Thermal expansion of YBa$_{2-x}$Me$_x$Cu$_3$O$_{7-\delta}$ (Me = Sr, Ca; $0.0 \leq x \leq 1.0$) solid solutions at elevated temperatures

A. I. CLYNDYUCK, G. S. PETROV, L. A. BASHKIROV
Department of Physical and Colloid Chemistry, Belarussian State Technological University, 220630, Minsk, Belarus
E-mail: root@bgtu.minsk.by

The thermal expansion of high-temperature superconductors (HTSC) solid solutions YBa$_{2-x}$Me$_x$Cu$_3$O$_{7-\delta}$ (Me = Sr, Ca; $0.0 \leq x \leq 1.0$) was investigated by dilatometric method in air at 293–1123 K. The temperatures of phase transitions: orthorhombic phase 1 to orthorhombic phase 2 and orthorhombic phase 2 to tetragonal phase were determined. The influence of isovalent substitution of barium by strontium or calcium on the crystal structure, temperature of phase transitions and values of linear thermal expansion coefficient (LTEC, α) of investigated solid solutions was analyzed.
© *2002 Kluwer Academic Publishers*

1. Introduction

Influence of isovalent substitution of ions, which are in different crystallographic positions of crystal lattice of YBa$_2$Cu$_3$O$_{7-\delta}$-type HTSC, on the temperature of transition into superconducting state of these phases (T_c) has been studied in detail. So, substitution of 10–20% of copper by ions of 3d-elements (Fe, Co, Ni, Zn *et al.*) results in suppression of superconductivity [1]. Substitution of barium by ions of other alkaline-earth metals leads to the significant decrease of T_c, however samples stay superconducting at temperatures above temperature of liquid nitrogen boiling even under substitution of a half of barium by the strontium or calcium [2–4]. But in the literature there are data on significant increase of density of critical current (j_c of YBa$_2$Cu$_3$O$_{7-\delta}$-type phases under partial substitution of barium by strontium [5]. Partial or full substitution of yttrium by ions of rare-earth elements practically has no influence on T_c, which for phases RBa$_2$Cu$_3$O$_{7-\delta}$ is near 90 K [6]. Influence of isovalent substitution of ions on the behaviour of these phases above room temperature has not been experimentally studied.

Meanwhile a study of physicochemical characteristics of YBa$_2$Cu$_3$O$_{7-\delta}$-type HTSC (and in particular of solid solutions) at high temperatures is of a significant interest due to a number of reasons. Firstly, this is possible expansion of HTSC applications, in particular, as possible materials for high-temperature electrochemical devices [7, 8] or catalysts of chemical reactions [9, 10]. Secondly, for the development of optimum technology of synthesis of HTSC materials with the possibility of variation of their characteristics with the given step over a wide range. Finally, a study of peculiarities of behaviour of HTSC at high temperatures, where the most intensive structural changes take place and oxygen nonstoichiometry of the samples

changes more appreciably, possibly, will be useful for the clarification of mechanism of superconductivity of these phases.

In the literature there are detailed data on the thermal expansion of YBa$_2$Cu$_3$O$_{7-\delta}$ over broad ranges of temperatures and partial pressures of oxygen [11–14]. It is found that LTEC of YBa$_2$Cu$_3$O$_{7-\delta}$ increases with temperature increase [11–14] and with reducing of partial pressure of oxygen [14] and LTEC values of YBa$_2$Cu$_3$O$_{7-\delta}$ are ranged from 14×10^{-6} K^{-1} to 23×10^{-6} K^{-1} at 673–1073 K [14]. Partial or full substitution of yttrium by rare-earth element, according to [14, 15], weakly influences on the value of LTEC of RBa$_2$Cu$_3$O$_{7-\delta}$-type phases. Literature data on the thermal expansion of solid solutions of YBa$_2$Cu$_3$O$_{7-\delta}$-type HTSC are not numerous [8, 15].

We studied thermal expansion of solid solutions YBa$_{2-x}$Me$_x$Cu$_3$O$_{7-\delta}$ (Me = Sr (I), Ca (II); $x = 0$; 0.2; 0.4; 0.6; 0.8; 1.0) at 293–1123 K in air.

