XRD-XRF SYSTEM FOR LOCAL ANALYSIS WITH HIGH AREA RESOLUTION

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Abstract

A setup for local XRD-XRF analysis simultaneously with high area resolution and high sensitivity in the same experiment has been developed on the basis of the microdiffractometer PSPC/MDG (Position Sensitive Proportional Counter and X-ray Micro Diffraction Goniometer). The main idea of the presented technique is to get information about phase and elemental composition in the same experiment. In order to record the diffraction pattern in angle interval 0-150^o (2) a curved position sensitive proportional counter was utilized. The fluorescent signal excited in the sample by a primary X-ray beam was measured by a portable energy dispersive detector XR100-CR with 185eV energy resolution. A narrow glass microcapillary of 50μ diameter length was applied as a collimator for narrow X-ray beams production. The efficiency of the presented technique was tested by thin-film microstructure AuTi/SiO_2 experiments and the experiments, carried out while meteorite material's micro inclusions investigations. During the last experiments we detected a homogenous composition region, which corresponded to pure Fe phase.

Introduction

The purpose of the present work is the development and the setting up of the local X-ray diffraction (XRD) [1] and X-ray fluorescence (XRF) analysis [2] in the same experiment with the usage of monocapillaries as collimators for narrow X-ray beams formation. Monocapillaries render the possibility to increase significantly the intensity of the primary beam and reduce the background [3]. The serial microdiffractometer PSPC/MDG (Position Sensitive Proportional Counter X-ray Micro Diffraction Goniometer) of Japan Corporation Rigaku [4] was used as the basic equipment for setting up the technique. Optical system of the microdiffractometer with X-Y-Z motorized sliding stage permit in enlarged view of the measuring area for easy alignment of the sample. Fluorescent signal was registered by means of a portable energy dispersive detector of the AMPTEK Company [5]. These two methods of diagnostics are well combined with each other and make it possible to receive simultaneously the information about the structure as well as the chemical composition of the investigated crystalline materials. The developed technique can be applied for local areas ~ 10 μm of various crystal materials, specifically for microinclusions of various chemical composition, surface pollution, thin-film structures, which have interfaces, inhomogeneous materials, etc.

Experimental equipment

We used serial microdiffractometer PSPC/MDG, which is an attachment to the universal Rigaku Rotaflex D/max-RC diffractometer, for the detection X-ray diffraction pattern from the area of interest of the sample. The distinctive feature of this device is the ability to form a narrow parallel X-ray beam for micro objects investigation and high speed measurement due to using a position-sensitive detector in combination with the powerful X-rays source.

The detection of a X-ray fluorescent signal for an elementary analysis was carried out on the basis of the portable energy dispersive detector XR 100-CR of the USA Company AMPTEK. The equipment is installed on the free left window of the X-ray source and can work independently of the main goniometer, which is installed on the right window of the source.

In order to eliminate parasitic fluorescent emission, which inevitably appears in the diaphragm material of the traditionally used iron collimators, collimators on the basis of glass monocapillaries were used [6, 7]. The main advantage is that intensity of the X-ray beam in the output of such a collimator becomes significantly higher due to the presence of an additional component caused by the beam mirror reflection from the inner wall of the glass monocapillary [8]. The diameter of the monocapillary is 50 μm.

The optical scheme of the technique for conducting local XRD and XRF analyses in the same experiment is presented on Fig. 1.

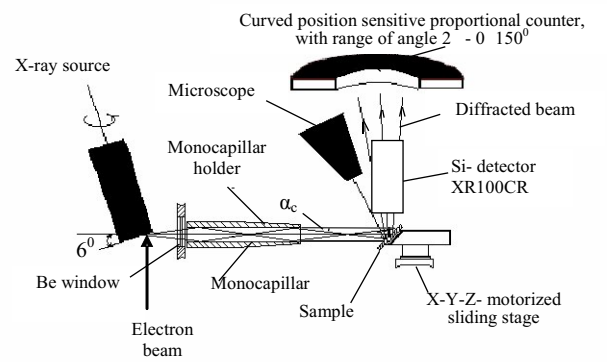

Figure 1. The optical scheme of the technique.

