-1212 superconductors

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Abstract

Eu-substituted $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$, for $x = 0.2$, 0.4, and 0.6 compounds were prepared and investigated by ^{151}Eu Mössbauer spectroscopy, XRD, SEM, EDAX and electrical resistance measurements. The ^{151}Eu isomer shift reflected trivalent Eu in all cases, but it decreased with increasing Eu content. The monotonous change of the principal component, V_{zz} of electric field gradient with Eu content can be attributed mainly to the change in the lattice parameters due to substitution of Eu for Ca. The correlation between the ^{151}Eu isomer shift and the superconducting critical temperature supports the hole filling mechanism (and change in the formal valence state of copper) to explain the suppression of superconductivity upon Eu substitution in this system.

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1. Introduction

The Tl-containing 1223 type high temperature superconductors are in the focus of the interest from the point of view of both science and technology. They are currently among the highest transition temperature bearing superconductors. The partial substitution of Tl by Pb and Ba by Sr results in a stable single phase 1223 compound [1]. It was found, however, that an attempt to incorporate Eu into Tl-containing 1223 superconductor results in the preferential formation of Eu-containing 1212 phase [2].

Mössbauer spectroscopy is a useful tool to study the local electronic and spin density, electric field gradient and lattice vibrations at the site of the Mössbauer active element. Mössbauer studies have contributed to the knowledge about the substitution effects in these types of high temperature superconductors [2–5]. Since ^{151}Eu is a Mössbauer nuclide, one can expect to get information about the substitution effect of Eu into Tl-containing 1212 compound by the help of ^{151}Eu Mössbauer spectroscopy.

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The aim of this work was to investigate the correlation between the superconducting properties and the local electronic density and electric field gradient at the Eu site of the lattice as a function of Eu substitution in $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2$-$(Ca_{1-x}Eu_x)Cu_2O_y$, for $x \leqslant 0.6$.

2. Experimental

2.1. Preparation

The samples were prepared following previously published procedure [1]. The nitrates of calcium, barium, strontium and copper were dissolved in hot distillated water. Eu-metal was dissolved in nitric acid and appropriate amounts were added to the solution containing the alkaline earth and copper nitrates. The mixture was evaporated to dryness and was converted into the oxides by calcination in air at 900 °C for 30 h and cooled down to room temperature in air. After calcination, the required amounts of volatile Tl_2O_3 and PbO were added to the precursor materials by co-milling. The powders were uni-axially compacted at 1 GPa, wrapped in Ag-foil and sintered in flowing oxygen at 925 °C for 0.2 h and at 910 °C for 10 h. Heating rates were 3 K min^{-1} up to 850 °C and 1 K min^{-1} up to 925 °C; cooling rates were 2 K min^{-1} to 910 °C and 5 K min^{-1} to room temperature.

2.2. Methods

^{151}Eu Mössbauer spectra of powdered samples were recorded in transmission geometry with a conventional Mössbauer spectrometer (Wissel). The γ-rays were provided by a $^{151}SmF_3$ source of 3×10^9 Bq activity. The measurements were carried out between 78 K and 300 K in a temperature-controlled cryostat (Leybold, Germany). Isomer shifts are given relative to EuF_3. The ^{151}Eu Mössbauer spectra were analyzed by using the full Hamiltonian of the excited $I_e = 7/2$ and ground $I_g = 5/2$ nuclear spin states by the help of MOSSWINN code [6]. The quadrupole moments of the excited and the ground state were fixed to $Q_e = 1.5 \times 10^{-28}$ m^2 and $Q_g = 1.14 \times 10^{-28}$ m^2.

The instruments for X-ray diffractometry, electron microscopy, EDAX and polarization light optical microscopy measurement have been described elsewhere [7,8]. T_c was measured by electrical resistance measurement with 1 μV cm^{-1} criterion to verify the superconducting state.

