Synthesis, structural and electrical characterizations of $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$

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ABSTRACT

A new compound $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ has been prepared by sol gel method and annealed at 1473 K in 1 atm of Ar gas flow. The X-ray diffraction (XRD) is used for phase identification. The sample shows to adopt the K_2NiF_4-type structure based on tolerance factor calculation. XRD analysis using the Rietveld method was carried out and it was found that $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ ($Dy_{0.33}Sr_{1.67}Ni_{0.8}Cu_{0.2}O_{4-\delta'}$) compound crystallizes in tetragonal symmetry with space group $I4/mmm$ ($Z=2$). The lattice parameters are found to be at room temperature $a=3.7696(5)$ Å and $c=12.3747(2)$ Å. The final reliability indices were: $R_B=5.219\%$ and $\chi^2=3.47$. Four probe electrical resistivity measurements were performed versus temperature in the range 294–579 K. A semiconducting behaviour over the whole range of temperature, with a conductivity maximum of 0.4 S cm^{-1} is observed at 510 K.

1. Introduction

Complex oxides with the general formula A_2BO_4 with rare earth, alkaline-earth elements on the A sites and $3d$-transition metals on the B sites, are well known for their catalytic activities, wide range of magnetic and electrical properties. A unique set of these properties makes them useful as electrode materials in the different electrochemical devices. Further investigations on these oxides have been carried out in order to find appropriate compositions with the best set of necessary properties. The traditional way of modifying the properties of materials is by partial substitution in different sub-lattices.

Following the discovery of superconductivity in the $La_{2-x}Sr_xCuO_4$ system [1], many authors have reported studies on nickel oxides having the same structure. In particular, extensive investigations have been carried out on the structural, magnetic and electrical properties of the $La_{2-x}Sr_xNiO_{4-\delta}$ [2–4] and $Nd_{2-x}Sr_xNiO_{4-\delta}$ [5,6] solid solutions. Despite claims for the onset of diamagnetism and superconductivity in the $La_{2-x}Sr_xNiO_{4-\delta}$ system [7–10], no pure superconducting nickel oxide phase has yet been isolated. A study of the $Ln_{2-x}Sr_xNiO_{4-\delta}$ system with the smaller Y^{3+} cation led to the point phase $YSr_5Ni_3O_{11}$ [11]. In one of our previous investigations [12] of the quaternary system Ln_2O_3–SrO–NiO–CuO, we have determined similar phases $LnSr_5Ni_{2.4}Cu_{0.6}O_{11}$ that form with the small lanthanides Ho, Er and Dy. A pure sample was obtained only for the Holmium compound at 1150 °C in 1 atm of O_2 gas flow using conventional solid state

methods. For Ln=Dy and Er, mixtures of Ln_2SrO_4, NiO, CuO and the new phase were found. We have chosen to detail only the refinement of the pure compound $HoSr_5Ni_{2.4}Cu_{0.6}O_{11}$ [12].

As far as we are more interested in mixed oxides based on neodymium rare earth, and then we have previously studied the series $NdSrNi_{1-x}Cu_xO_{4-\delta}$, $0 \le x \le 1$ [13,14]. A systematic substitution of Ni by Cr in $NdSrNiO_4$ parent compound has been reported, in our previous works, and we have synthesized new compounds in the $NdSrNi_{1-x}Cr_xO_{4-\delta}$, with $0 \le x \le 1$ by solid state method [15] and by modified sol gel method and subsequent annealing in 1 atm of Argon gas flow [16]. Therefore, we realized that experiments in fully oxygenated atmosphere, in order to prepare an oxygen deficient compound ($Ln_{0.33}Sr_{1.67}Ni_{0.8}Cu_{0.2}O_{4-\delta}$), always produced multiphase samples, but the preparation under a 1 atm of Argon gas flow resulted in the formation of the pure compound.

In this paper, we demonstrate that considerable attention to the precise synthetic conditions, and detailed confirmation of single phase by Rietveld analysis of high-quality powder X-ray diffraction data is required for the synthesis of pure phases in the two-dimensional K_2NiF_4 structure. We report, the synthesis, the structural characterization and also the resistivity measurements at high temperature of the compound $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$.

