^{119}Sn AND ^{151}Eu MÖSSBAUER STUDY OF $EuBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ PEROVSKITES

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Eu and Sn Mössbauer spectroscopy was used to study $EuBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ metallic oxides. The spectra are characteristic for Eu^{III} and Sn^{IV} states in all cases. The existence of at least two different Sn states was determined by decomposition of the Sn Mössbauer spectra. These Sn sites can be associated with nonequivalent Cu sites replaced by Sn atoms in the perovskite type lattice. Anomalous changes were observed in the isomer shifts and area fractions in the spectra measured at room temperature and at 77 K. It can be interpreted assuming low temperature phase transformation and phonon softening. Time dependent changes were found in the Sn spectra recorded at 77 K in the case of highest Sn concentration. The observed changes are consistent with a transitional stage of the low temperature phase transformation.

Introduction

High-T_c superconductivity has already been found in case of several metallic oxide materials [1-3]. A specially high T_c could be observed in the $EuBa_2Cu_3O_{7-y}$ material [1]. The conditions of the sample preparation were found to strongly affect the electronic and magnetic properties of this class of compounds [1,2]. Additionally, the as-prepared superconductors often loose their superconductivity after a certain time [4,5].

In the structure model of these perovskites the position of the rare-earth element (e.g. Eu) was found to be between CuO_{2+y} layers [6]. Only very slight differences could be observed in the X-ray diffraction patterns due to the modification of preparation circumstances of the same sample [1].

It is possible to get informations about the surroundings and states of the atoms through the hyperfine interactions by means of Mössbauer spectroscopy by replacing Eu, Fe, Co, and Sn atoms into superconducting cuprates.

In our previous Mössbauer study of $EuBa_2Cu_3O_{7-y}$ perovskite [7] we found time dependent changes in the Eu Mössbauer spectra recorded at 76 K. In order to better understand this behaviour, we replaced

the Cu atoms partially by Sn atoms.

The aim of the present work was to obtain information about the state of incorporated tin and europium atoms and its dependence on temperature and time, in $EuBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ (x=0.05, 0.10, 0.20) tripled perovskite by the help of Eu and Sn Mössbauer spectroscopy.

Experimental

Samples of $EuBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ with x=0.05, 0.10 and 0.20 were prepared by carefully mixing and sintering Eu_2O_3, $BaCO_3$ CuO and SnO_2 at 920±20 °C for 14 h in air and cooled slowly to room temperature. The reacted powders were annealed at 420±10 °C for 4 h in air. These powders served as samples for Mössbauer measurements.

Electric resistivity measurements were also carried out by conventional four-point technique.

X-ray diffraction and scanning electron microscopy characterisation showed that these samples could be considered as homogeneous, well sintered, single phase systems with orthorombic structure.

The powdered samples of equal surface densities were dispersed into paraffin for the Mössbauer measurements. Transmission spectra of ^{151}Eu and ^{119}Sn were taken at room temperature and at around the temperature of liquid nitrogen. A temperature-controlled cryostat (Leybold) was applied for the low temperature measurements. 10^9 Bq activity $Ca^{119}SnO_3$ source as well as 10^{10} Bq $^{151}SmF_3$ source provided the γ-rays. Isomer shifts are given relative to the sources.

The evaluation of the Mössbauer spectra were carried out by least-square fitting of lines.

Results and discussion

Fig. 1 shows ^{151}Eu Mössbauer spectra of $EuBa_2Cu_3O_{7-y}$ sample recorded at room temperature (a), and at 76 K immediately after the preparation (b) and four weeks later (c). It represents two different

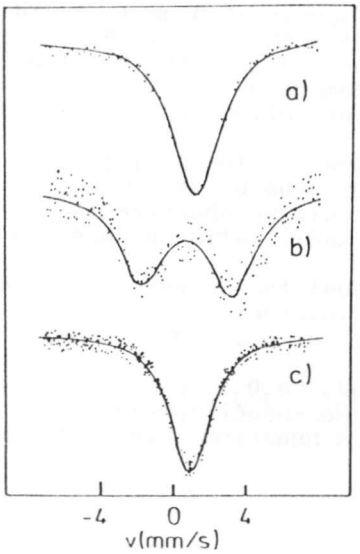

Fig. 1. ^{151}Eu Mössbauer spectra of $EuBa_2Cu_3O_{7-y}$ sample recorded at room temperature (a) and at 76 K immadiately after the preparation (b) and four weeks later (c).

