
EPR Study of Water Induced Decomposition of the SrCuO₂ and Sr₂CuO₃ Ceramics Surface. The Role of Carbon Dioxide

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Processes of SrCuO₂ and Sr₂CuO₃ ceramics decomposition induced by contact with water and carbon dioxide were studied by EPR. The dominant signals in the spectra were found to originate from Sr₂Cu(OH)₆ (for Sr₂CuO₃) and SrCu(OH)₄·H₂O (for SrCuO₂) compounds. The thermally induced conversion of SrCu(OH)₄·H₂O into Sr₂Cu(OH)₆ was analysed, and its product CuO was found to exist in the nanocrystalline form. The presence of CO₂, reacting with Sr(OH)₂, was shown to modify the decomposition process leading to the appearance of SrCu(OH)₄·H₂O, some hydroxycarbonates and Cu(OH)₂ on the surface of ceramics studied. At temperatures higher than 300°C CuO reacts back with Sr(OH)₂. For the samples being in contact with atmospheric moisture this compound, deposited on a surface of SrCuO₂, decomposes to Sr₂Cu(OH)₆. The presence of the antiferromagnetic compounds Cu(OH)₂, CuO, and Cu₂[(OH)₂CO₃] in the samples can influence the results of magnetic measurements of the studied ceramics.

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1. Introduction

The fact that the EPR signal was recorded for SrCuO₂ and Sr₂CuO₃ compounds, which are expected to be EPR silent as they are assumed to represent

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ideal systems of 1D $S = 1/2$ antiferromagnetic Heisenberg chains with the exchange interaction J of about 2200 K [1], gave rise to various speculations concerning structural defects in these compounds [2, 3]. The EPR signal of SrCuO_2 was ascribed to the centres with axial symmetry, while that of Sr_2CuO_3 was supposed to originate from the centres with orthorhombic symmetry [2]. Intensity of both signals can be strongly increased by the exposure of the samples to the humid air or hot steam. In Refs. [4, 5] the interactions of the Sr_2CuO_3 ceramic with water was studied and it was shown that the orthorhombic EPR signal of this ceramic can be assigned to the product of partial decomposition of Sr_2CuO_3 with the structure of $\text{Sr}_2\text{Cu}(\text{OH})_6$ [5]. The EPR signal and its parameters for pure $\text{Sr}_2\text{Cu}(\text{OH})_6$ [6] are identical to that observed for Sr_2CuO_3 ceramics.

The ceramic SrCuO_2 was found to be less sensitive to humid air, and in Ref. [4] there was no information about X-ray diffraction (XRD) identification of any traces of phases being products of SrCuO_2 reaction with water. However, our recent EPR investigations shortly published in [7] allow the assignment of the signal observed for SrCuO_2 ceramics to $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$. The EPR signal of a pure $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ compound [8] is identical to that observed by us [7].

Hydroxides $\text{Sr}_2\text{Cu}(\text{OH})_6$ and $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ have been known since the 1930s when they were synthesized for the first time [9]. Their structure [10] and properties were studied by various methods [11]. In the 1990s they attracted interest as precursors of Sr_2CuO_3 and SrCuO_2 used for the low temperature synthesis [12–14]. In these papers the process of thermal decomposition of hydroxides was studied and the products identification was made by the X-ray phase analysis. In order to obtain crystallites sufficient for X-ray diffraction the samples were annealed for hours at various temperatures. As a result the early stages of decomposition process were not monitored.

EPR application is limited to the paramagnetic species. However, just EPR can detect very small amounts of products and is not restricted by the grain size. Therefore, it can be very useful in the study of contamination by paramagnetic species.

The present paper reports the results of our study of the processes of SrCuO_2 and Sr_2CuO_3 ceramics interaction with the humid air (and/or water). Additional information was obtained from thermal decomposition of the products appearing in the samples due to contact with water. This allows both the observation of the new, more weak and broad EPR signals and identification of the other products of ceramics decomposition. The presence of one of these products, namely, CuO is very crucial as it can significantly influence the results of magnetic measurements.

2. Experiment

2.1. Synthesis

The stable compounds, namely, orthorhombic SrCuO_2 and Sr_2CuO_3 found in the SrO-CuO system, treated under ambient pressure, were prepared. In the

process of investigation it was shown that the third variety, $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, appears in the SrO–CuO system as a self-dependent locally occurring phase resulting in a small deviation of the component from the stoichiometry. Therefore, this compound was also synthesized. The SrCuO_2 and Sr_2CuO_3 ceramics were first synthesized by Teske and Müller-Buschbaum [15]. $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ was found as a by-product in the synthesis of high- T_C superconductors [16].