2. Experimental procedure

All samples were prepared by the ceramic method from Y$_2$O$_3$ (super pure), CuO (super pure), BaCO$_3$ (pure), SrCO$_3$ (pure for analysis) and CaCO$_3$ (pure for analysis), taken in corresponding stoichiometric proportions. After carefully grinding in an agate mortar, tablets were pressed, having diameter 19 and height 5–7 mm. For better compaction isobutanol or ethanol was added to the mixtures. After pressing tablets were dried in air for 1–2 hours at 373–473 K to remove the alcohol and then annealed in boats of alumina in air for 40–80 hours at 1173 K with several intermediate regrindings. For dilatometric measurements from powders we pressed rods (of $5 \times 5 \times 30$ mm^3) under pressure 100–150 MPa, which then were sintered in air for 15–20 hours at 1223 K. After sintering samples were annealed in the

flow of oxygen at the 718 ± 5 K for 10 hours. Density of samples after sintering and annealing was about 90–95% of the theoretical X-ray density.

Identification of prepared samples was conducted by X-ray phase analysis at room temperature using diffractometer DRON-3 (Cu K_α-radiation, Ni-filter). Oxygen nonstoichiometry of samples was determined iodometrically [16].

Thermal expansion of (I) and YBaCaCu$_3$O$_{7-\delta}$ was studied by a quartz dilatometer DI-24 ADAMEL-LHOMARGY systems in air at heating and cooling rate equal to 2 K/min [17]. Samples (II) were studied by a quartz dilatometer having clock-type indicator (accuracy of scale of indicator was ± 0.001 mm) in air at 293–1023 K during step-by-step heating and cooling of the samples with their keeping at each temperature for 15 minutes [18].

3. Results and discussion
3.1. X-ray analysis
All samples after annealing at 1173 K and sintering at 1223 K were, within accuracy of X-ray method, monophase and they were, depending on the composition, tetragonal (for large values of x) or orthorhombic (for small x). After oxygenation all samples had orthorhombic structure.

Calculation of parameters of unit cells of samples was made using (200), (020), (006) reflexes. Values of parameters of unit cells, index of oxygen nonstoichiometry (δ), X-ray (ρ_c) and experimental (ρ_e) (determined by mass and geometric sizes of samples) density of solid solutions are given in Table I.

As is clear from the data of Table I, in the YBa$_2$Cu$_3$O$_{7-\delta}$ crystal lattice substitution of larger barium ions by smaller strontium ions ($r_{Ba^{2+}} = 0.166$, $r_{Sr^{2+}} = 0.146$ nm for coordination number (C.N.) equal

to 10) [19] results in expected decrease of the parameters a, b and c as well as volume of unit cell V. Values of parameters and volumes of unit cells of solid solutions YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$, obtained by us, are in satisfactory agreement with previous data [2–4]. We observed increase of index oxygen nonstoichiometry (δ) with increase of strontium content in solid solutions of HTSC YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$, which, is probably due to the change of nature of interionic interactions in the crystal lattice of samples, particularly, between (CuO$_2$)-(BaO)-(CuO)-layers (Fig. 1), containing
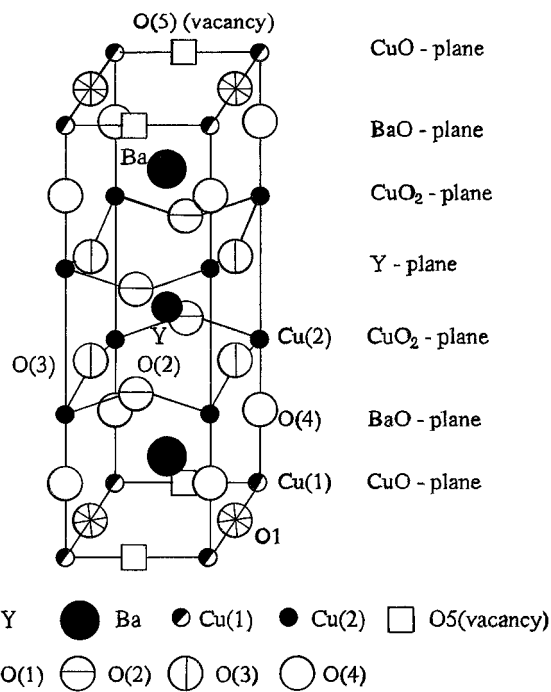

Figure 1 The crystal structure of HTSC of YBa$_2$Cu$_3$O$_{7-\delta}$-type [20].

