Available online at www.sciencedirect.com

ScienceDirect

Thermochimica Acta 467 (2008) 113–116

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Synthesis and physico-chemical properties of phase-pure ceramic $LuBa_2Cu_3O_{7-\delta}$

Nata Matskevich[a,*], Thomas Wolf[b]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia

[b] Karlsruhe Research Center GmbH, Institute of Solid State Physics, Hermann-von-Helmholtz-Plaz, 1, Karlsruhe D-76334, Germany

Received 4 September 2007; received in revised form 17 October 2007; accepted 22 October 2007
Available online 1 November 2007

Abstract

Up to now all ceramics of $REBa_2Cu_3O_{7-\delta}$ (RE = Y and rare-earth elements) were prepared at temperatures of about 900–950 °C except Lu123. $LuBa_2Cu_3O_{7-\delta}$ could not be prepared as single-phase ceramic. In the present study, we have developed the preparation conditions to synthesize phase-pure Lu123 ceramics. We have measured the resistivity of Lu123 ($T_c = 92.1$ K) at different temperatures, determined the enthalpies of reaction including $LuBa_2Cu_3O_{7-\delta}$ by solution calorimetry and have studied the thermodynamic stability of this compound.

Keywords: Lu123 pure ceramic phase; Solid-phase synthesis; Calorimetry; Thermodynamic stability

1. Introduction

Due to the potential application of high-T_c superconductors, much effort has been directed at sintering the high-temperature superconductors and related phases in complex oxide systems [1–3]. Rotors and stators for electric motors and generators, elements for superconductor bearing and levitation systems could be produced from the bulk materials with high enough critical current. The high-T_c superconductors, $REBa_2Cu_3O_{7-\delta}$ (RE123, RE, rare-earth elements) are the most promising compounds for high-temperature applications owing to strong flux-pinning capability under high magnetic fields. It has been believed that the flux-pinning capability of RE123 is determined mainly by oxygen deficiency, impurities, twin boundaries, and cation-site substitution.

Almost all ceramics of $REBa_2Cu_3O_{7-\delta}$ (RE = Y and rare-earth elements) were prepared at temperatures of about 900–950 °C except Lu123. $LuBa_2Cu_3O_{7-\delta}$ could not be prepared as single-phase ceramics [4–10]. According to the theory of phase stability [5], the stability of $REBa_2Cu_3O_{7-\delta}$ is lowered significantly as the ionic radius of RE^{3+} decreases. The field of thermodynamic stability is narrowest for $LuBa_2Cu_3O_{7-\delta}$ [5]. High-temperature decomposition of $LuBa_2Cu_3O_{7-\delta}$ occurs at temperatures >900 °C ($P_{O_2} = 0.21$ bar) [7,8].

Synthesis of $LuBa_2Cu_3O_{7-\delta}$ by direct combination of the reactants was attempted at several temperatures between 900–1000 °C both in air and in pure O_2 [6]. The resulting products were a mixture of $BaCuO_2$, Lu_2BaCuO_5 and CuO. The Lu123 phase did not form under the conditions described above even though its neighboring ytterbium compound formed easily [6]. Samoylenkov et al. [9] observed no XRD peaks of $LuBa_2Cu_3O_{7-\delta}$ after annealing the ceramic precursor in an oxygen atmosphere at 850–920 °C for 5 h. They concluded that the successful preparation of $LuBa_2Cu_3O_{7-\delta}$ is only possible from the melt. Authors of papers [10] reported that they obtained ceramic mixture of 70% 123Lu phase and 30% of Lu_2BaCuO_5, $BaCuO_2$.

In the present study, for the first time we report the synthesis and physico-chemical properties of phase-pure Lu123 ceramic. We have measured the resistance of Lu123 at different temperatures, determined the enthalpies of reaction including $LuBa_2Cu_3O_{7-\delta}$ and have studied the stability of this compound.

---

[*] Corresponding author. Tel.: +7 3833 306449; fax: +7 3833 309489.
E-mail address: nata@che.nsk.su (N. Matskevich).