2. Experimental

2.1. Synthesis

The $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ sample was prepared in polycrystalline form using a water-soluble complex method. Prior to use,

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Nd_2O_3 (Aldrich, 99.99%) was calcined at 1273 K for 10 h in air to remove any hydrogeno-carbonate impurities. NiO and CuO (Aldrich, 99.99%) were used as obtained. Stoichiometric amounts of Nd_2O_3, $SrCO_3$, NiO and CuO were dissolved in a minimum quantity, typically 150 mL, of a 1:1 solution of analar 6 M nitric acid and distilled water. For each mole of transition metal used 3 mol equivalents of citric acid (Riedel-de-Han, 99.5%) solution were added along with 5 cm³ of ethylene glycol with magnetic stirring. The whole mixture was then stirred at 373 K until the solution became completely transparent, containing metal ion and citric acid complexes. During the continuous heating, the solution became more viscous with a change of colour from green to brown, but without any visible formation of precipitation or turbidity. The resin was pyrolized in a porcelain crucible at 473 K for 4 h in an electrical furnace. The resulting product was ground and calcined in an alumina crucible at 1173 K for 24 h. The obtained black powder was pressed into pellets (about 2 mm thickness, 13 mm diameter) which were annealed in a tube furnace (Vecstar) under flowing argon, which had been dried by passage over concentrated sulphuric acid at 1473 K for 8 days with several intermittent grindings. The polycrystalline black product has been allowed to cool under the argon flow at the rate of the furnace, typically 12 h, before being removed. In order to avoid any loss of reactants due to their reactivity with alumina, direct contact with the crucible was prevented by putting the pellets in a platinum crucible.

2.2. Diffraction and electrical measurements

The X-ray powder diffraction was carried out using the Diffractometer Empyrean of Panalytical equipped with an incident-beam curved Ge (1 1 1) Johansson monochromator to obtain Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å) radiation. Data were collected at each 0.007° step width for 50 s over a 2θ range from 10.003° to 150.017° and a PIXcel³D solid-state X-ray detector was used in the Bragg–Brentano geometry. The pattern matching and Rietveld refinement were performed with FullProf software [17].

The electrical direct current resistivity measurements were carried out on sintered pellet using a Lucas Labs 302 four point probe with a Keithley 2400 digital Source Meter (Keithley Instruments, Inc., Cleveland, Ohio) in the temperature range 294–579 K.

The oxygen content of the compound has been determined indirectly at room temperature after calculation of the valence average of the transition metal ions obtained by iodometric titration under flowing nitrogen gas taking into account that Ni^{3+} and Cu^{3+} can be present in the sample with Ni^{2+} and Cu^{2+}. In fact, 60 mg of sample was dissolved in a solution of 6 M hydrochloric acid in the presence of excess KI, leading to reduction of Ni^{3+} into Ni^{2+} and all the copper ions (Cu^{3+} and Cu^{2+}), into Cu^{+} ions with formation of iodine that was titrated with $Na_2S_2O_3$ solution using starch as indicator. Sodium thiosulfate solution was standardized using pure copper wire.

3. Results and discussion

3.1. Structural study and oxygen stoichiometry analysis

The exact temperature, gas atmosphere and duration of reaction were found to be crucial in obtaining pure phase containing no traces of the starting materials. In fact the $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ sample has been successfully synthesized under flowing argon at 1473 K for 8 days, in different conditions compared with the analogue family $Ln_{2-x}Sr_xNi_{0.8}Cu_{0.2}O_{4-\delta}$ ($0 < x < 2$) [12] and $NdSrNi_{1-x}Cu_xO_{4-\delta}$ ($0 \leq x \leq 1$), which has been prepared by Chaker et al. [13,14] at 1423 K for period of

4 days in 1 atm of O_2 gas flow. Inspection of the X-ray patterns at intermediate stages of the synthesis appeared to indicate phase purity. The confirmation of successful synthesis requires a satisfactory single-phase Rietveld refinement.