All samples were prepared by a conventional solid-state reaction technique from mixtures of high purity raw materials: CuO and SrCO_3 (Specpure, Johnson, Matthey Chemicals Limited).

a) To get SrCuO_2 , CuO and SrCO_3 were mixed in appropriate proportions to obtain the stoichiometric material [17, 18]. The powder mixture was calcined initially in air at 950°C for 10 h, and then the material was reground, pressed into tablets and sintered in air at 950°C for 20 h. The sample was next cooled in furnace to 500°C and quenched to room temperature.

b) To get Sr_2CuO_3 , a mixture of CuO and SrCO_3 at appropriate ratio was used. The synthesis sequence was (in air): calcination at 927°C for 10 h, then the material was mixed, ground, pressed into tables and sintered at 1000°C for 10 h. The sample was then cooled in furnace to room temperature.

c) To get pure $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ compound, the initial mixture of the nominal stoichiometry ($\text{Sr}_{14}\text{Cu}_{24}\text{O}_{38}$) was at first calcined at 1200 K for 10 h, then grounded, pressed into tablets and sintered in flowing O_2 gas for about 20 h at 1200 K and cooled to room temperature.

All products were brown-black in colour.

2.2. Structural analysis

Powder X-ray diffraction patterns were obtained with a DRON-2 diffractometer using Fe K_α radiation with beta filter. The data were analysed by the full profile analysis of the Rietveld method. The program MAUDI.9992 [19] was used.

2.3. EPR

EPR measurements were carried on the X-band RADIOPAN spectrometer with 100 kHz modulation at room temperature and at 77 K.

3. Results

3.1. Structural characterization of the samples

XRD diagrams of the SrCuO_2 and Sr_2CuO_3 samples and the results of X-ray phase analysis are shown in Fig. 1. The results of the phase analysis of these and other samples are presented in Table I.

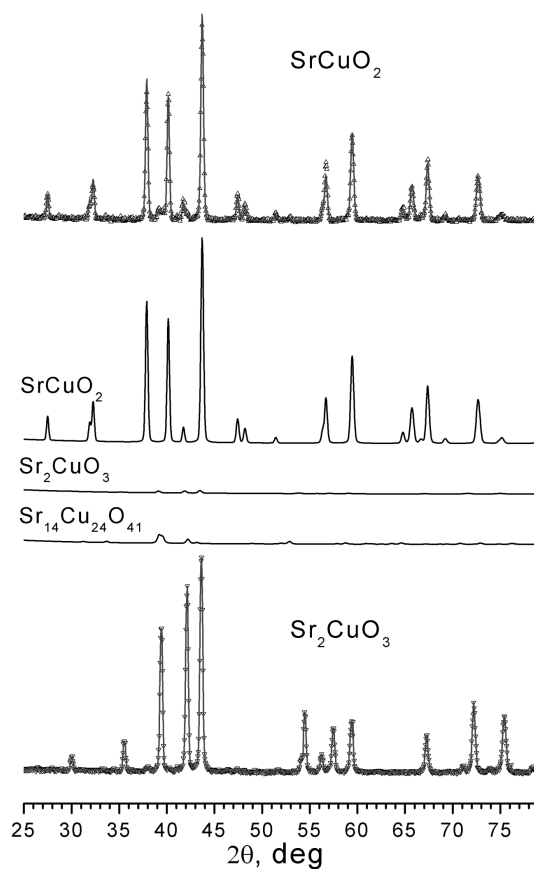


Fig. 1. An example of X-ray structural phase analysis of diffraction pattern ($\text{Fe } K_{\alpha}$ radiation) of SrCuO_2 . The diffraction pattern of Sr_2CuO_3 ceramic is also shown. Symbols show the experimental data.

In SrCuO_2 (sample *A*) the admixture of 6.3 molar % of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ [16] was found together with 1.4 molar % of Sr_2CuO_3 . (The $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ compound was thoroughly studied in [20, 21], where the existence of intensive EPR signals from this compound was shown. It is clear that even its small admixture should influence the EPR of sample *A*.)

Sr_2CuO_3 (sample *B*) is the purest one (among those studied) and contains only about 1 molar % of SrCuO_2 . The presence of hydroxide $\text{Sr}_2\text{Cu}(\text{OH})_6$ and $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ contaminations was not detected. This fact can be explained either by a too low amount of these products in the sample or by a too small size of the crystallites to be suitable for effective XRD analysis.

3.2. EPR study of the process of ceramic surface decomposition

Measurements of the fresh samples were started in about 2 h after the end of the synthesis process. Materials taken out from the oven were handled in the

TABLE I

Results of X-ray phase analysis.