0040-6031/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.10.013

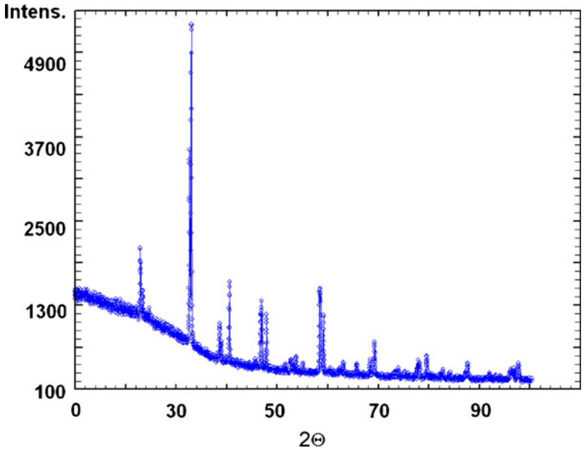

Fig. 1. Powder X-ray diffractogram of $LuBa_2Cu_3O_{6.92}$.

Table 1
Power X-ray diffraction data for $LuBa_2Cu_3O_{6.92}$

Nr.	2*Θ*, obs.	*h*	*k*	*l*	2*Θ*, calc.	Int.	*d*, obs.	*d*, calc.
1	22.862	0	0	3	22.854	38.7	3.8866	3.8881
2	23.368	0	1	0	23.384	26.8	3.8038	3.8011
3	32.594	1	0	3	32.604	65.0	2.7450	2.7442
4	32.958	0	1	3	32.927	100	2.7155	2.7180
		1	1	0	32.989			2.7131
5	38.587	0	0	5	38.561	19.2	2.3313	2.3329
		1	0	4	38.615			2.3297
6	40.505	1	1	3	40.511	29.9	2.2253	2.2249
7	45.625	0	1	5	45.589	9.4	1.9867	1.9883
		1	1	4	45.636			1.9863
8	46.683	0	0	6	46.686	22.3	1.9442	1.9440
9	46.875	2	0	0	46.870	24.9	1.9367	1.9368
10	47.828	0	2	0	47.821	21.7	1.9003	1.9005
11	53.660	0	2	3	53.633	10.6	1.7067	1.7075
		2	1	1	53.644			1.7071
		1	2	0	53.675			1.7062
12	55.073	0	0	7	55.068	8.6	1.6662	1.6663
13	58.359	1	1	6	58.347	29.4	1.5799	1.5802
14	59.092	1	2	3	59.078	21.0	1.5621	1.5624
15	63.073	0	2	5	63.038	8.8	1.4727	1.4735
		1	2	4	63.076			1.4727
16	65.709	1	1	7	65.708	8.3	1.4199	1.4199
17	68.311	2	0	6	68.306	9.5	1.3720	1.3721
18	69.208	2	2	0	69.200	14.1	1.3564	1.3565
19	73.918	2	2	3	73.942	7.1	1.2812	1.2808
20	79.546	1	3	0	79.532	10.6	1.2041	1.2042
21	87.641	2	2	6	87.644	8.8	1.1125	1.1125
22	96.170	3	1	6	96.195	7.0	1.0352	1.0350
23	96.857	3	2	3	96.824	7.2	1.0296	1.0299
24	97.695	2	3	3	97.705	8.7	1.0230	1.0229
		1	0	11	97.729			1.0228

2. Experimental part

2.1. Sample preparation

$LuBa_2Cu_3O_{7-\delta}$ was prepared from Lu_2O_3, CuO, and $BaCO_3$, all of the purity 99.999%. In a first step $BaCO_3$ has been calcined at 850 °C for 18.5 h, and then at 900 °C for 65 h in a continuously pumped vacuum. At the end of this process the pressure was less than 3×10^{-5} bar. From weight loss a complete decomposition to BaO could be confirmed. In a second step about 7 g of a stoichiometric mixture of oxides was ground in a planetary mill (PULVERISETTE, Fritsch Company) with a rate of 50–250 rpm for one week to obtain an extremely fine-grained powder mixture. Finally, the powder has been pressed into 7 pellets with a diameter of 10 mm and then reacted at 850 °C for 150 h and then at 900 °C for more than 100 h in an atmosphere of 100 mbar flowing oxygen. A subsequent oxidation treatment at 450 °C for more than 23 h in 1 bar O_2 resulted in Lu123 with optimal superconducting properties. The low peritectic melting point, and the thus resulting slow reaction kinetics are the main challenges of the synthesis of Lu123. They have been overcome by the preparation of a highly reactive BaO powder, by a grinding and milling step down to the <1 μm level, and finally, by a gradual increase of the reaction temperatures to avoid a loss of melt of eutectic composition before the completed synthesis. The sample was shown to be a phase-pure ceramic with an orthorhombic structure (space group Pmmm) by X-ray powder diffraction (STADI-P, Stoe, Germany, Cu $K\alpha_1$) performed at the Institute of Solid State Physics (Karlsruhe Research Centre) (Fig. 1 and Table 1). The fractional atomic coordinates are given in Table 2. The initial coordinates of atoms for the structural refinements have been used from reference [11] for Y123. The method to determine atom sites was the same as described in paper [12] in detail.