In order to determine the oxygen nonstoichiometry we have carried out iodometric titration using $Na_2S_2O_3$ standard solution. The oxygen nonstoichiometry (δ) is directly correlated to Ni^{3+} and Cu^{3+} contents according to the formulation $DySr_5(Ni_{1-\tau}^{3+} Ni_{\tau}^{2+})_{2.4}(Cu_{1-\tau}^{3+} Cu_{\tau}^{2+})_{0.6}O_{12-\delta}$, with $\delta = (3/2)\tau$. The content $(1-\tau)$ of the average of cations transition metals Ni^{3+} and Cu^{3+} was then determined by iodometric titration. I^- anions reduce Ni^{3+} into Ni^{2+} and all the copper ions (Cu^{3+} and Cu^{2+}), into Cu^+.
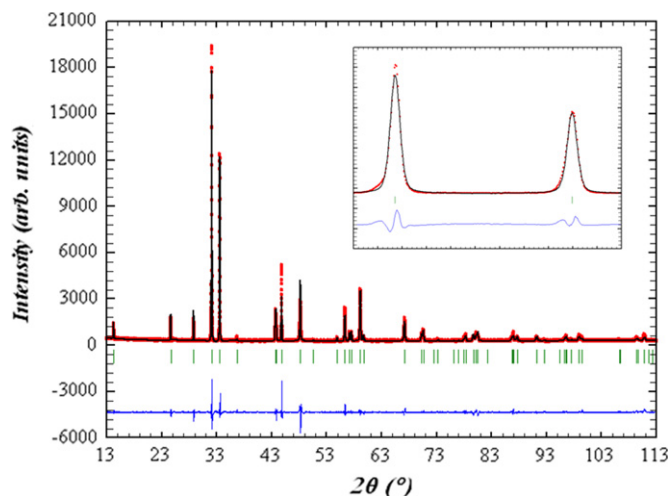

Fig. 1. Observed, calculated, and difference profiles for the Rietveld refinement of $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound.

Table 1
Acquisition conditions and refinement results.

Crystallographic data	Unit cell parameters
Formula: $Dy_{0.33}Sr_{1.67}Ni_{0.8}Cu_{0.2}O_{4-\delta'}$	$a = 3.7696(5)$ Å
Stœchiometric: $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$	$b = 3.7696(5)$ Å
Formula weight (g/mol): 323.617	$c = 12.3747(2)$ Å
Crystal system: tetragonal	$\alpha = \beta = \gamma = 90°$
Space group: $I4/mmm$	$V = 175.848(4)$ Å³
Cell formula units: $Z = 2$	**Profile parameters**
Acquisition conditions	Thompson–Cox–Hastings
Diffractometer: Empyrean of	Pseudo-Voigt function
Panalytical	$H_G^2 = U\tan^2(\theta) + V\tan(\theta) + W$
Monochromator: Ge(111)	$H_L = X\tan(\theta) + (Y/\cos(\theta))$
Wavelength: $\lambda = 1.54056$ Å	$U = 0.1299(1)$
Angular range: $10.003° < 2\theta < 150.017°$	$V = -0.0263(1)$
Step (°2θ): 0.007	$W = 0.0055(4)$
Mean constant count time per point: 50 s	$X = -0.0044(1)$
Conditions and results of the refinement	
Refinement program: FULLPROF 2005	
Zero shift (°2θ): $-0.0084(5)$	
Number of refined parameters: 113	
Background description: Linear interpolation between 100 refined points	
Asymmetric parameters ($2\theta < 50°$): 0.0384, 0.0118	
Preferred Orientation according to [001]: 0.9682	
Agreement factors:	
$R_B = 0.052$	
$R_p = 0.252$	
$R_{wp} = 0.117$	
$R_F = 0.034$	
$\chi^2 = 3.47$	

The titration of the resulting I_2, by a solution of $Na_2S_2O_3$ sodium thiosulfate leads to determine, by considering the average of cations transition metals Ni^{3+} and Cu^{3+}, the value $\tau = 0.36$ and therefore $\delta = 0.54$. The obtained result indicates that the compound is oxygen-deficient.

Profile analysis of X-ray diffraction pattern for $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound has been performed on the basis of a tetragonal system (space group $I4/mmm$). A good fit was obtained using a pseudo-Voigt peak shape function. First, refinement of instrument zero point, unit cell parameters, half-width parameters U, V, W, shape and X converged to $\chi^2 = 2.59$. Secondly, the background was fitted with a linear interpolation between 100 chosen points. The lattice parameters deduced from the whole pattern profile refinement of the X-ray data are found to be $a = 3.7696(5)$ Å and $c = 12.3746(2)$ Å.

