X-Ray Characterization of La – Sr – Cu – O System

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The high-temperature (38 K) superconducting La – Sr – Cu – O sample was investigated by X-ray diffractometry with diffracted beam monochromator. Four phases were identified. It is possible that the interaction between two of them can influence the superconducting properties of the sample. The EPMA analysis revealed the precipitates enriched by Sr up to 97%. The compositions of the matrix and the area with excess of Cu were estimated. The correlations between X-ray diffraction and EPMA results are discussed.

I. Introduction

The search for high-temperature superconducting materials is one of the most important tasks of condensed matter physics lately. The identification of the structure and calculation of the lattice parameters could be helpful for explaining superconducting behavior of a sample. The aim of this paper was to examine the structure and composition of the superconducting La – Sr – Cu – O sample ($T_c = 38$ K). Till now some samples with similar composition were investigated by many workers [1–3]. The very precise X-ray diffraction methods for phases identification as well as for lattice parameters measurements were used. The composition of the sample in the different areas detected by X-ray wavelength dispersive analysis were compared with structural investigation results.

II. Sample Preparation

The sample was prepared by solid state reaction. The appropriate amounts of La$_2$O$_3$, SrCO$_3$, and CuO (purity La$_2$O$_3$ - 99.9%, SrCO$_3$ - 99.99%, CuO - 99% - the main impurities in CuO were Fe - 0.3%, Cd - 0.2%, Cr - 0.1%, Ni - 0.1%, Mn - 100 ppm) were carefully grind and mixed according to chemical formula La$_{1.8}$Sr$_{0.2}$CuO$_4$ - S. The mixture was annealed at 1000 °C for 6 days with several regrindings during annealing (usually 2 times per day). Afterwards the powder was ground again and pressed into the pellet form. The diameter of the pellet was 15 mm and thickness 3 mm and the applied pressure was $10^7$ Pa. Subsequently the sample was annealed at 1100 °C for 6 h and after this was removed from the furnace and cooled to room temperature. In next step the pellet was sealed in the quartz tube under pressure $1.3 \times 10^4$ Pa (O$_2$) and was annealed at 1000 °C for 24 h.

Accordingly to the resistance and susceptibility measurements the onset of the superconducting transition temperature $T_c = 38$ K was obtained. At higher temperatures the sample had metallic character and resistivity [4].

III. X-Ray Diffraction Measurements

X-ray Siemens Diffractometer Kristalloflex 4 was used for obtained diffraction patterns. The diffractometer was supplied with the precise bent quartz diffracted beam monochromator ((1011) reflection – Johansson type) to cut out the $K_{22}$ line as well as for
increasing the ratio between diffraction lines intensity and background (this configuration increases this ratio 100 times in case of a big fluorescent and incoherent background radiations). As a detector NaI(Tl) scintillation counter with pulse height analyser was used.

The measurements were carried out at temperature 23 °C. The most of lines positions were read from slow-scanned (0.1°/min) diffractogram. In cases of very weak lines, an additional step scanning measurement was made (0.05° steps, 10 min counting time). The intensities were measured using a logarithmic counting ratemeter with statistic error 1% (time constant). The peaks and background intensities were measured directly from the diagram. The relative accuracy of logarithmic counting ratemeter response was lower than 3% for all over the scale. The precision of the goniometer was tested using ultrapure silicon and germanium powder samples.

IV. X-Ray Diffraction Results

The fragment of diffraction patterns is given in Fig. 1. The diffraction lines can be divided into two groups. The first one – strong and very sharp lines and the second one – much more weaker, diffused lines. We were able to index all strong lines using a tetragonal body centered cell. Using the least-squares Cohen method we obtained the following lattice parameters: \( a = 3.7783 \pm 0.0002 \, \text{Å} \), \( c = 13.229 \pm 0.001 \, \text{Å} \) (later called phase A). Phase A was identified as \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), \( x = 0.07 \) (\( \text{K}_2\text{NiF}_4 \) type). The group of weak peaks could be interpreted assuming presence of three additional phases. First of them (phase B) had orthorhombic unit cell and lattice parameters \( a = 3.91 \pm 0.02 \, \text{Å} \), \( b = 4.52 \pm 0.02 \, \text{Å} \), \( c = 13.3 \pm 0.1 \, \text{Å} \). Second of them was identified as \( \text{La}_2\text{O}_3 \) phase (phase C) with cubic unit cell and lattice parameter \( a = 11.320 \pm 0.003 \, \text{Å} \). The third (phase D) was identified as monoclinic \( \text{CuO} \) phase with lattice parameters: \( a = 4.65 \pm 0.02 \, \text{Å} \), \( b = 5.18 \pm 0.02 \, \text{Å} \), \( c = 3.40 \pm 0.01 \, \text{Å} \), \( \beta = 80.31 \pm 0.50 \, \text{°} \). In Tables 1–4 are given measured and calculated interplanar distances and intensities for phases A, B, C, D respectively. The approximate concentrations of the phases B, C, D were 4%, 1.5%, 2% respectively.

V. EPMA Measurements and Results

The investigation of the chemical composition of the precipitates observed and their surroundings in the sample were carried out using one-crystal spectrometer of the Johann type in the electron probe microanalyser JXA-50A (EPMA). For analysis of copper and