The refined cell parameters obtained for $LuBa_2Cu_3O_{6.92}$: $a = 3.8737(6)$ Å, $b = 3.8011(7)$ Å, $c = 11.664(3)$ Å, cell volume: 171.75(7) $Å^3$. These parameters are in a good agreement with parameters for single crystal of Lu123 obtained by a flux growth method ($c = 11.69$ Å) [10] and for $LuBa_2Cu_3O_{7-x}$ thin films prepared by metal organic chemical vapour deposition ($c = 11.67$ Å) [9]. It was possible to expect following to data for $YbBa_2Cu_3O_{7.02}$ ($c = 11.607$ Å) [13] that lattice parameters could be smaller. Nevertheless sample obtained by us had oxygen content (6.92) smaller than oxygen content of Yb123 (7.02) in paper [13] and the superconductivity transition (92.1 K) higher than T_c of $YbBa_2Cu_3O_{7.02}$ sample (90 K) [13]. There are no data for Lu123 in paper [13].

All compounds were characterized by X–ray power diffraction (STADI-P, Cu $K\alpha_1$) and chemical analysis. For analysis of Lu, a spectrophotometric method (spectrophotometer SF-46) was used. Ba was determined by flame photometry, and Cu by atomic absorption (air–acetylene flame, Hitachi Z-8000) methods. The following results were obtained (wt. %): Lu, found

Table 2
Fractional atomic coordinates of $LuBa_2Cu_3O_{6.92}$

Atom	*x*	*y*	*z*
Lu	0.5	0.5	0.5
Ba	0.5	0.5	0.1888 (4)
Cu1	0	0	0
Cu2	0	0	0.3601 (4)
O1	0	0	0.1570 (3)
O2	0	0.5	0.3801 (4)

23.17 ± 0.12 (calculated 23.29); Ba, found 36.30 ± 0.26 (calculated 36.57); Cu, found 25.28 ± 0.18 (calculated 25.38). The oxygen content was determined by iodometric titration. The oxygen index for $LuBa_2Cu_3O_{7-\delta}$ was 6.92 (±0.03). According to the results of the analyses the Lu123 phase was found to be single phase with an accuracy of about 1%.

2.2. *Calorimetric investigations*

Solution calorimetry was carried out in an automatic calorimeter with an isothermal jacket. The calorimeter consists of a glass Dewar reaction vessel (200 ml) with a brass cover. This instrument has a 100 Ω platinum thermometer, 60 Ω calibration heater, cooler, mixer, and a device to hold and to break ampoules, which were mounted on the lid closing the Dewar vessel. The platinum thermometer and device to input power were connected with voltmeter Solartron 7061. The voltmeter was computer-controlled using interface PCI-GRIB (IEEE 488) and Matlab program written in our laboratory. The calorimetric vessel was maintained at 323.15 K with temperature drift less than 0.0003 °C for 10 h. The experimental procedure was described earlier in detail [14,15]. The apparatus has been tested several times by the dissolution of KCl in water. The obtained dissolution heat of KCl (17.529 ± 0.009 kJ mol^{-1}, the molality of the final solution was 0.028 mol kg^{-1}) was in a good agreement with the value recommended in the literature. The certified values are 17.42 ± 0.02 kJ mol^{-1}) [16], 17.47 ± 0.07 kJ mol^{-1} [17].

6.0 M HCl (aq) (reagent grade) was chosen after several trials of other concentrations since it dissolves the superconducting oxides and related phases readily. The experiments were performed at 323.15 K. At lower temperature the rate of dissolution of CuO is small. First of all we tried to dissolve Lu_2O_3 in different concentrations of HCl. However, it was impossible. Therefore we chose a thermochemical cycle designed in such a way that it was possible to compare the enthalpy of solution of $LuBa_2Cu_3O_{7-\delta}$ with the enthalpy of solution of the mixture $0.5Lu_2BaCuO_5 + 1.5BaCO_3 + 2.5CuO$.