T A B L E I The parameters (a, b, c, nm) and volume (10^3 V, nm^3) of unit cell, oxygen nonstoichiometry (δ), X-ray (10^{-3} ρ_c, kg·m^{-3}) and experimental (10^{-3} ρ_e, kg·m^{-3}) density of YBa$_{2-x}$Me$_x$Cu$_3$O$_{7-\delta}$ (Me = Sr, Ca) solid solutions

No	Me=	x=	a	b	c	V	δ	ρ_c	ρ_e	Ref.
1	Sr	0.0	0.3828	0.3886	1.169	173.959	0.07	6.35	5.71	Our data
2	Sr	0.0	0.3823	0.3886	1.1687	173.624	–	–	–	[2]
3	Sr	0.0	0.3823	0.3892	1.1684	173.848	0.1	–	–	[3]
4	Sr	0.2	0.3821	0.3882	1.166	172.984	0.09	6.28	5.65	Our data
5	Sr	0.2	0.3817	0.3880	1.1656	172.645	–	–	–	[2]
6	Sr	0.2	0.3805	0.3875	1.1624	171.388	0.2	–	–	[3]
7	Sr	0.4	0.3815	0.3870	1.165	171.927	0.11	6.22	5.66	Our data
8	Sr	0.4	0.3809	0.3877	1.1640	171.894	–	–	–	[2]
9	Sr	0.4	0.3792	0.3859	1.1578	169.425	0.2	–	–	[3]
10	Sr	0.5	0.3804	0.3873	1.1623	171.240	–	–	–	[4]
11	Sr	0.6	0.3806	0.3870	1.161	170.973	0.13	6.16	5.61	Our data
12	Sr	0.6	0.3804	0.3870	1.1614	170.975	–	–	–	[2]
13	Sr	0.8	0.3805	0.3859	1.158	169.964	0.16	6.09	5.60	Our data
14	Sr	0.8	0.3800	0.3857	1.1589	169.855	–	–	–	[2]
15	Sr	1.0	0.3802	0.3847	1.154	168.818	0.19	6.03	5.58	Our data
16	Sr	1.0	0.3793	0.3857	1.1558	169.089	–	–	–	[2]
17	Sr	1.0	0.3780	0.3850	1.1548	168.058	–	–	–	[4]
18	Ca	0.2	0.3830	0.3886	1.168	173.877	0.11	6.16	5.61	Our data
19	Ca	0.4	0.3828	0.3892	1.167	173.928	0.14	5.97	5.55	Our data
20	Ca	0.5	0.3823	0.3878	1.1689	173.296	–	–	–	[4]
21	Ca	0.6	0.3827	0.3888	1.166	173.553	0.17	5.79	5.41	Our data
22	Ca	0.75	0.3817	0.3871	1.1670	172.431	–	–	–	[4]
23	Ca	0.8	0.3819	0.3867	1.164	171.903	0.20	5.65	5.34	Our data
24	Ca	1.0	0.3817	0.3876	1.163	172.979	0.23	5.46	5.19	Our data
25	Ca	1.0	0.3822	0.3872	1.1694	173.057	–	–	–	[4]

in planes (CuO) so-called weekly-fixed oxygen (positions O1 in Fig. 1) [20]. When substitution of barium by calcium parameters a, b and volume of unit cell V of solid solutions $YBa_{2-x}Ca_xCu_3O_{7-\delta}$ were decreased slightly. Parameter c was decreased noticeably with increase of degree of substitution of barium by calcium and with decrease of oxygen content in samples.