3. Results

The X-ray diffraction patterns of $(Tl_{0.58}Pb_{0.4})$-$(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$, $x = 0.2$, 0.4 and 0.6 are shown in Fig. 1. Almost all of the reflections may be assigned to the 1212 structure. Very minute amounts of calcium–strontium cuprate were found as a secondary phase. The parameters of the unit cells are shown in Table 1.

The measured diffractograms are in agreement with those of simulated ones (using Carine Crystallograpy 3.1 software) by taking into consideration the substitution of Eu into Ca site (Fig. 2).

Uniformly distributed well developed crystallites observed by scanning electron (Fig. 3) and polarization light micrography of Eu-substituted materials reflect the appropriately sintered superconducting material. The EDAX-analysis confirmed the composition and showed some small variation of Eu content in correlation with the Ca content.

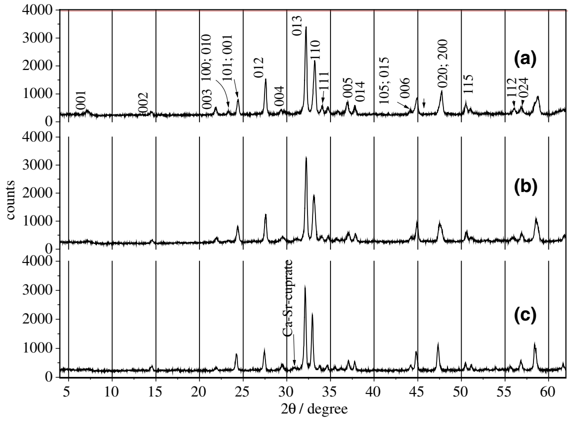

Fig. 1. X-ray diffraction patterns of $(Tl_{0.58}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2$-$(Ca_{1-x}Eu_x)Cu_2O_y$, (a) $x = 0.2$, (b) $x = 0.4$ and (c) $x = 0.6$. Ni-filtered Cu K_α radiation.

Table 1
Composition, lattice parameters and T_c values of $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$—1212 superconductors

Sample	Composition	a/nm	c/nm	V/nm^3	$T_{c\,(0)}$
	$Tl_{0.6}Pb_{0.4}Sr_{1.8}Ba_{0.2}CaCu_2O_y$	0.38103	1.22069	0.17722	98
A	$(Tl_{0.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})_2(Ca_{0.8}Eu_{0.2})Cu_2O_y$	0.38258	1.21148	0.17732	90
B	$(Tl_{0.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})_2(Ca_{0.6}Eu_{0.4})Cu_2O_y$	0.38286	1.21000	0.17604	73
C	$(Tl_{0.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})_2(Ca_{0.4}Eu_{0.6})Cu_2O_y$	0.38413	1.20517	0.17783	[a]

[a] non-superconducting material.

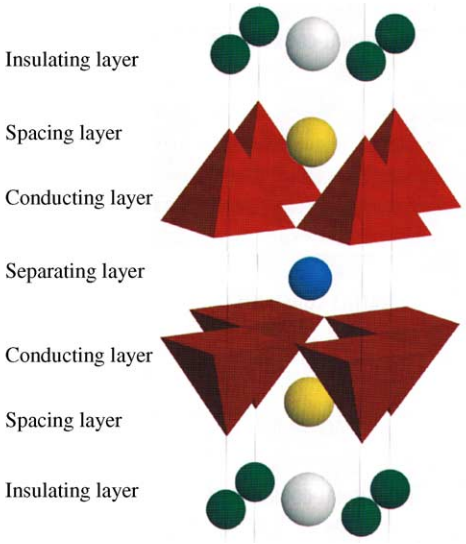

Fig. 2. Structure of a 1212 superconductor. Eu can be substituted for Ca in the separating layer between the Cu–O conducting layers. Cu atoms are in the center of the basal plane of pyramids of the conducting layers. In the spacing layer Ba atoms are shown. Oxygen atoms are situated both in the corners of the pyramids and in the insulating layer, surrounded by Tl atoms.