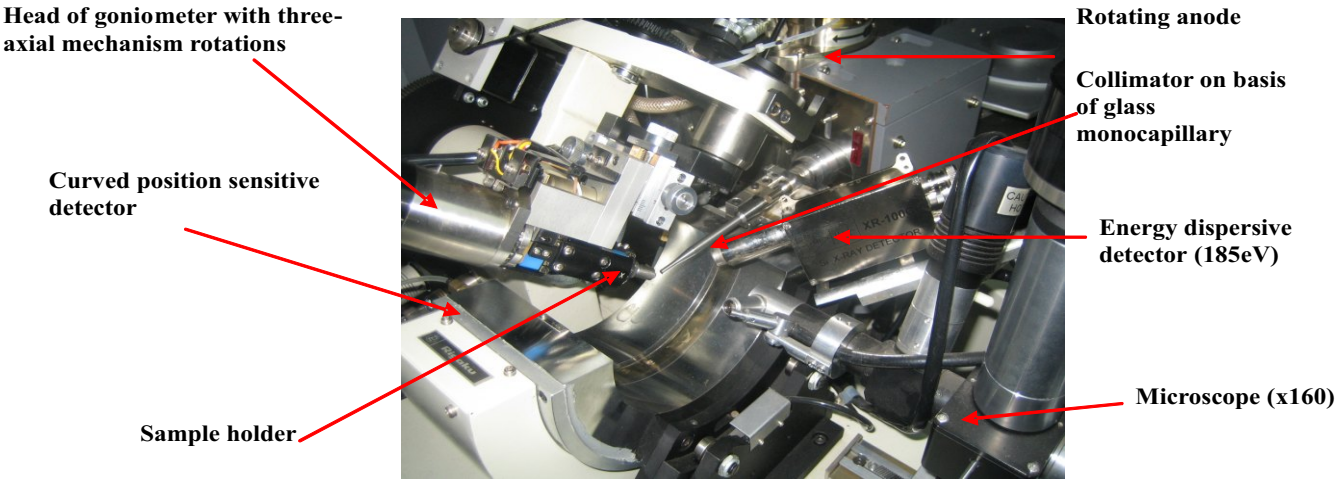

Figure 2. Photo of the microdiffractometer PSPC/MDG and energy dispersive detector XR-100CR.

An X-ray beam from the powerful 12kW source (Cu-K , E = 8,86 keV; Mo-K , E = 20 keV) falls on the input aperture of the monocapillary, passes through it and gets to fall on the sample. The diffraction pattern from the sample is registered by the curved position sensitive proportional counter in the range of 0-150 2 .

The treatment of the recorded diffraction patterns for performing phase analysis is realized with standard programs, which are attached to the microdiffractometer. The calibration of the true position of diffraction lines by 2 angle was performed using standard NIST SRM640c (silicon powder).In order to register the maximal number of diffraction reflexes (the presence of texture, monocrystal impurity) the sample holder can be rotated to three , , angles.

Simultaneously with the recording of the diffraction pattern, the fluorescent signal, excited in the sample by the characteristic line of the incident X-ray beam transmitted through the monocapillary, was registered. The fluorescent spectrum was registered by an energy dispersive detector, which was mounted with a specially produced tripod and installed at the distance of 100 mm from the sample (Fig.2). The distance from the input aperture of the counter to the sample is selected in a special way, in order to allow recording the diffraction pattern. The intensity of the fluorescent signal can be varied changing the power of the X-ray source in the range from 200W to 12kW. The fluorescent signal was recorded with a multichannel analyzer, connected with the computer through a standard port. The spectrum treatment for elemental composition definition was performed with the usage of XRF-FP program package [9].

XRD and XRF technique tryout on the test sample of the microstructure Au,Ti//Si(100)

XRD and XRF technique was tried out on a test sample Au,Ti//Si(100). This structure was produced by the method of optical lithography with preliminary metal evaporation on silicon bottom layer, applying method of high-frequency magnetron spraying of titanic and golden targets. The thickness of applied layer is 70 nm. These structures are used as connectors of the lead wires for micro- and nanostructures. Sample's image, got by dint of scanning electron microscope JEOL, is shown in Fig. 3.

The experiment was performed in such a way that the X-ray beam falled on the 80 μm wide metal lane in one case and in the region outside the lane (pointed with the arrow on Fig. 3) in the other case. The adjustment for the investigated area was performed manually using the microdiffractometer optical microscope and motion of the sample holder. For diffraction, the emission of the copper anode was used. The diameter of the incident beam on the local region formed by the 50 μm diameter glass monocapillar was 55 μm. The recording time of diffraction pattern was 30 minutes. Measurements were carried out with fixed angles of the three-axis rotational mechanism.