As far as ion radius of calcium ($r_{Ca^{2+}} = 0.142$ and 0.126 nm for C.N. 10 and 8 respectively [19]) is closer to the ion radius of yttrium ($r_{Y^{3+}} = 0.116$ and 0.124 nm for C.N. 8 and 9 respectively [19]), than to the ion radius of barium, when forming of solid solutions $YBa_{2-x}Ca_xCu_3O_{7-\delta}$ calcium ions can occupy (and, possibly does, occupy) not only positions of barium as well as positions of yttrium, displacing a part of yttrium ions into vacant lattice sites of barium sublattice. That is to say, partial breach of ordering in the arrangement of ions of yttrium and barium (Ba(Ca,Y)-Y(Ca)-Ba(Ca,Y) instead of Ba-Y-Ba) at A-positions of perovskite-like (ABO_3) cell of $YBa_2Cu_3O_{7-\delta}$ (Fig. 1) takes place, which is similar to the disordering in the arrangement of lanthanum and barium ions in $LaBa_2Cu_3O_{7-\delta}$ [20]. Thus, formula of solid solutions $YBa_{2-x}Ca_xCu_3O_{7-\delta}$ (taking into account distribution of cations over different sublattices) may be written as $(Y_{1-z}Ca_z)(Ba_{2-x}Ca_{x-z}Y_z)Cu_3O_{7-\delta}$.

3.2. Thermal expansion

Typical dependence of relative elongation ($\Delta l/l_0$) and LTEC (α) for the solid solutions (I–II) is given in Fig. 2. For some compositions hysteresis was observed an heating-cooling, which was small for temperature dependences of $\Delta l/l_0$ and vastly greater for LTEC dependences. This hysteresis, was probably, due to the slow oxygen exchange between samples and environment (air) [13]. Values α for solid solutions (I–II) at partial substitution of barium by strontium or calcium were about $(1.2 - 1.4) \times 10^{-5}$, $(1.8 - 2.4) \times 10^{-5}$ and $(1.6 - 1.8) \times 10^{-5}$ K^{-1} for temperature intervals 293–593, 593–893 and 893–1023 K respectively. These data
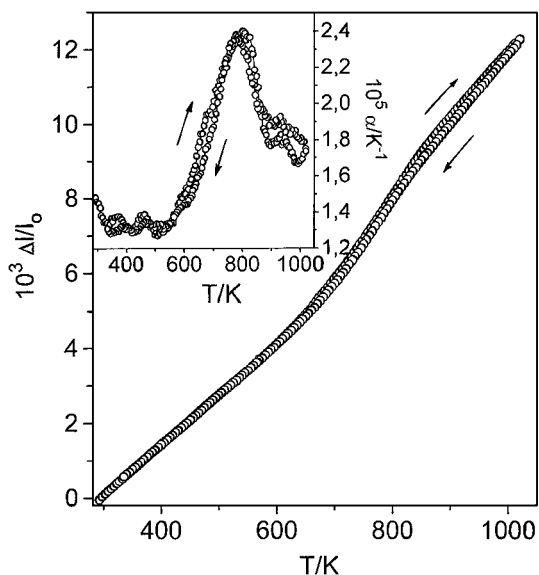
TABLE II The temperatures of phase transitions of orthorhombic 1 to orthorhombic 2 (T_1, K) and orthorhombic 2 to tetragonal phase (T_2, K) of solid solutions (I–II), determined for T_1 from $\Delta l/l_0 = \mathrm{f}(T)$ and for T_2 - from $\alpha = \mathrm{f}(T)$ dependences

No	Sample	T_1	T_2
1	$YBa_2Cu_3O_{7-\delta}$	768	903
2	$YBa_{1.8}Sr_{0.2}Cu_3O_{7-\delta}$	748	888
3	$YBa_{1.6}Sr_{0.4}Cu_3O_{7-\delta}$	743	878
4	$YBa_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	738	888
5	$YBa_{1.2}Sr_{0.8}Cu_3O_{7-\delta}$	738	878
6	$YBaSrCu_3O_{7-\delta}$	738	888
7	$YBa_{1.8}Ca_{0.2}Cu_3O_{7-\delta}$	733	898
8	$YBa_{1.6}Ca_{0.4}Cu_3O_{7-\delta}$	730	890
9	$YBa_{1.4}Ca_{0.6}Cu_3O_{7-\delta}$	720	884
10	$YBa_{1.2}Ca_{0.8}Cu_3O_{7-\delta}$	688	878
11	$YBaCaCu_3O_{7-\delta}$	673	868

are in a good accordance with results of [12–14] for the unsubstituted phase $YBa_2Cu_3O_{7-\delta}$. LTEC values of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ (I) were essentially larger, than those of $YBa_{2-x}Ca_xCu_3O_{7-\delta}$ (II) for the temperature interval studied.