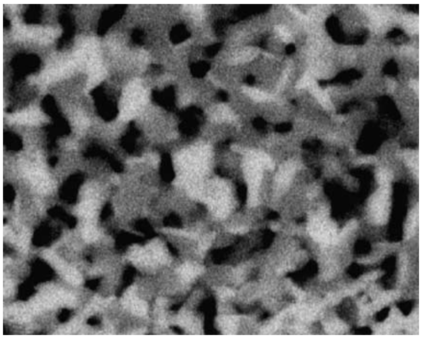

Fig. 3. Secondary electron image, reflecting only the morphology, of the $Tl_{0.6}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_{0.4}Eu_{0.6}Cu_2O_y$ sample.

The dependence of $T_{c(0)}$ on the Eu content for $x = 0.2$ and 0.4 is shown in Table 1.

As Fig. 4 illustrates, the isomer shifts of ^{151}Eu Mössbauer spectra of all samples, recorded in a wide velocity range, undoubtfully show that no Eu is in 2+ valence state (since no line can be found with isomer shifts between −13 and −11 mms^{-1} [9]). At the same time, the isomer shift values of the spectral lines are in the range reflecting the oxidation state of +3 for Eu [9] in these Eu-substituted Tl,Pb-1212 cuprates.

Fig. 5 shows the room temperature ^{151}Eu Mössbauer spectrum of a $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2$-$(Ca_{1-x}Eu_x)Cu_2O_y$ sample recorded in narrower velocity range for higher resolution. The shape of this spectrum is typical of all samples.

The ^{151}Eu Mössbauer spectra of samples exhibit a broad slightly asymmetric envelope. This envelope can be decomposed into eight lines taking into consideration the quadrupole interactions between the Eu nucleus and the electrons. The

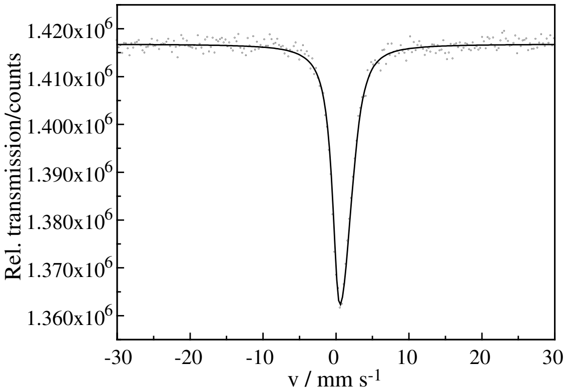

Fig. 4. Room temperature Mössbauer spectrum of a $Tl_{0.6}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_{0.4}Eu_{0.6}Cu_2O_y$ sample recorded in a wide velocity range.

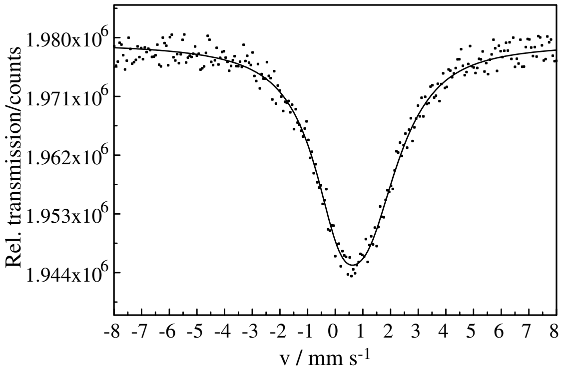

Fig. 5. Room temperature Mössbauer spectrum of a $Tl_{0.6}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_{0.6}Eu_{0.4}Cu_2O_y$ sample.