/ 2 scan of the test sample is presented on the Fig. 4. On the diffractogram there are only two narrow reflexes (111) and (222) from the gold-film and broadened reflex (400) of the reflection from the silicon substrate. The presence of the reflection points order proves that metal film is textured ((111) - texture). In the case of the absence of the information about chemical composition the phase analysis on two reflexes is complicated. The complete information about phase composition can be given only having information about the elemental composition of the investigated sample, obtained using the fluorescence measurement. The results of the performed fluorescent analysis with the usage of detector XR-100CR in two different local regions of the test sample are presented in Table 1.

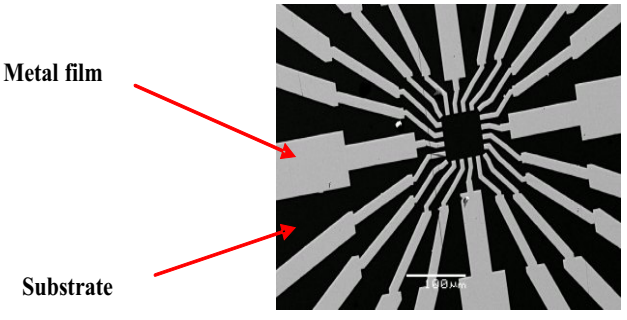

Figure 3. The image of structure Au,Ti//Si(100), obtained by dint of scanning electronic microscope JEOL.

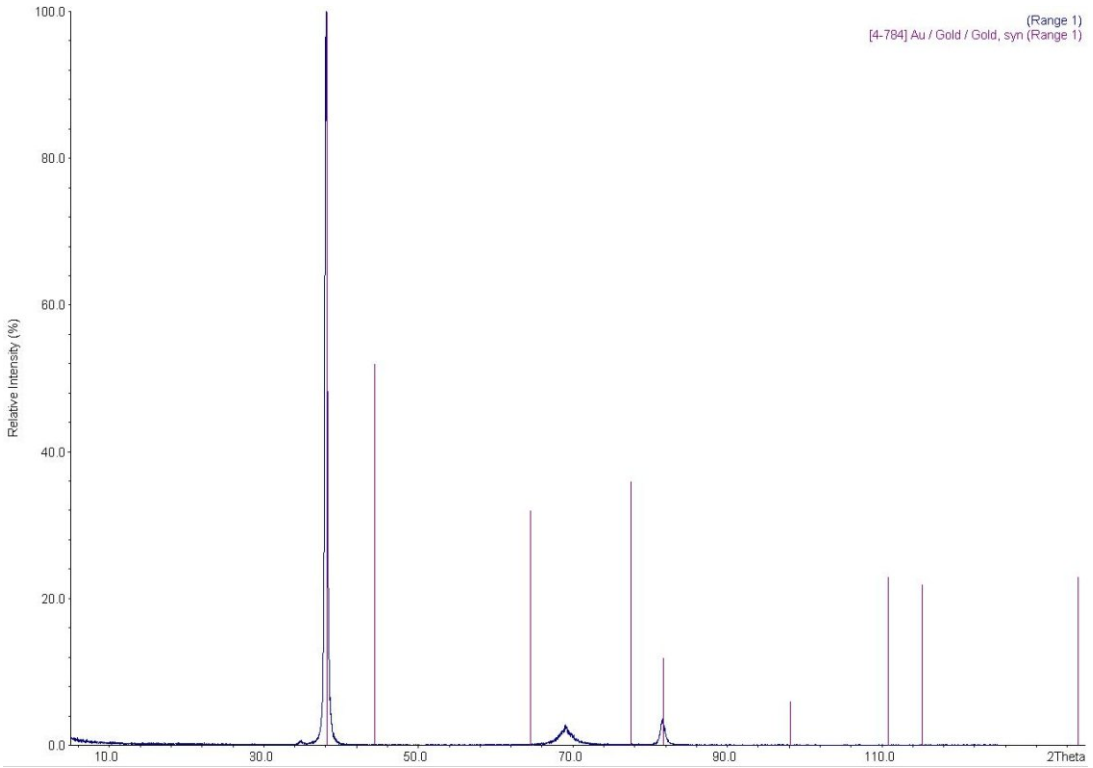

Figure 4. Diffraction pattern of the test sample and results of the phase quantitative analysis. (Weak reflexes in the vicinity of angles 33° and 69° are from the substrate.)