Sample	SrCuO ₂		Sr ₂ CuO ₃		Sr ₁₄ Cu ₂₄ O ₄₁	
	Molar [%]	Unit cell parameters [Å]	Molar [%]	Unit cell parameters [Å]	Molar [%]	Unit cell parameters [Å]
SrCuO ₂ sample A	92.3	$a = 3.5713$ ± 0.0002 $b = 16.324$ ± 0.001 $c = 3.9117$ ± 0.0002	1.4	$a = 3.93$ ± 0.01 $b = 3.51$ ± 0.01 $c = 12.84$ ± 0.03	6.3	$a = 11.47$ ± 0.01 $b = 13.39$ ± 0.01 $c = 27.66$ ± 0.03
Sr ₂ CuO ₃ sample B	1	$a = 3.5711$ ± 0.0002 $b = 3.4970$ ± 0.0003 $c = 12.6951$ ± 0.0009	99	$a = 3.9130$ ± 0.0006 $b = 3.869$ ± 0.007 $c = 16.41$ ± 0.04		

normal atmospheric conditions; ceramics were cut into the small pieces and the samples prepared in this way were placed in the quartz tubes. Some of them were closed with paraffin, the others were left opened. EPR spectra were recorded for all the samples (Fig. 2), and their parameters are listed in Table II. We observed that SrCuO₂ (sample A) and Sr₂CuO₃ (sample B) readily absorb water. Even moderate heating of the bottom of the tubes with fresh samples resulted in the condensation of water drops on the cool parts of the tubes. This effect was not observed for Sr₁₄Cu₂₄O₄₁ ceramics.

Then we have studied the influence of H₂O on the materials properties. An exposure of A and B samples to warm (about 35°C) steam, hot (100°C) steam, and liquid water resulted in the appearance or in the increase in the signal intensity. A limit of this intensity increase corresponding to about 2–3 molar % of Cu²⁺ ions in the sample was observed. We did not observe any influence of water on the spectra of Sr₁₄Cu₂₄O₄₁ ceramics.

For a detailed study of thermal evolution of the EPR spectra, samples with the strong water induced signals were isolated with silicone oil or Al₂O₃ powder and gradually heated from room temperature up to 370°C. After 15 min of annealing at each temperature the samples were cooled to the room temperature and the EPR spectra were recorded.

The main repeatable results can be summarized as follows:

— *Sample A* — SrCuO₂. A signal with tetragonal g -factor, $g_{\parallel} = 2.259(2)$; $g_{\perp} = 2.055(2)$ (Table II) was observed in the fresh samples, which were not isolated

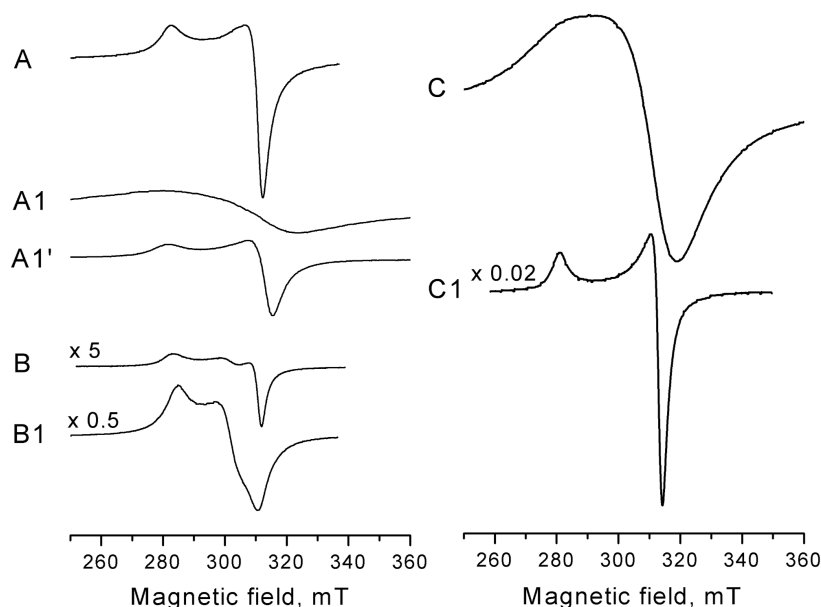


Fig. 2. EPR spectra of “as prepared” samples. *A* — a fresh sample *A* with nominal composition SrCuO_2 ; *A1* — the sample *A* stored for 2 months in a closed container and named *A1* sample; *A1'* — the sample *A1* at 77 K; *B* — a fresh sample *B* (Sr_2CuO_3); *B1* — the sample *B* stored in air for two months; *C* — a sample *C* ($\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$) at room temperature; *C1* — the sample *C* at 77 K. Intensities of the presented spectra reflect differences between samples with comparable weight.