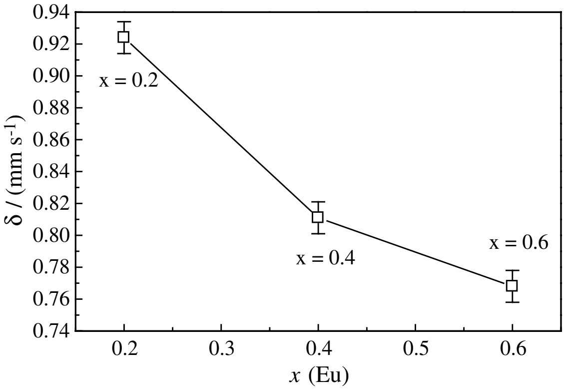

Fig. 6. ^{151}Eu isomer shift vs. the Eu-content of the $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$ samples.

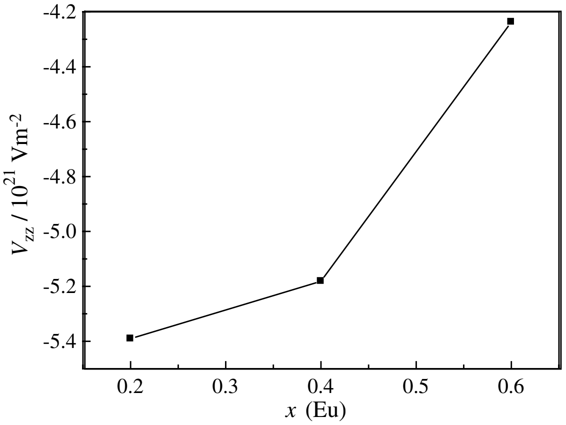

Fig. 7. The change of the principal component of the electric field gradient (V_{zz}) with the Eu-content of $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$.

evaluation of the Mössbauer spectra gives the isomer shift and the principal component of the electric field gradient (V_{zz}) and the asymmetry parameter ($\eta = (V_{xx} - V_{yy})/V_{zz}$). The Mössbauer parameters are shown in Table 2.

No changes were observed in the ^{151}Eu spectra of the samples recorded at lower temperature (up to 78 K) besides the regular second order Doppler shift.

The ^{151}Eu isomer shift decreases with the Eu concentration as depicted in Fig. 6. However, all isomer shift values remain within the interval characteristic of oxidation state of +3 for Eu.

This change in the isomer shift reflects an increase of the 4f-electron density at the site of Eu. This can be interpreted as that the oxidation state of Eu is shifted from +3 toward +2 when an increasing amount of Eu^{3+} substitutes for Ca^{2+} in the lattice of Tl-1212 compound.

V_{zz} increases monotonously with increasing Eu content as shown in Fig. 7. Simultaneously, the almost linear increase of η was observed with the Eu content (Fig. 8).

We have found a linear correlation between V_{zz} and lattice parameter c as shown in Fig. 9. In order to explain the observed changes in the V_{zz} and η with the Eu content, we have developed an evaluation method for the calculation of components of the electric field gradient tensor based on the point charge model. The atomic positions in the unit cell

Table 2
The Mössbauer parameters of Eu-substituted $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$—1212 superconductors

x	0.2	0.4	0.6
δ/(mm s^{-1})	0.924 ± 0.011	0.811 ± 0.012	0.768 ± 0.012
V_{zz}/(10^{21} V m^{-2})	−5.390 ± 0.099	−5.180 ± 0.093	−4.230 ± 0.087
η	0.456 ± 0.043	0.618 ± 0.039	0.761 ± 0.048

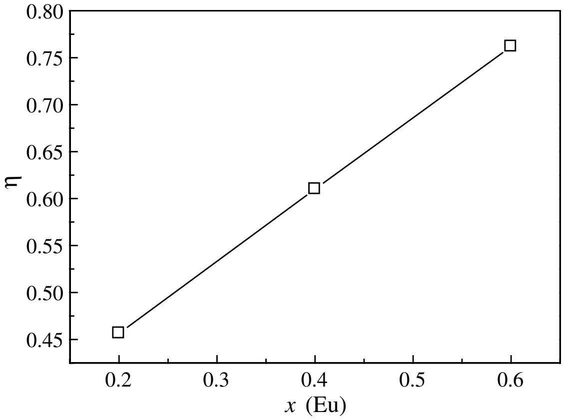

Fig. 8. The asymmetry parameter η vs. Eu content curve of the samples $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$.