Table 1. Results of X-ray fluorescence analysis

Element, concentration	Au, %	Ti, %	Si, %
Metal film	30.09	3.33	66.58
Substrate			99.8

As one can see from the Table 1, local area of the lane corresponds to the composition of gold with titan impurity. Quantitative analysis showed that the ratio of gold content and titan is 10:1. The local region outside the film structure corresponds to the silicon bottom layer. From the data of the X-ray diffraction analysis within the range of method sensitivity there was no separate titan phase detected. This unambiguously indicated that the structure of the film is a solid solution of titan in gold.

Investigation of submicron inclusions of a meteoritic material

Using the presented technique, investigations of microinclusions in meteorite PCA 91085 found in Antarctica in 1991 were performed. The sample of the meteoritic material is 10 7mm^2 and presents a metallographic section in glass cover. The image of the 1.8 1.3 mm^2 region of meteoritic material obtained with scanning electron microscope in back scattered electrons regime is presented in Fig. 5. As one can see from the figure there are some regions on the sample surface with different electron density. The size of impurities changes in the limits from units to hundreds of microns. The diffraction pattern of meteoritic

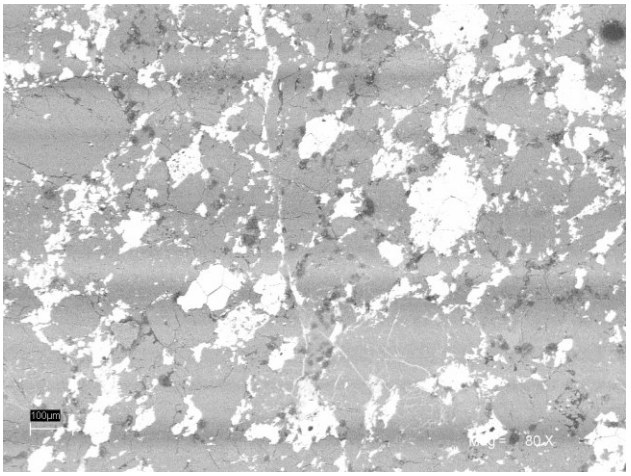

Figure 5. The image of the 1.8 1.3 mm^2 region of meteoritic material obtained with scanning electron microscope in back scattered electrons regime JEOL JSM5610LW.

material, taken from the whole surface of the sample is presented in Fig. 6. It was established that the investigated material is multiphase and one of the phases is (Fe Ni) phase. The detailed local analysis with the developed technique revealed the 80 µm region which corresponds to the phase of the pure iron (-Fe JCPDS PDF2 card No.6-696). The diffraction pattern of this local region is represented on Fig. 7. In the input of the figure the photograph of the whole sample surface with indication of microinclusions' location of the same composition and the photo of microinclusions as such are presented.