kind of changes in this perovskite:

i.) A time dependence of Eu state. The spectrum in Fig. 1/b (representing two unusual Eu states) can be associated with a metastable state in which electron hopping process takes place [7].

ii.) An anomalous temperature dependence of the isomer shift. Comparing the isomer shifts measured at room temperature and at temperature of liquid nitrogen we found a significant difference opposite to the temperature shifts. It reflects different chemical states of Eu atom at 300 K and at 76 K. Consequently, this anomalous change (which could be reproduced on several samples) indicates a low temperature phase transformation (similar to that found in the case of T_c of 40 K superconductors [9]).

Table 1.
Some Mössbauer parameters of $EuBa_2(Cu_{1-x}Sn_x)O_{7-y}$

Mössbauer source	x	Measuring temperature °C	Isomer shift mm/s	Quadrupole splitting mm/s
^{151}Eu	0	300	0.81	
^{151}Eu	0	76	0.74	
^{151}Eu	0.05	300	0.805	
^{151}Eu	0.05	77 K	0.73	
^{119}Sn	0.20	77 K	0.03 0.14	0 0.75

Similar behaviour could be observed in the ^{119}Sn Mössbauer spectra of $EuBa_2Cu_{2.9}Sn_{0.1}O_{7-y}$ metallic oxide, too.

In the $EuBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ type compounds the Sn can occupy both Cu sites. It is in accordance with the optimal decomposition of Sn spectra (Fig. 2) which resulted in three lines. From these lines the outermost ones proved to be a quadrupole doublet [8] representing Sn atoms being in Cu(1) sites of the perovskite lattice. The central singlet is attributed to Sn atom in Cu(2) position.

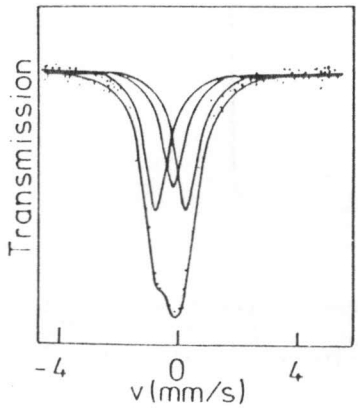

Fig. 2. ^{119}Sn Mössbauer spectra of $EuBa_2(Cu_{0.8}Sn_{0.2})_3O_{7-y}$ sample recorded at 77 K.

Both isomer shifts in ^{119}Sn spectra indicates Sn^{IV} valence states.

The temperature dependent changes in the line positions also support the existence of the low temperature phase transformation. Our conclusion is in fair agreement with that of Dunlap et al. [9] who found similar phenomena in case of a superconducting compound of $(La_{1.85}Sr_{0.85})(Cu_{0.95}Sn_{0.05})$.

The area fractions of ^{119}Sn spectra exhibited an anomalous temperature dependence. It can be understood by supposing a decrease in the Debye temperature at 77 K. It can be considered as a phonon softening which was also found by others [9,10] in superconducting materials.

We observed also metastable states in $EuBa_2Cu_{2.4}Sn_{0.6}O_{7-y}$ cuprate by ^{119}Sn Mössbauer spectroscopy [8]. This observation could be reproduced. Results of such a reproduced experiment are illustrated in Fig. 3, which shows the changes in the Sn Mössbauer spectra (recorded at 77 K) taken 12 h, 24 h, 36 h, and 48 h after a resintering process. No similar changes could be observed at room temperature. The time dependent changes of the Mössbauer parameters can be seen in Fig. 4.