from atmosphere (spectrum *A* in Fig. 2) and practically did not change during the time of investigation (more than two months). Its intensity increased with exposure to H_2O and even hot steam (with $T \leq 100^\circ\text{C}$) did not change the signal shape. Annealing at temperatures growing from 110°C up to $180\text{--}200^\circ\text{C}$ resulted in the transformation of this signal into the one characterized by orthorhombic g -factor with $g_z = 2.245(3)$; $g_x = 2.051(3)$, $g_y = 2.115(3)$ (Fig. 3). A further heating between 250 and 300°C resulted in the gradual decrease in this signal intensity and revealed a broad asymmetric signal at room temperature (Fig. 4a), whose linewidth decreased on cooling. The g -values of the signal recorded at 77 K: $g_{\parallel} = 2.277(2)$ and $g_{\perp} = 2.045(2)$ are characteristic of the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ compound [20, 21] (compare the spectrum shown in Fig. 4a with the spectra *C* and *C1* in Fig. 2; the g -values are presented in Table II); the room temperature spectrum could be fitted with $g_{\parallel} = 2.265$ ($\Delta B_{\parallel} = 43.0$ mT) and $g_{\perp} = 2.040$ ($\Delta B_{\perp} = 28.0$ mT). The shape and intensity of this signal were not affected by final heating up to $350\text{--}370^\circ\text{C}$. A gradual reappearance of the EPR signal with orthorhombic g -factor was observed in the sample stored after thermal treatment in air.

TABLE II

EPR parameters of signals observed for the fresh samples, after exposure to water, and after annealing at various temperatures.

Sample	T [K]	g -values
SrCuO ₂ — <i>A</i> Fresh and after exposure to water Heated up to 180°C Heated up to 300°C	293, 77	$g_{\parallel} = 2.259 \pm 0.002$, $g_{\perp} = 2.055 \pm 0.002$
	293, 77	$g_z = 2.245 \pm 0.003$, $g_y = 2.115 \pm 0.003$, $g_x = 2.051 \pm 0.003$
	293	$g_{\parallel} = 2.265$ ($\Delta B = 43.0$ mT) ^b , $g_{\perp} = 2.040$ ($\Delta B = 28.0$ mT) ^b
	77	$g_{\parallel} = 2.277 \pm 0.002$, $g_{\perp} = 2.045 \pm 0.002$
SrCuO ₂ — <i>A1</i>	293	$g_{\parallel} = 2.280$ ($\Delta B = 45.0$ mT) ^b , $g_{\perp} = 2.055$ ($\Delta B = 30.0$ mT) ^b
	77	$g_{\parallel} = 2.277 \pm 0.002$, $g_{\perp} = 2.045 \pm 0.002$
		$g_{\text{eff}} = 2.106$ ($\Delta B = 17.0$ mT)
Sr ₂ CuO ₃ — <i>B</i> Fresh and after exposure to water Annealed at $T > 300^{\circ}\text{C}$	293, 77	$g_z = 2.245 \pm 0.002$, $g_y = 2.115 \pm 0.002$, $g_x = 2.051 \pm 0.002$, $g_{\parallel} = 2.259 \pm 0.003^a$, $g_{\perp} = 2.055 \pm 0.003^a$
	293	$g_{\text{eff}} = 2.110$ ($\Delta B = 29.0$ mT)
	77	$g_{\text{eff}} = 2.108$ ($\Delta B = 18.0$ mT)
Sr ₁₄ Cu ₂₄ O ₄₁ — <i>C</i>	293	$g_{\parallel} = 2.280$ ($\Delta B = 25.0$ mT) ^b , $g_{\perp} = 2.055$ ($\Delta B = 16.5$ mT) ^b
	77	$g_{\parallel} = 2.277 \pm 0.002$, $g_{\perp} = 2.045 \pm 0.002$,

^asignals observed in the fresh Sr₂CuO₃ samples

^b g -values and ΔB were obtained by spectra fitting

— *Sample A1* — SrCuO₂ (a part of sample *A* placed immediately after synthesis in a closed container and stored for 3 months). At room temperature the EPR spectrum of this sample consisted of a broad slightly asymmetrical single line with $\Delta B \approx 33$ mT (see spectrum *A1* in Fig. 2 and Table II), without any traces of the above described signal with tetragonal g -factor. At 77 K sample *A1* exhibited the spectrum (*A1'* in Fig. 2) with g -values characteristic of Sr₁₄Cu₂₄O₄₁ ($g_{\parallel} = 2.277(2)$ and $g_{\perp} = 2.045(2)$) [20, 21] (compare the spectra *A1'* and *C1* in Fig. 2 and data in Table II). This spectrum is identical with that observed for sample *A* after thermal treatment. Exposure of this sample to water results in the appearance of the EPR signal, whose properties are the same as those of sample *A*.