The stability of the $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound having K_2NiF_4-type structure can be discussed in terms of the value of the tolerance factor defined by Goldschmidt [18], where

$$t = \frac{(0.33r_{Dy^{3+}} + 1.67r_{Sr^{2+}})/2 + r_{O^{2-}}}{\sqrt{2}[0.8r_{Ni^{3+}} + 0.2r_{Cu^{2+}} + r_{O^{2-}}]}$$

The K_2NiF_4-type structure is stable over the range $0.866 \leq t < 1$. The T (tetragonal) structure exists for $0.88 \leq t \leq 0.99$ and the T/O (tetragonal/orthorhombic) structure is present for $0.866 \leq t < 0.88$. Based on Shannon's ionic radii [19], ($r_{Dy^{3+}} = 1.083$ Å, $r_{Sr^{2+}} = 1.31$ Å in a nine fold coordination and $r_{Ni^{3+}} = 0.56$ Å, in low spin case, $r_{Cu^{2+}} = 0.73$ Å and $r_{O^{2-}} = 1.4$ Å in a six fold coordination), the calculated tolerance factor for $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ is $t = 0.948$, this value was included in the tetragonal symmetry stability range.

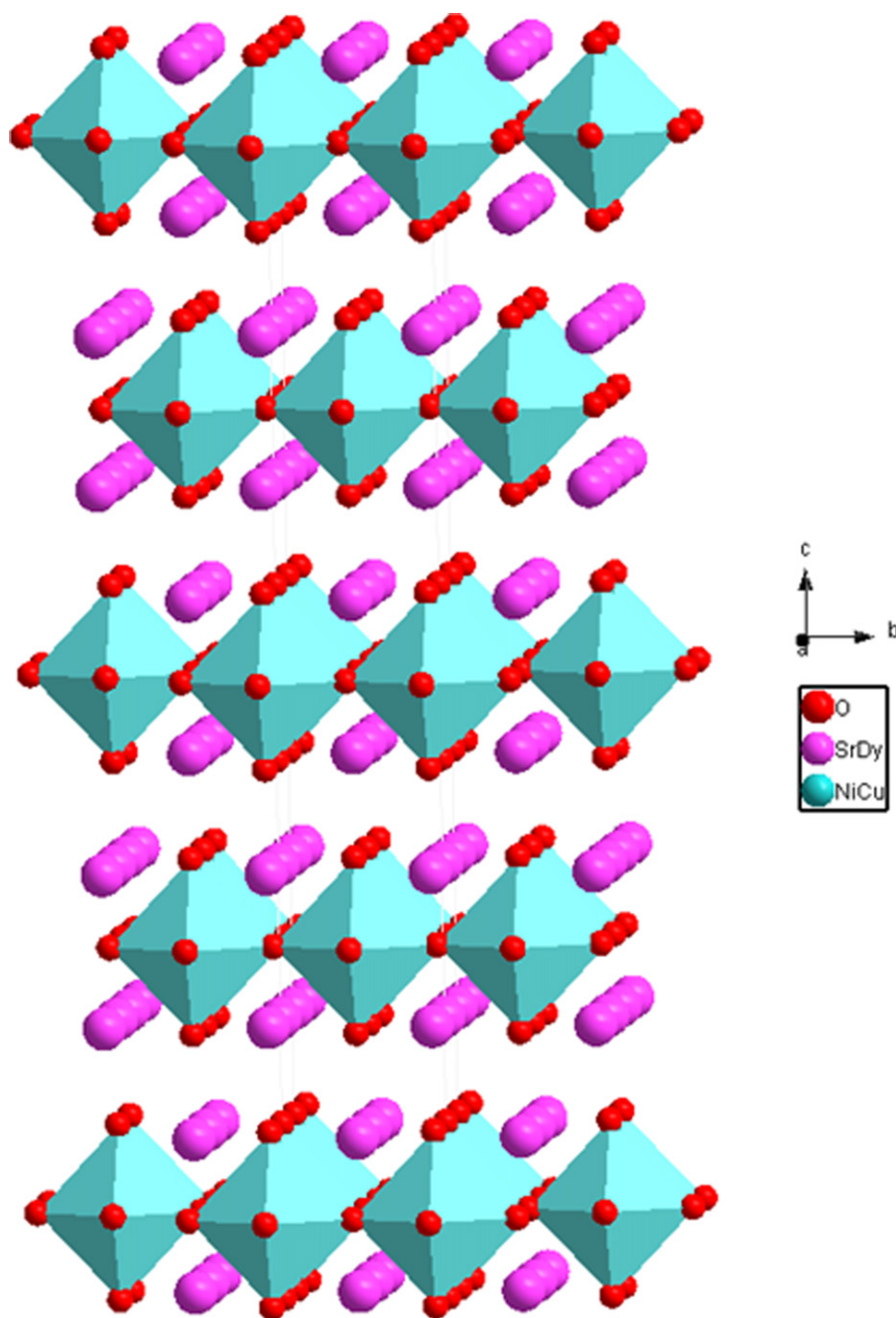**Fig. 2.** Crystal structure of $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ sample with the tetragonal K_2NiF_4-type structure.