The enthalpies of solution of five samples of Lu_2BaCuO_5 (about 0.08 g), five samples of $BaCO_3$ (about 0.08 g), five samples of CuO (about 0.05 g), six samples of $LuBa_2Cu_3O_{7-\delta}$ (about 0.2 g) in 6.0 mol dm^{-3} HCl (aq) (200 ml) at 323.15 K are reported. Samples were stored under dry N_2 before use.

The calorimetric scheme for determination of the enthalpy of $LuBa_2Cu_3O_{7-\delta}$ is described by Eqs. (1)–(5) (see Table 3). "Soln" refers to 6.0 M HCl (aq) in all of these equations.

The measured enthalpies of solution of Lu_2BaCuO_5, $BaCO_3$, CuO, $LuBa_2Cu_3O_{6.92}$ were determined as: $\Delta_{sol}H_1^\circ$ (323.15 K) = −464.7 ± 2.2 kJ mol^{-1}, $\Delta_{sol}H_2^\circ$ (323.15 K) = −15.3 ± 1.3 kJ mol^{-1}, $\Delta_{sol}H_3^\circ$ (323.15 K) = −51.1 ± 0.7 kJ mol^{-1}, $\Delta_{sol}H_4^\circ$ (323.15 K) = −730.7 ± 3.1 kJ mol^{-1}, respectively. The dissolution enthalpies were calculated as average values of five or six calorimetric experiments. Errors were calculated for the 95% confidence interval using the Students coefficient.

These enthalpies of dissolution were used for calculating the enthalpy of the reaction

$$0.5Lu_2BaCuO_5(s) + 1.5BaCO_3(s) + 2.5CuO\,(s) + 0.21O_2(g) = LuBa_2Cu_3O_{6.92}(s) + 1.5CO_2(g)$$

$$\Delta_r H_5^\circ(323.15\,K) = +347.6 \pm 4.2\,kJ\,mol^{-1},$$

where

$$\Delta_r H_5^\circ = 0.5\Delta_{sol}H_1^\circ + 1.5\Delta_{sol}H_2^\circ + 2.5\Delta_{sol}H_3^\circ - \Delta_{sol}H_4^\circ.$$

It is possible to write this equation if solution obtained after dissolution of mixture $0.5Lu_2BaCuO_5 + 1.5BaCO_3 + 2.5CuO$ and solution obtained after dissolution of $LuBa_2Cu_3O_{6.92}$ are assumed to be identical. The identical state of these solutions, however, needs some proof due to possible presence of various oxidation states of Cu (Cu^{2+}, Cu^{3+}) in $LuBa_2Cu_3O_x$. In the present study the electronic spectra of solutions have been investigated in the range of 10^4–3×10^4 cm^{-1} in air atmosphere. It was shown that in experiments conducted in air the spectra of solutions became identical in 1–2 min after dissolution was finished.

Literature data for the heat of the reaction of $BaO + CO_2 = BaCO_3$ ($\Delta_r H_5^\circ$ (323.15 K) = −272.4 ± 1.5 kJ mol^{-1} [16]) were used to calculate the enthalpies of the following reaction

$$0.5Lu_2BaCuO_5(s) + 1.5BaO(s) + 2.5CuO\,(s) + 0.21O_2(g) = LuBa_2Cu_3O_{6.92}\,(s)$$

$$\Delta_r H_5^\circ\,(323.15\,K) = -61.0 \pm 4.8\,kJ\,mol^{-1}.$$

Our experimental data and measured or estimated entropies of all the substances employed in reaction above [16,18] permit one to conclude that the formation of Lu123 phase from the mixture Lu_2BaCuO_5, BaO, CuO is thermodynamically favourable at room temperature.