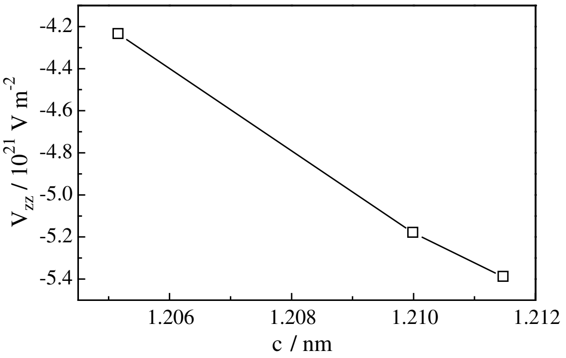

Fig. 9. The V_{zz} vs. lattice parameter c curve of the samples $(Tl_{0.6}Pb_{0.4})(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$.

and the charges of the atoms (according to valence states required by the stochiometry) were taken into consideration in the neighborhood of a central Eu-atom up to 50 unit cells in all directions. The relative atomic positions of a 1212 unit cell was obtained from the work of Putilin et al. [10]. Our calculation used the cell parameters obtained from the evaluated XRD-data.

The values of the components of V_{zz} tensor [11] were calculated for the statistical distribution of atoms supposedly corresponding to $(Tl_{0.6}Pb_{0.4})$-$(Sr_{0.9}Ba_{0.1})_2(Ca_{1-x}Eu_x)Cu_2O_y$, for $x = 0.2$, 0.4, and 0.6 with homogeneous distribution of Eu.

The result of this calculation for the dependence of V_{zz} on Eu content is in fairly good agreement with the experimental results ($V_{zz}/(10^{20}\ \mathrm{V\ m^{-2}}) = -6.91$, -6.40 and -5.28 for $x = 0.2$, 0.4 and 0.6, respectively, without taking into consideration the Sternheimer factor). This indicates that the point charge calculation may be suitable for the rough description of the trends in the electric field gradient at the Eu site in these cases. As the trend of change in the V_{zz} can be satisfactorily modeled simply by taking into account only the change in the lattice parameters due to Eu substitution, this latter change seems to be the main cause of the dependence of V_{zz} on the Eu concentration.

Since we can obtain a nearly linear correlation between the ^{151}Eu isomer shift and the T_c it is plausible to assume that the increase of the 4f electron density of the Eu (reflected by the decrease in the isomer shift) and the decrease of the transition temperature can have a common origin, when the hole filling mechanism is mainly responsible for suppression of the superconductivity, similarly to that observed when Pr was substituted either for Eu or Ba in $Eu_{1-x}Pr_x$-$Ba_{2-y}Pr_yCu_3O_{7-d}$ [12]. Nevertheless, the changes in the lattice parameters (Table 1) can have their own contribution to the decrease of the T_c. In the case of Pr^{3+} substitution for Ba^{2+} in the 123 system the considerable increase of the population of antichain O(5) oxygens has a major contribution to the charge compensation [13]. In the present case, however, changes in the composition (oxygen stoichiometry and defects in the Tl layer) can hardly compensate for the extra charges when a substantial amount of Ca^{2+} is replaced by Eu^{3+} because the 1212 structure is still preserved. Therefore, it appears that there is some decrease in the oxidation state of copper in the Eu substituted sample as compared to the Eu-free one. Consequently, our experiment can indicate the existence of copper of variable oxidation states in the 1212 type superconductors.

Acknowledgments

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