On temperature dependences of relative elongation and LTEC two anomalies were observed for all samples. According to [12, 13], these anomalies were due to the solid-state phase transitions: orthorhombic phase 1 to orthorhombic phase 2 (of "order-disorder" type, connected with the disordering of oxygen ions at different crystallographic positions of the unit cell of the samples and accompanied by beginning of oxygen loss by samples at heating) at T_1 and orthorhombic phase 2 to tetragonal phase at T_2. Temperatures of phase transitions (for the heating) T_1 (determined using kinks on temperature dependences of $\Delta l/l_0$) and T_2 (determined using kinks on temperature dependences of α) of (I–II) solid solutions are given in Table II. As can be seen from these data, monotonous decrease of temperatures of phase transitions of solid solutions (I) and (II) with increase of strontium or calcium content is observed. It is interesting to note that orthorhombic 1 to orthorhombic 2 phase transition for the strontium-substituted solid solutions occurs at practically the same temperature. Temperatures of phase transitions of (I–II), obtained in this work, agree satisfactorily with those determined by us earlier using thermogravimetric data (on the loss of oxygen by samples) for the same compositions [21].

In Table III LTEC values of the samples studied are given for some temperatures for the heating process. For better clarity in Figs 3–4 three-dimensional α-T-x diagrams and their projections on the plane T-x for (I) and (II) are shown. As can be seen from the data obtained, at the heating LTEC of solid solutions (I) in orthorhombic 1 and tetragonal modifications decreases slightly with content of strontium in samples increasing, but in orthorhombic 2 modification as a whole it does not change appreciably, having a minimum for $x = 0.4$ composition. It is interesting to note, that LTEC of sample with $x = 0.8$ is closed to the LTEC of unsubstituted phase. When cooling one can observe very similar results, but a minimum on dependences of LTEC on the composition at $x = 0.4$ and near 800 K becomes more observable. LTEC of solid solutions (II) for the

Figure 2 The temperature dependence of relative elongation ($\Delta l/l_0$) and LTEC (α) of $YBa_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$ solid solutions.

5383

TABLE III Values of the LTEC ($10^5 \, \alpha \cdot K^{-1}$) at different temperatures (T, K)