Consequently, Rietveld refinement of $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ X-ray data has been performed to confirm the K_2NiF_4-type structure.

The structural refinement was carried out in the space group $I4/mmm$ starting with atomic positions taken from $HoSr_5Ni_{2.4}Cu_{0.6}O_{11}$ [12], with Dy/Sr and O2 atoms situated at special positions $4e$ with coordinates $(0, 0, z)$. The Ni and Cu atoms are located at $(0, 0, 0)$ in sites $2a$, and the O1 atoms at $(0, 1/2, 0)$ in sites $4c$.

Atomic positions have been refined for all the atoms, together with scale factor and profile parameters. Then we tried to allow the occupation factors of the two oxygen sites to vary with the thermal displacement factors. In this way, the least squares analysis converged quickly to provide a good fit to the diffraction pattern with an overall oxygen nonstoichiometry in the $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ phase $\delta \approx 0.46$, value which is very close to that obtained by iodometric titration, which is at first sight not surprising given that the phase can be prepared only under argon, and oxygen vacancies are forming under the argon synthesis atmosphere. However, it is well known that in Rietveld refinements of heavy-atom structures, using X-ray diffraction data, much problematic intensity may be hidden in the thermal displacement factors of relatively light atoms. That is why we have undertaken the refinement of oxygen atoms with fixed occupancies at 0.125 and thermal displacement factors fixed to values bigger than those of heavy atoms. It was also impossible to refine the Ni/Cu ratio, due to the similar X-ray scattering powers of these elements.

3.2. Structure description

The observed, calculated, and difference profiles for the Rietveld refinement of $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound are shown in Fig. 1. An enlargement of the fit to the 2θ region between $31°$ and $34°$ 2θ is also presented in Fig. 1. The structural refined parameters for $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ are summarized in Table 1.

As shown in Fig. 2, the structure can be described as an ordered intergrowth of alternating perovskite $(Dy/Sr)(Ni/Cu)O_3$ and rock salt $(Dy/Sr)O$ layers stacked along the tetragonal c axis. The $(Ni/Cu)O_6$ octahedra share corners in the ab plane forming a two-dimensional array of $(Ni/Cu)–O–(Ni/Cu)$ bonds, which is responsible for a variety of interesting physical phenomena, as for example, the anisotropic electrical transport and magnetic exchange interactions [20,21].

3.3. Electrical conductivity

A very dense ceramic is required in order to perform the electric measurements. Powder was grounded for 3 h in ethanol medium. A pellet (13 mm in diameter and 1.8 mm thick) was fabricated using uniaxial pressing (100 MPa). It was sintered at 1173 K for 1 h, with a heating rate of 5 K min^{-1} and a cooling rate of 10 K min^{-1}.