— *Sample B* — Sr₂CuO₃. For the pieces of a fresh Sr₂CuO₃ ceramic no EPR signal was detected. Exposure to the warm steam produced a weak spectrum consisting of both tetragonal ($g_{\parallel} = 2.259(2)$; $g_{\perp} = 2.055(2)$) and orthorhombic

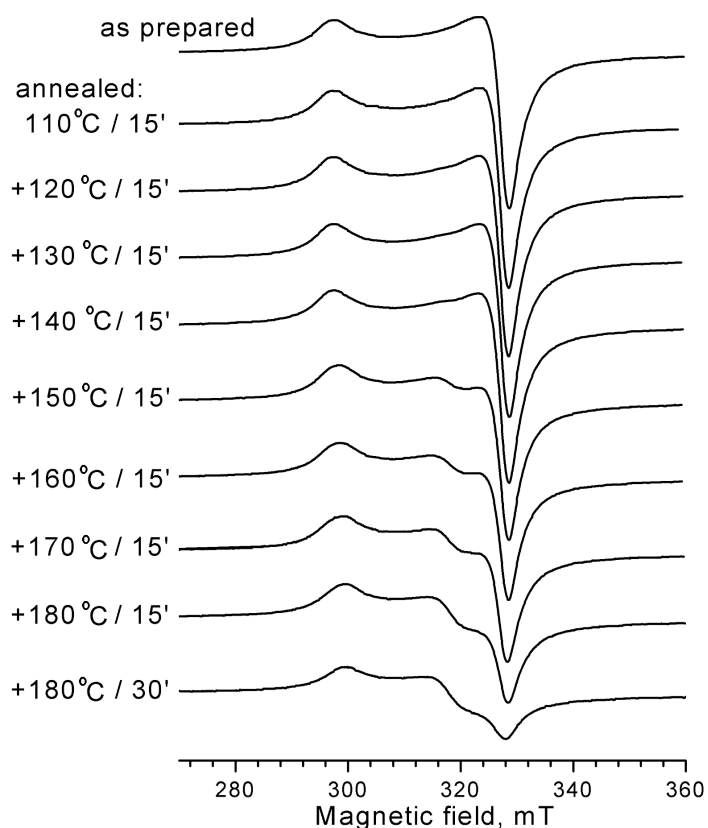


Fig. 3. Transformation of the room temperature EPR spectra from sample *A* induced by gradual annealing in the temperature range 110–180°C. The symbol “+” before following temperatures indicates additional annealing of the same sample.

($g_z = 2.245(3)$; $g_x = 2.051(3)$; $g_y = 2.115(3)$) signals (spectrum *B* in Fig. 2). Analysis of this spectrum (Fig. 5) has shown that the content of centres with tetragonal g -factor reaches 36%. In the powder sample of the fresh ceramic these signals are observed at once. Under the influence of hot steam the intensity of these signals is nearly 50 times increased. The ratio of intensities of the signals of tetragonal and orthorhombic g -factors was the same as for the fresh powder samples and did not change after exposition to the hot steam. Storage in air resulted in a decrease in the intensity of the first type of signals accompanied by an increase in the intensity of the second one, and finally no traces of the signal of tetragonal g -factor were visible (the spectrum *B1* in Fig. 2). Additionally the hot steam produced on a surface of the ceramic a thin layer of a blue-green phase. However, we have not observed any correlation between the amount of this phase and the EPR signal intensity and/or shape of the spectra. The blue-green colour of the layer clearly indicates a divalent copper compound and the lack of the signal

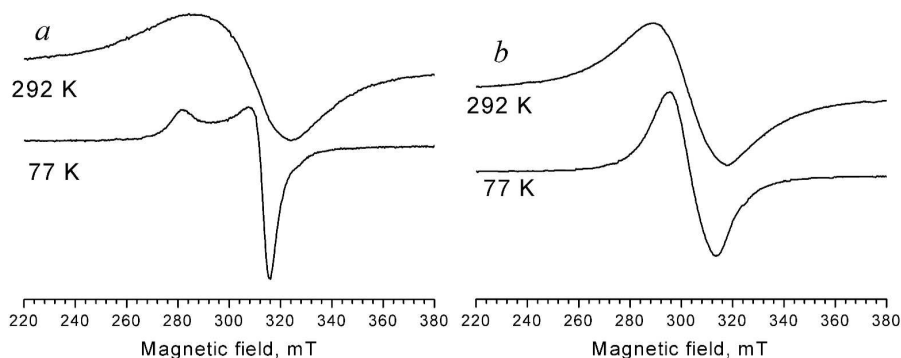


Fig. 4. EPR spectra of samples *A* (a) and *B* (b) annealed at temperatures higher than 300°C registered at room (292 K) and liquid nitrogen (77 K) temperatures.