As it was mentioned in papers [7,8] the decomposition of Lu123 takes place at temperatures higher than 900 °C. On the basis of experimental data of this paper, earlier data measured by us for the reaction $BaCuO_2 + CO_2 = BaCO_3 + CuO$

Table 3
Thermochemical cycle for the determination of the enthalpy of reaction of $LuBa_2Cu_3O_{6.92}$

Nr.	Reactions	$-\Delta H^\circ$ (kJ mol^{-1})
1	$0.5Lu_2BaCuO_5(s) + 5HCl\,(soln) = LuCl_3(soln) + 0.5BaCl_2\,(soln) + 0.5CuCl_2\,(soln) + 2.5H_2O(soln)$	464.7 ± 2.2
2	$1.5BaCO_3(s) + 3HCl\,(soln) = 1.5BaCl_2(soln) + 1.5CO_2\,(g) + 1.5H_2O\,(soln)$	15.3 ± 1.3
3	$2.5CuO(s) + 5HCl\,(soln) = 2.5CuCl_2\,(soln) + 2.5H_2O\,(soln)$	51.1 ± 0.7
4	$LuBa_2Cu_3O_{6.92}\,(s) + 13HCl\,(soln) = LuCl_3\,(soln) + 2BaCl_2(soln) + 3CuCl_2(soln) + 6.5H_2O(soln) + 0.21O_2\,(g)$	730.7 ± 3.1
5	$0.5Lu_2BaCuO_5(s) + 1.5BaCO_3(s) + 2.5CuO\,(s) + 0.21O_2(g) = LuBa_2Cu_3O_{6.92}\,(s) + 1.5CO_2(g)$	−347.6 ± 4.2

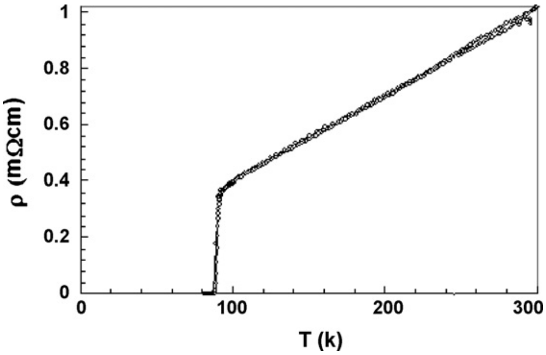

Fig. 2. The resistivity, ρ (T), of $LuBa_2Cu_3O_{6.92}$ up to 300 K.

($\Delta_r H_5{}^\circ$ (323.15 K) = −201.1 ± 1.9 kJ mol^{-1} [19]) and measured or estimated entropies of the compounds [16], we calculated the enthalpy and estimated the temperature of reaction of Lu_2BaCuO_5 with $BaCuO_2$ and CuO forming Lu123.

$$0.5Lu_2BaCuO_5(s) + 1.5BaCuO_2(s) + CuO\,(s) + 0.21O_2(g)$$
$$= LuBa_2Cu_3O_{6.92}$$

$$\Delta_r H_7{}^\circ\,(323.15\,K) = +45.9 \pm 5.0\,kJ\,mol^{-1}.$$

This reaction takes place above 1067 K (≅794 °C) where $\Delta_r G_7{}^\circ = 0$ ($P_{O_2} = 1$ bar).

Taking into account this result and data [7,8] about the decomposition of Lu123 at temperature higher than 900 °C, it can be concluded that the temperature field where Lu123 forms is rather narrow. It was one of the difficulties encountered in preparing pure ceramic Lu123.

There is increasing number of reports that superconducting oxides are unstable with respect to atmospheric H_2O and CO_2. A typical reaction for $REBa_2Cu_3O_{7-\delta}$ [20] is given in the equation below, where the end products are the stable

$$REBa_2Cu_3O_{7-\delta}\,(s) + 1.5H_2O(g) + 5CO_2(g)$$
$$= 0.5RE_2(CO_3)_3(s) + 2BaCO_3(s) + 1.5[CuCO_3 . Cu(OH)_2](s)$$
$$+ yO_2(g)$$

Morrs et al. [20] estimated $\Delta_r G^\circ = -355$ kJ mol^{-1} for the decomposition reaction above with RE = Y, confirming the instability with respect to water and CO_2.

It is possible to use our experimental data to calculate a similar reaction for $LuBa_2Cu_3O_{7-\delta}$ in the future.