The total electrical conductivity σ of the sintered ceramic was determined, under air using the four-probe technique, in the temperature range of 294–579 K [22]. The corresponding curve to σ versus $1000/T$ is reported in Fig. 3. The conductivity, first, increases with temperature to reach a maximum observed between 493 and 510 K, then, above this temperature, the conductivity decreases, due to the decrease of the oxygen content and correspondingly of the density of Ni^{3+} and Cu^{3+} carriers [23,24]. We choose to study the conduction mechanism only in the temperature range up to 510 K (where the maximum of conductivity is achieved). Fig. 4 shows the relationship of $Ln(\sigma T)$ versus $1000/T$ for temperature range of 294–510 K. The increase of $Ln(\sigma T)$ with increase in temperature indicates that the compound
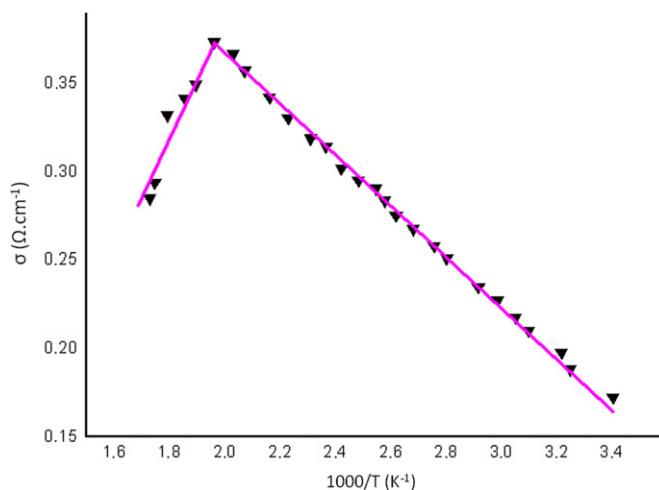

Fig. 3. Thermal variation of the electronic conductivity σ_e for the $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound $(294 \leq T(K) \leq 579)$.

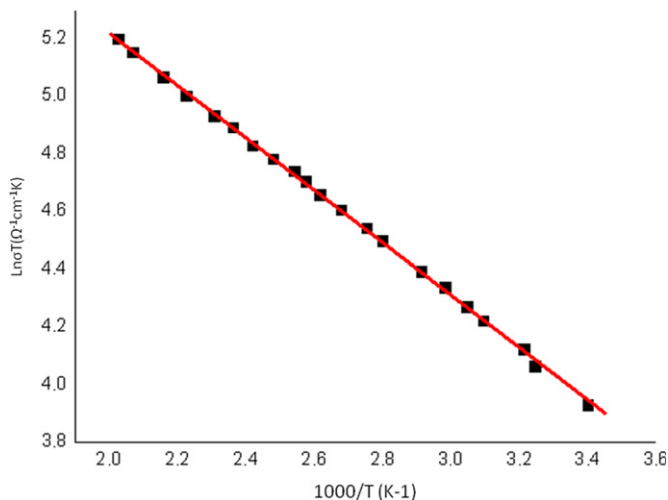**Fig. 4.** Arrhenius relations of $Ln(\sigma T)$ vs $1000/T$ for the $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$.

exhibits a semi-conducting behaviour over the chosen temperature range. To determine the conduction mechanism, we tried to use the thermal activated adiabatic small polaron hopping as conduction model [25,26–28]:

$$\sigma = \sigma_0 T^{-1} \exp\left(\frac{-E_a}{k_B T}\right)$$

with E_a is the activation energy (polaron formation and hopping energy), σ_0 is a constant related to polaron concentration and diffusion. In the analysis of simulated curve: $Ln(\sigma T)=f(1000/T)$, we found that convergence of curve fitting is achieved in the whole range of temperature. This suggests that the charge transport in $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ ceramic, in the temperature range of 294–510 K, is described by adiabatic small polaron hopping model, with activation energy, after fitting, is $E_a=0.078$ eV.

4. Conclusions

Pure $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ compound was successfully formed at 1473 K in argon atmosphere. Rietveld refinement using powder X-ray diffraction data shows that the title compound crystallizes in the tetragonal K_2NiF_4 type structure in space group $I4/mmm$.

Results obtained by iodometric titration indicate that the compound is oxygen-deficient. The transport mechanism in $DySr_5Ni_{2.4}Cu_{0.6}O_{12-\delta}$ has been investigated. On heating, under air, first the conductivity increases with temperature to reach a maximum at 510 K. Above this temperature, the oxide starts to lose oxygen; consequently holes concentration is reduced and resistivity increased. The fitting shows that the adiabatic small polaron hopping model describes the experimental data in the temperature range of 294–510 K.

Acknowledgment

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