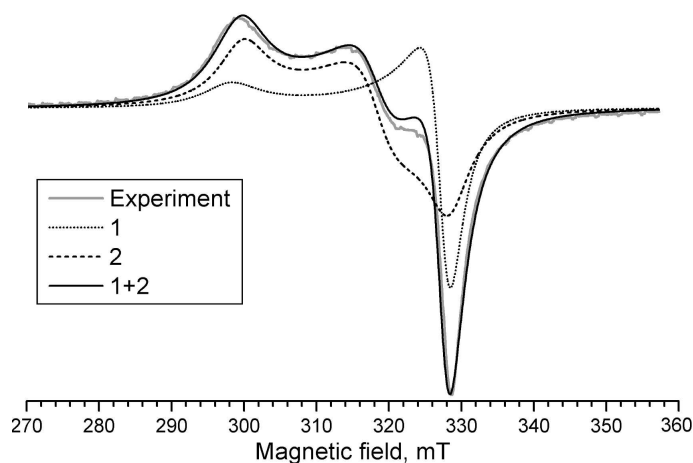


Fig. 5. Analysis of the EPR spectrum from sample *B* (Sr_2CuO_3) stored in air recorded in 20 h after the end of the synthesis process. It corresponds to 36% content of centres with tetragonal symmetry (line 1); line 2 indicate centres with orthorhombic symmetry.

suggests strong antiferromagnetic correlations. This phase was not detected by X-ray diffraction probably due to a very small thickness of the layer.

An immersion of Sr_2CuO_3 ceramic directly into water leaved the blue sediment (see also [5]). The EPR signal of these precipitations, dried immediately on the filter-paper, has shown to originate from the centres with axial symmetry with $g_{\parallel} = 2.259(3)$ and $g_{\perp} = 2.055(3)$.

The signal of sample *B*, with orthorhombic g -factor, was not sensitive to annealing at temperatures 110 – 180°C . The intensity of the signal of orthorhombic g -factor decreased on annealing at temperatures higher than 250°C , and finally this signal disappeared after heating to 300°C ; instead the structureless broad signal was observed (see Fig. 4b and Table II for parameters). A final heating of

sample *B* up to 350–370°C resulted in 2.5 times increase in the intensity of the remaining signal. The g -factor and line width of this signal are: $\Delta B \approx 29$ mT; $g_{\text{eff}} = 2.110$ at room temperature (RT) and $\Delta B \approx 18$ mT; $g_{\text{eff}} = 2.108$ at 77 K.

— *Sample C* — $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$. This sample was synthesized in order to obtain the experimental spectrum of the ceramic and to compare it to the signal observed in samples *A* and *A1*. Relatively strong and broad RT spectrum of this sample (with best fit parameters $g_{\parallel} = 2.280$ ($\Delta B = 25.0$ mT); $g_{\perp} = 2.055$ ($\Delta B = 16.5$ mT)) transformed at 77 K into the signal with tetragonal g -factor: $g_{\parallel} = 2.277(2)$; $g_{\perp} = 2.045(2)$ (see spectra *C* and *C1* in Fig. 2 and Table II). The g -factors and linewidths of the EPR signal of sample *C* obtained with the best fit procedure practically coincide with parameters measured in [20, 21]. Neither exposure to H_2O nor annealing had any influence on the EPR spectra of this ceramic.

4. Discussion

4.1. Identification of the origin of EPR signals

The results obtained have shown a strong correlation between water acting on SrCuO_2 and Sr_2CuO_3 ceramics and the appearance of the EPR signal. The fact of the water induced decomposition of the Sr_2CuO_3 compound is known [4, 5]. One of the products of such decomposition was identified as polycrystalline compound $\text{Sr}_2\text{Cu}(\text{OH})_6$. It exhibits a strong EPR signal with the orthorhombic g -factor ($g_1 = 2.24$, $g_2 = 2.11$, and $g_3 = 2.05$) [6] identical to that observed for the sample *B*. We shall note that according to the crystal structure of the $\text{Sr}_2\text{Cu}(\text{OH})_6$ compound [10], the $\text{Cu}(\text{OH})_6$ complex has approximately tetragonal symmetry, and the EPR signal with the tetragonal g -factor could be expected. The observed signal of the orthorhombic g -factor is due to the exchange averaging of signals of two magnetically inequivalent complexes in the crystal lattice. Therefore, the signal of orthorhombic g -factor, observed in Sr_2CuO_3 after interaction with water, indicates that $\text{Sr}_2\text{Cu}(\text{OH})_6$ forms crystallites with well organized structure on the surface of ceramics even in the samples, in which their presence is not detected by X-ray diffraction (probably due to the small amount and small crystallites dimensions).

The products of SrCuO_2 reaction with water had not been identified earlier [4]. However, knowing that $\text{Sr}_2\text{Cu}(\text{OH})_6$ is a precursor of Sr_2CuO_3 used for the low temperature synthesis [12, 13] we had supposed that another hydroxide, the $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ used for the synthesis of SrCuO_2 [13, 14], could be responsible for the signal observed for this ceramic.

The EPR signal of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ compound is characterized by $g_{\parallel} = 2.26$ and $g_{\perp} = 2.06$ [8]. These values are identical with those observed in our experiment for SrCuO_2 ceramic.