Sample	350	400	450	500	550	600	650	700	750	800	850	900	950
$YBa_2Cu_3O_{7-\delta}$	1.29	1.32	1.33	1.36	1.38	1.48	1.68	1.94	2.31	2.21	1.43	2.21	1.55
$YBa_{1.8}Sr_{0.2}Cu_3O_{7-\delta}$	1.26	1.33	1.37	1.35	1.37	1.44	1.75	2.02	2.37	2.56	2.41	1.91	1.78
$YBa_{1.6}Sr_{0.4}Cu_3O_{7-\delta}$	1.29	1.28	1.35	1.30	1.31	1.37	1.56	1.80	2.10	2.09	1.81	1.67	1.62
$YBa_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	1.37	1.32	1.37	1.31	1.35	1.45	1.61	1.90	2.27	2.32	1.99	1.88	1.84
$YBa_{1.2}Sr_{0.8}Cu_3O_{7-\delta}$	1.26	1.29	1.35	1.24	1.26	1.41	1.68	2.18	2.49	2.51	2.07	1.95	1.86
$YBaSrCu_3O_{7-\delta}$	1.22	1.26	1.31	1.32	1.29	1.35	1.44	1.70	1.91	1.86	1.82	2.12	1.82
$YBa_{1.8}Ca_{0.2}Cu_3O_{7-\delta}$	–	0.88	1.04	1.02	1.02	0.97	0.91	1.06	1.57	1.83	1.46	1.23	1.28
$YBa_{1.6}Ca_{0.4}Cu_3O_{7-\delta}$	0.72	1.07	1.40	1.22	1.33	1.30	1.39	1.54	1.93	2.06	1.86	1.66	1.52
$YBa_{1.4}Ca_{0.6}Cu_3O_{7-\delta}$	0.80	0.81	0.99	1.08	1.09	0.98	0.69	0.64	1.76	2.10	1.82	1.27	1.00
$YBa_{1.2}Ca_{0.8}Cu_3O_{7-\delta}$	1.22	1.52	1.19	1.22	1.24	1.24	1.53	1.78	2.25	2.45	1.81	1.96	1.51
$YBaCaCu_3O_{7-\delta}$	1.13	1.15	1.24	1.24	1.14	1.18	1.29	1.47	1.49	1.41	–	1.22	1.26
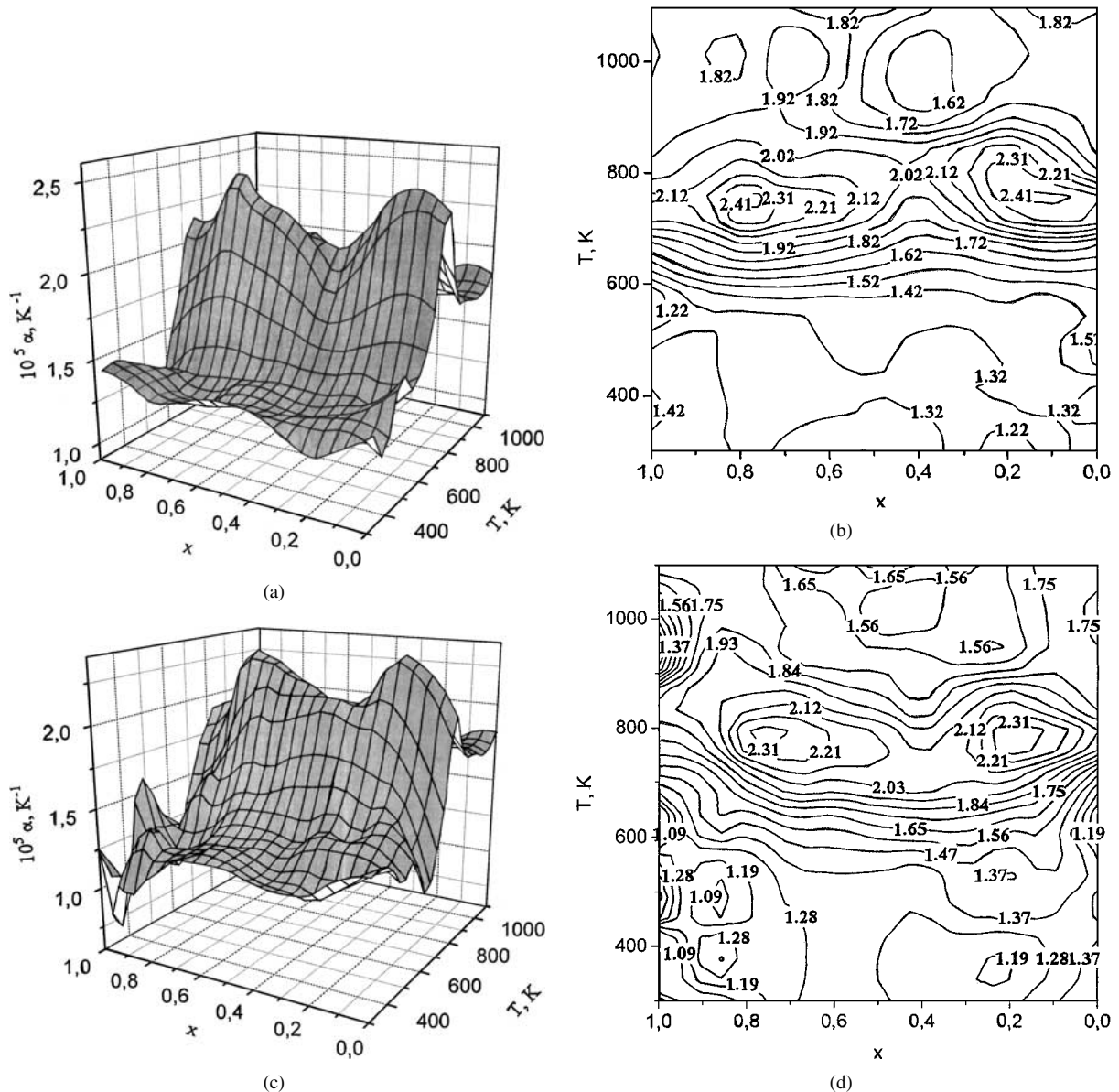
Figure 3 The LTEC (α) of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ solid solutions: α-T-x-diagram (a, c) and projections of this diagram on the T-x-plane (b, d) for heating (a, b) and cooling (c, d).