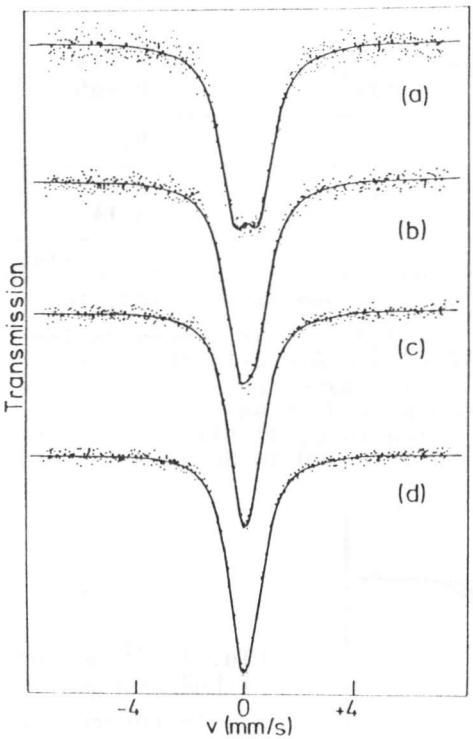

Fig. 3. ^{119}Sn Mössbauer spectra of the resintered $EuBa_2Cu_{2.4}Sn_{0.6}O_{7-y}$ recorded at temperature of liquid nitrogen 12 h (a), 24 h (b), 36 h (c), and 48 h (d) after the resintering of sample (920 ^{o}C/14h + 420 ^{o}C/4h).

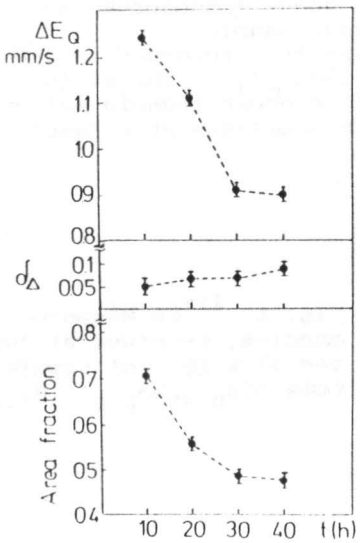

Fig. 4. Time dependence of line positions and area fractions of ^{119}Sn Mössbauer doublet lines after the resintering of sample $EuBa_2(Cu_{0.8}Sn_{0.2})_3O_{7-y}$.

Additional phases (e.g. SnO_2) can be excluded based on the consideration of the corresponding X-ray results as well as the carefully evaluated Mössbauer spectra.

To explain our findings a model was proposed involving an extraordinary tin position near to the Eu atom (Fig. 5) [8]. The time dependent changes are consistent with the consideration that the extraordinary Sn atoms at 77 K are in a transitional stage of low temperature phase transformation and the change of Mössbauer parameters (Fig. 3 and Fig. 4) show that these extraordinary tin atoms gradually occupy the regular Cu(2) sites [8].

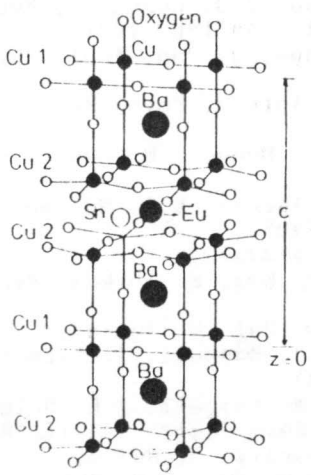

Fig. 5. Structure model of $EuBa_2(Cu_{1-x}Sn_xO_{7-y})$ perovskite. Metastabil Sn position assumed at temperature of liquid nitrogen in $EuBa_2(Cu_{0.8}Sn_{0.2})_3O_{7-y}$ is included. Regular Cu(1) and Cu(2) positions can be replaced by Sn atoms.

The time dependent changes of parameters are consistent with the consideration that the extraordinary tin atoms at 77 K are in a transitional stage of a low temperature phase transformation.

Eu^{III} state could be detected in each sample.

Fig. 6 shows the ^{151}Eu Mössbauer spectra, recorded at 300 K (a) and at 77 K (b), of sample of $EuBa_2Cu_{2.9}Sn_{0.1}O_{7-y}$. The evaluations confirmed the existence of low temperature phase transformation, indicating anomalous changes in the line positions as a function of temperature.

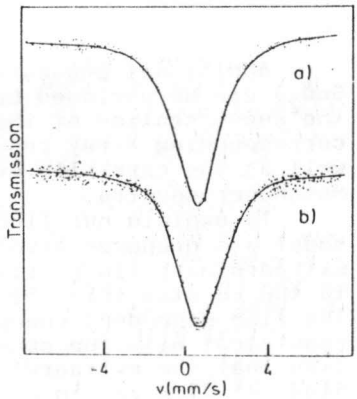

Fig. 6. ^{151}Eu Mössbauer spectra, recorded at 300 (a) and 77 K (b), of sample of $EuBa_2(Cu_{0.95}Sn_{0.05})_3O_{7-y}$.

The line width of the ^{151}Eu spectra increased with increasing Sn content of the samples. It can be explained in terms of modified quadrupole interaction influenced by tin atoms.

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