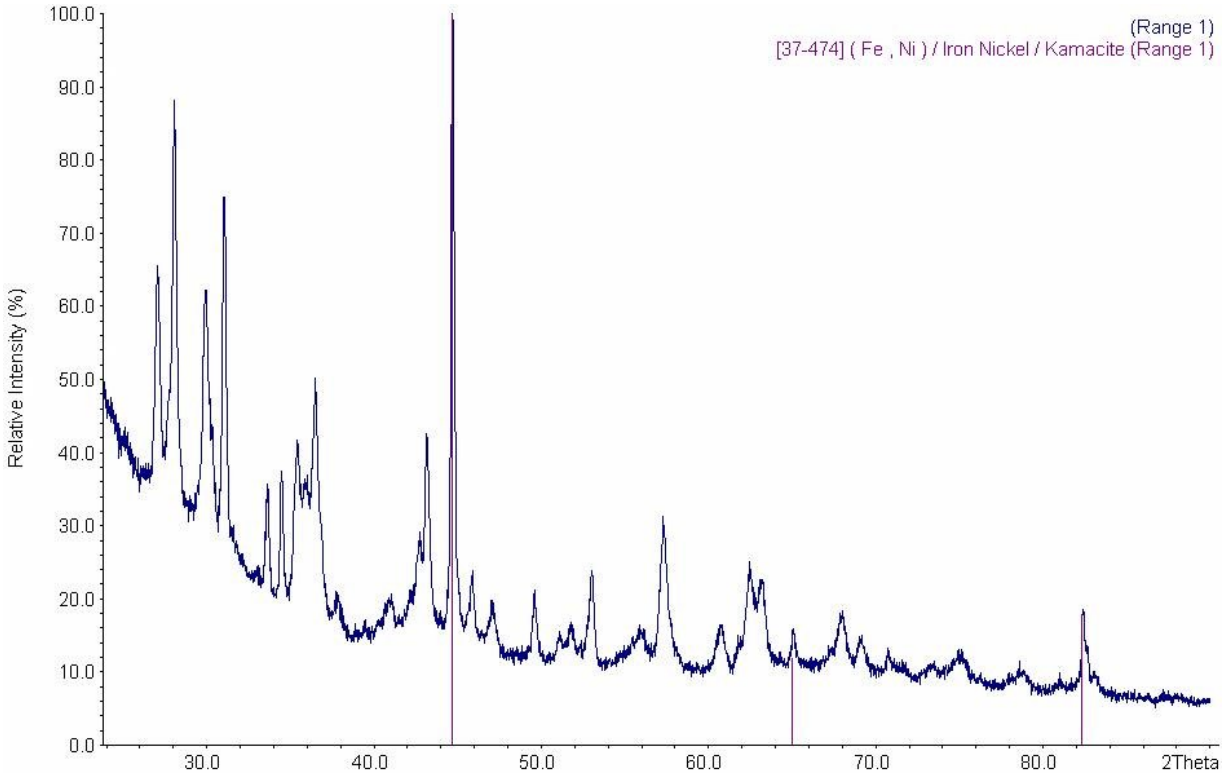

Fig ure 6. The dif frac tion pat tern of me te or itic ma te rial taken from the whole sur face of the sam ple and the re sults of the phase anal y sis which has shown the pres ence of phase (Fe Ni) JCPDS PDF2 card No. 37-474 in the in ves ti gated sam ple.