heating process decreases with increasing of calcium content, with the exception of samples with $x = 0.4$ and $x = 0.8$, for which LTEC values of orthorhombic 2 modification are approximately equal or even more, than those of unsubstituted phase $YBa_2Cu_3O_{7-\delta}$. The most significant decrease of LTEC for calcium-substituted samples in contrast with the unsubstituted phase is observed for the samples with $x = 0.2$ and $x = 1.0$ (for cooling process).

Explanation of such dependences of (I) and (II) LTEC on composition and temperature, in our opinion, may be made taking into account two factors: distribution
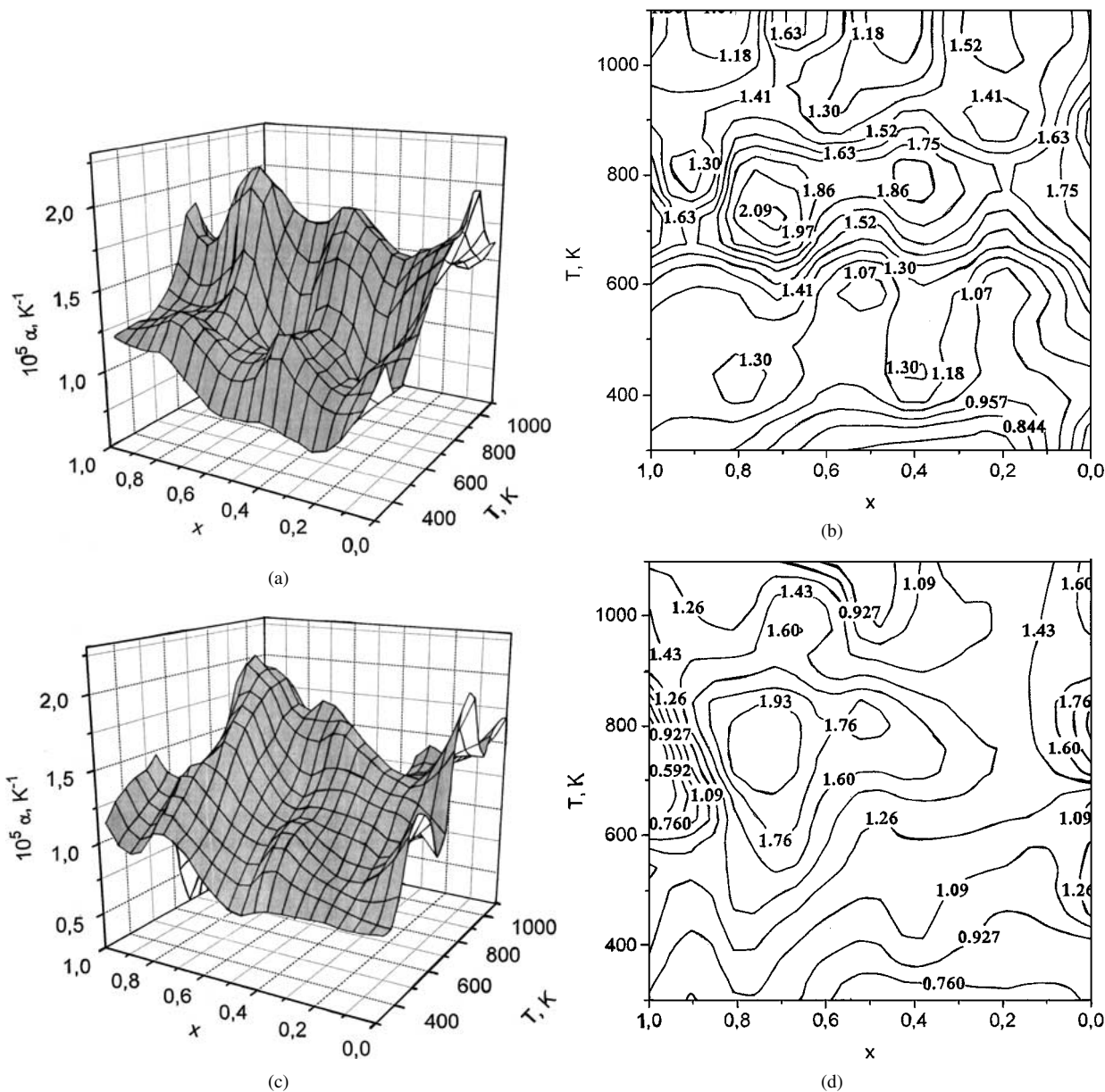
Figure 4 The LTEC (α) of $YBa_{2-x}Ca_xCu_3O_{7-\delta}$ solid solutions: α-T-x-diagram (a, c) and projections of this diagram on the T-x-plane (b, d) for heating (a, b) and cooling (c, d).