2.3. Resistivity

We have carried out an investigation of the electrical resistivity of a $LuBa_2Cu_3O_{7-\delta}$ ceramic sample. ρ (T) has been measured up to 520 K using the four probe method [21]. Fig. 2 shows the ρ (T) dependence for the $LuBa_2Cu_3O_{7-\delta}$ pure ceramics. Measurements were carried out at rate 5 K/min. The value of the electrical resistivity equals 1 mΩ cm at 300 K, which is typical for single-phase samples. The midpoint of the superconductivity transition is 92.1 ± 1.1 K (10–90%).

Acknowledgments

We are grateful for financial support from NATO programme (ref. CBR.NR.NRCLG 982559), Karlsruhe Research Center, DFG programme (grant LO 250/24-1) and "Program of Fundemental Investigation of Siberian Branch of the Russian Academy of Sciences".

References

[1] Th. Zeiske, R. Sonntag, D. Hohlwein, N.H. Andersen, Th. Wolf, Nature 353 (1991) 542.
[2] D.A. Cardwell, N. Hari Babu, Physica C 445–448 (2006) 1.
[3] G. Krabbes, Th. Hopfinger, C. Wende, P. Diko, G. Fuchs, Supercond. Sci. Technol. 15 (2002) 665.
[4] K.I. Gnanasekar, R. Pinto, A.S. Tamhane, L.C. Gupta, S.P. Pai, P.R. Apte, M. Sharon, R. Vijayaraghavan, Phys. Rev. B 52 (1995) 1362.
[5] S. Somasundaram, A.M. Ram, A.M. Umarji, C.N.R. Rao, Mater. Res. Bull. 25 (1990) 331.
[6] E. Hodorowicz, S.A. Hodorowicz, H.A. Elick, J. Alloy Compd. 181 (1992) 445.
[7] V.K. Janovskyi, V.I. Voronkova, I.V. Vodolazskaja, L.N. Leont'eva, T.P. Petrovskaya, Supercond. Phys. Chem. Technol. 2 (1989) 30.
[8] G.V. Bazuev, Supercond. Phys. Chem. Technol. 5 (1992) 171.
[9] S.V. Samoylenkov, O.Yu. Gorbenko, I.E. Graboy, A.R. Kaul, Yu.D. Tretyakov, J. Mater. Chem. 6 (1996) 623.
[10] M.Yu. Kameneva, L.P. Kozeeva, N.A. Myrzina, V.S. Danilovich, V.E. Fedorov, Chem. Subst. Dev. 6 (2002) 699.
[11] W.-J. Jang, H. Mori, M. Watahiki, S. Tajima, N. Koshizuka, S. Tanaka, J. Solid State Chem. 130 (1997) 42.
[12] L.P. Kozeeva, M.Yu. Kameneva, N.V. Podberezskaya, D.Yu. Naumov, N.F. Beizel, U.H. Paek, V.E. Fedorov, J. Ceram. Pros. Res. 3 (2002) 123.
[13] M. Guillaume, P. Allenspach, W. Henggeler, J. Mesot, B. Roessli, U. Staub, P. Fischer, A. Furrer, V. Trounov, J. Phys. Condens. Matter. 6 (1994) 7963.
[14] N.I. Matskevich, F.A. Kuznetsov, D. Feil, K.-J. Range, Thermochim. Acta 319 (1998) 1.
[15] N.I. Matskevich, M.V. Chuprova, R. Punn, C. Greaves, Thermochim. Acta 459 (2007) 125.
[16] D.R. Stull, H. Prophet, JANAF Thermochemical Tables, second ed., NSRDS-NBS, 37 US Govt. Printing Office, Washington, DC, 1971.
[17] C. Gunter, R. Pfestorf, M. Rother, J. Seidel, R. Zimmermann, G. Wolf, V. Schroder, J. Therm. Anal. Calorim. 33 (1988) 359.
[18] J. Buan, B.P. Stojkovich, N.E. Israeloff, A.M. Goldman, C.C. Huang, O.T. Valls, J.Z. Liu, R. Shelton, Phys. Rev. Lett. 72 (1994) 2632.
[19] N.I. Matskevich, Th. Wolf, Thermochim. Acta 421 (2004) 231.
[20] L.R. Morss, D.C. Sonnenberger, R.J. Thorn, Inorg. Chem. 27 (1988) 2107.
[21] V.N. Naumov, G.I. Frolova, A.I. Romanenko, O.V. Anikeeva, N.I. Matskevich, Yu.G. Stenin, Physica C 408–410 (2004) 733.