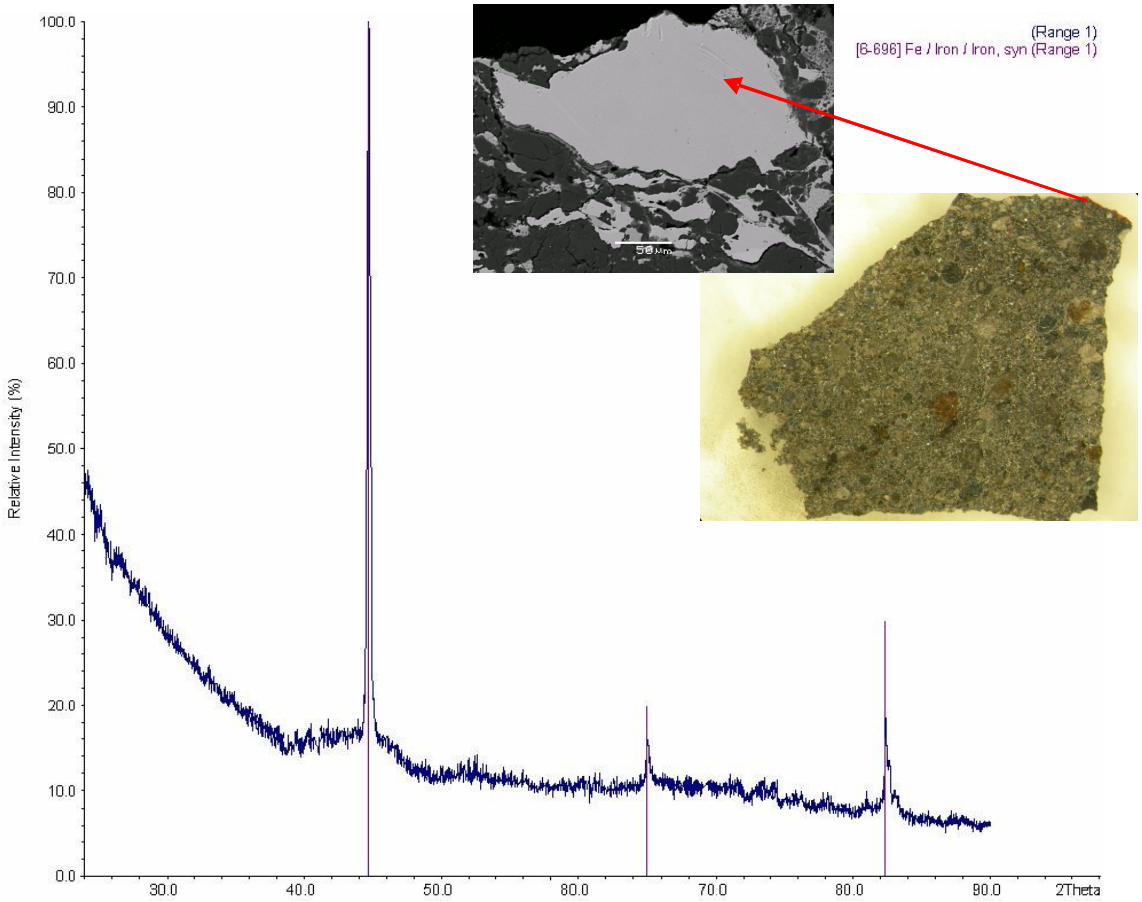

Figure 7. The diffraction pattern of the local region of ~ 80 μm sample (pointed with the arrow on an insert), received on microdiffractometer with use of glass monocapillary 50 μm.

Conclusions

A setup for combined X-ray diffraction and fluorescence analysis has been developed. The technique was tested on a microstructure of gold on silicon substrate and by measuring a meteoritic material. The presented technique can be used for investigations of samples with large area, specifically multilayer structures, thin surface layers, powders, ceramics, for depth profile analysis where the knowledge of the definite component is required. The usage of glass monocapillary allows to increase the integral intensity of the beam and to raise signal/background ratio. The technique proved its efficiency while investigating meteoritic material, during which a phase impurity of homogeneous composition, corresponding to pure iron, was detected.

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NEUTRON DIFFRACTION STUDY OF $La_{0.6}Sr_{1.4}CoO_4$ AT HIGH PRESSURE UP TO 4.3 GPa

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Abstract

The structural and magnetic properties of the layered cobaltite $La_{0.6}Sr_{1.4}CoO_4$ have been studied by the neutron diffraction at the temperature range 16-290 K and high-pressure up to 4.3 GPa. The observed spectra of $La_{0.6}Sr_{1.4}CoO_4$ at 16 K have not shown any new line that could be a signature of an antiferromagnetic order. The ferromagnetic contribution to some diffraction peaks reveals that the magnetic moments are oriented perpendicular to the CoO_6 octahedral layers and their magnitude are increase from 0.7 $_B$ at ambient pressure to 0.9 $_B$ at 4.3GPa. The calculation of the linear compressibilities ($k_i = -(1/a_{i0})(da_i/dP)_T$) shows that the lattice compressibility is lower along *c*, i.e., between the perovskite layers.

Introduction

The mixed-valent cobalt oxides $La_{1-x}Sr_xCoO_4$ with the layered perovskite structure [1] is a recent subject of great interest, because of the strong correlation between electronic, magnetic, transport and structural properties [2-7]. In the $La_{2-x}Sr_xCoO_4$ system, the valence of Co can be varied over large range, hypothetically from Co^{2+} for x = 0 to Co^{4+} for x = 2. Extensive data are available for the $Co^{2+/3+}$ region x = 0–1. La_2CoO_4 (x = 0, Co^{2+}) is an antiferromagnetic insulator with T_N = 275 K [3, 4]. The mixed $Co^{2+/3+}$ valency in the 0 < x < 1 region brings about magnetic disorder, and spin-glass behavior is found below 100 K for these systems. The electric conduction remains of an activation character. The absolute resistivity steeply decreases with increasing Co^{3+} content. The magnetic and electronic data suggest that Co^{2+} ions are in HS state while Co^{3+} ions gradually change with x from HS to IS state [4-6]. On the other hand, there are less reports concerning the $Co^{3+/4+}$ region of $La_{2-x}Sr_xCoO_4$ in a composition range x > 1.0. Very recently, a systematic low-temperature investigation in the range *x* = 1.0–1.5 was published by Shimada et al. [7]. The magnetic measurements revealed a formation of the ferro-