An additional support of our thesis comes from the temperature-induced evolution of the spectra. This transformation started in a ceramic sample at about 120°C and completed at about 180°C is shown in Fig. 3 and occurs in the same temperature range as the thermal decomposition of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ crystals into

$\text{Sr}_2\text{Cu}(\text{OH})_6$ in the static air studied in [8]. Therefore, we conclude that the signal with tetragonal g -factor, observed for SrCuO_2 (sample *A*) ceramic, can be assigned to $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ hydroxide (these results were described in brief in [7]).

The surprising effect of reappearance of the EPR signal with orthorhombic g -factor in the samples, stored in air after thermal treatment, can be easily explained. The thermal decomposition of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ hydroxide yields $\text{Sr}(\text{OH})_2$ and CuO , which in a temperature range of 300–400°C react to form Sr_2CuO_3 . Therefore, after the thermal treatment of SrCuO_2 ceramic the Sr_2CuO_3 phase exists on the surface of SrCuO_2 ceramic as contamination, together with the excess of CuO [8] and SrCO_3 [4]. These last two components form a passivation layer on a surface of the ceramic and stop its reaction with water, when Sr_2CuO_3 , present on the surface, reacts readily with water yielding $\text{Sr}_2\text{Cu}(\text{OH})_6$.

In the sample *A* the EPR signal of CuO cannot be revealed. In samples heated up to 180°C its presence is masked by a much stronger signal of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$. In samples annealed at 350°C the EPR signal of CuO is masked by the presence of the signal of a 6 molar % of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ admixture.

The signal which can be assigned to CuO is observed in sample *B* annealed at 350°C. It should be present there due to $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ transformation into $\text{Sr}_2\text{Cu}(\text{OH})_6$ and the thermal decomposition of the latter compound [8]. However, the Néel temperature of the bulk CuO is about 230 K [22], and below this temperature in the phase with strong antiferromagnetic correlations the linewidth of the EPR signal is expected to increase so strongly that in the X-band experiment no EPR signal should be detected. Instead, at the temperature lowered down to 77 K we observed the narrowing of the EPR signal. We can understand such temperature dependence of the EPR signal taking into consideration that precipitated CuO grains arise due to the decomposition of very small nanocrystals of $\text{Sr}_2\text{Cu}(\text{OH})_6$, which were not detectable in the X-ray analysis. A decrease in the Néel temperature with a decrease in the grain size was observed, and for the grains as small as 6.6 nm the Néel temperature is about 40 K [22]. Therefore, the observed narrowing of the EPR signal with temperature lowering is due to the phenomena characteristic of the paramagnetic phase.

Summarising this part we can conclude that according to our results the reaction of SrCuO_2 and Sr_2CuO_3 ceramics with water is responsible for the appearance of paramagnetic contaminations: $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$, $\text{Sr}_2\text{Cu}(\text{OH})_6$, $\text{Cu}(\text{OH})_2$ and CuO on the ceramic surface.

At the same time there are results which cannot be explained in the scheme based on the reaction with H_2O only. These are:

- a) the presence of two types of signal (with tetragonal and orthorhombic g -factor) in the spectra of the fresh Sr_2CuO_3 ceramic sample *B*;
- b) the increase in the intensity of the broad isotropic resonance line observed for sample *B* on heating from 300 to 370°C.

These problems are discussed in the next section.

4.2. Reaction with CO₂

The role of CO₂ in the process of decomposition of Sr₂CuO₃ ceramic was discussed by Wang et al. [4]. IR absorption due to CO₃ groups was observed and the diffraction peaks associated with SrCO₃ were found in the XRD diagrams of the ceramic stored in the humid air. The authors of the paper [4] suggested the existence of either a very fast high temperature reaction with atmospheric CO₂ leading to the appearance of SrCO₃ or a low temperature route to this contamination. However, because of the methods of investigation they stated that processes of reaction with CO₂ could not be observed at early stages of decomposition [4]. The possibility of high temperature carbonation reaction leading to SrCO₃ formation, considered by Wang et al., is brought into question as Luhrs et al. [23] have found that in a temperature range of 20–1000°C pure Sr₂CuO₃ ceramic did not react with dry CO₂. Some new pieces of information, concerning the role of atmospheric and water dissolved CO₂, were obtained by Hill et al. [5]. They have studied a decomposition process of Sr₂CuO₃ during exposure of samples to CO₂-free hydrated O₂ and N₂ gases. The main product of this reaction was identified as Sr₂Cu(OH)₆, but small amounts of Cu(OH)₂ and Sr(OH)₂, and traces of SrCO₃ were also detected. However, when Sr₂CuO₃ was reacted directly with de-ionised water stirred vigorously for several minutes the products were Cu(OH)₂ and SrCO₃. This showed that the precipitations of Sr(OH)₂ or Sr(OH)₂ · 8H₂O readily react with atmospheric and water soluble CO₂.

We have also performed an experiment with Sr₂CuO₃ reaction with liquid water, but instead of steering and waiting for the reaction completing, we have immediately dried the resulting blue precipitations. Due to the EPR signal with tetragonal *g*-factor we have identified them to be SrCu(OH)₄·H₂O, not Sr₂Cu(OH)₆ as it was assumed by Hill et al. [5]. The results of this experiment can be understood assuming that water induces decomposition of Sr₂CuO₃ ceramic to Sr(OH)₂ (or rather Sr(OH)₂ · 8H₂O) and Cu(OH)₂, which then should react to form the Sr₂Cu(OH)₆ hydroxide. However, when a part of Sr(OH)₂ · 8H₂O reacts with CO₂ dissolved in water, the stoichiometry of the solution changes and the rest of Sr(OH)₂ · 8H₂O reacts with Cu(OH)₂ yielding SrCu(OH)₄·H₂O.

Similar conditions are realized on the surface of a ceramic being in contact with atmospheric CO₂ and water (atmospheric moisture or steam, which also contains CO₂). Due to the above described reactions leading to the formation of SrCO₃, the surface layer of Sr₂CuO₃ ceramic suffers a local deficit of strontium, and in further reactions between Sr(OH)₂ and Cu(OH)₂, the SrCu(OH)₄·H₂O hydroxide can appear together with Sr₂Cu(OH)₆. In the EPR spectra this results in the presence of signals with both, tetragonal and orthorhombic *g*-factors.

The last problem to be discussed in this section is an increase in intensity of the EPR signal originating from CuO observed for sample *B* annealed in a temperature range of 300–380°C. We have identified two sources of CuO in the heated up to 300°C Sr₂CuO₃ sample: the thermal decomposition of Cu(OH)₂

(left due to the deficit of $\text{Sr}(\text{OH})_2$ which had partly reacted with CO_2), and the thermal decomposition of $\text{Sr}_2\text{Cu}(\text{OH})_6$ hydroxide. This determines the intensity of the EPR signal originated from CuO . Due to the low temperature synthesis of Sr_2CuO_3 [12, 13], the amount of CuO should decrease on the heating from 300 to 380°C. Instead, we observe a 2.5 times increase in the corresponding EPR signal intensity. This indicates that among the products of the reaction with water and CO_2 there are other strongly correlated copper compounds with decomposition temperatures higher than 300°C. The unidentified pale blue-green phase observed by Wang et al. [4] and by us as well can be due to the $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$ (malachite) precipitations, which can be the product of Sr_2CuO_3 reaction with water and CO_2 . Such a reaction is possible in the alkaline medium, and this is provided by the presence of the strongly alkaline $\text{Sr}(\text{OH})_2$ hydroxide.

For $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$ with antiferromagnetic ordering [24] the EPR signal is not detected at X-band. A multistep decomposition of malachite yielding CuO , H_2O , and CO_2 takes place between 300 and 380°C [25]. The resulting CuO can be responsible for the increase in the EPR signal intensity.

5. Conclusions

EPR has been used for investigation of crystals and other materials with paramagnetic impurities. The presence of impurities takes on special significance in the study of magnetic materials, as even traces of such impurities can seriously influence results of measurements and lead to false interpretation. The study is performed for the centres observed in the SrCuO_2 and Sr_2CuO_3 ceramics, where strong antiferromagnetic interactions occur. The EPR signals were identified on the basis of experiments in which their appearance and temperature induced evolution was studied. The obtained results were collated with literature data yielded by XRD, differential thermogravimetry (DTG), differential thermal analysis (DTA) and IR spectroscopy.

We have shown that the signals, dominating the spectra, originate mainly from $\text{Sr}_2\text{Cu}(\text{OH})_6$ (in the case of Sr_2CuO_3) and $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ (in the case of SrCuO_2), which are the products of water decomposition of these ceramics. The formation of these hydroxides is observed from very early stages. We have found also that the presence of CO_2 strongly modifies the decomposition process leading to the appearance of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ and some hydroxycarbonates, probably malachite $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$, on the surface of Sr_2CuO_3 and of $\text{Cu}(\text{OH})_2$ on both ceramics studied. The thermal decomposition of $\text{Sr}_2\text{Cu}(\text{OH})_6$, $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$, malachite, and copper hydroxide results in the formation of CuO . Information on the presence of $\text{Cu}(\text{OH})_2$, CuO , and $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$ contamination is very important, as the temperature characteristics of these antiferromagnetic compounds differ significantly from those of the ceramics under study. At temperatures higher than 300°C CuO reacts back with $\text{Sr}(\text{OH})_2$, which is also a product of hydroxide decomposition to form Sr_2CuO_3 . This compound becomes an additional contami-

nation on the surface of SrCuO₂, and for the samples being in contact with atmospheric moisture it decomposes to Sr₂Cu(OH)₆, which results in the appearance of the EPR signal with the orthorhombic *g*-factor.

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