of ions of yttrium and alkaline-earth elements between different crystallographic positions (which is important for substitution of barium by calcium) as well as oxygen nonstoichiometry of samples.

The first factor, probably, is responsible for the appearance of minimum on dependences "α-T-composition" for (II). It is obviously, that at small degrees of substitution distribution of cations takes place by a normal way, i.e, Ca^{2+} ions in the $YBa_2Cu_3O_{7-\delta}$ crystal lattice occupy A-positions in (BaO)-planes of perovskite-like ABO_3 structure. Here an expected decrease of LTEC of the samples within whole studied temperature interval occurs. Substitution of a major part of barium ions by calcium ions leads, as it was shown above, to essential distortion of crystal structure of $YBa_2Cu_3O_{7-\delta}$-type phases, accompanying by changing of a nature of interaction between (Me)- and (MeO)-planes, forming a structure of these phases. Because of this "compressing" function of small (in comparison with barium) Ca^{2+} ions is changed into "loosening" and an increase of LTEC of the samples takes place.

In the case of substitution of barium by strontium a picture is somewhat different. For a major part of investigated temperatures and compositions, as it was mentioned above, substitution of barium ion by smaller strontium ion leads to the expected decrease of LTEC, however, here increase of LTEC of phases (I) at $x = 0.6 - 0.8$ (from 5 up to 30% depending on temperature and composition) is not quite clear. Such a phenomenon was not bound to take place under statistical filling of positions in (BaO)-planes by Ba^{2+} and Sr^{2+} ions. Taking into account above considerations, it is possible to suppose that in this case at $x = 0.4$ (that corresponds to the substitution of 25% of barium by strontium) ordering of ions of alkaline-earth elements along c-axis with formation of (Ba-Ba-Ba-Sr)-type superstructure occurs. This ordering leading to the increase of interactions between (Me)- and (MeO)-planes, possibly, may define a significant decrease of LTEC of (I) for $x = 0.4$.

Above we did not take into account oxygen non-stoichiometry of the samples. However, in opinion of a

number of authors [2, 4, 7, 12–15, 20–23], namely non-stoichiometry to a considerable degree defines many properties of $YBa_2Cu_3O_{7-\delta}$-type phases.

When detailed considering obtained results, taking into account above remarks, it is possible to reveal an influence of oxygen nonstoichiometry and oxygen ordering on the thermal expansion and LTEC of samples (I–II). Influence of the second factor is the most pronounced in the following cases. It is known that LTEC of $YBa_2Cu_3O_{7-\delta}$-type phases increases with decrease of oxygen content in the samples [23]. Namely low content of oxygen (Table I) can explain high values of LTEC at low temperatures for samples (I) with large content of strontium ($x = 0.8 - 1.0$), though, taking into consideration "compressing" role of smaller in comparison with barium ions strontium ions, here one can expect smaller LTEC values, than those for compositions with $x = 0 - 0.4$. Ordering of oxygen, probably, is responsible for hysteresis of LTEC of the samples at high temperatures, which is connected with unequivalent filling by the oxygen of different crystallographic positions (O(1), O(5)) at heating–cooling. In the crystal structure of $YBa_2Cu_3O_{7-\delta}$-phases there is five unequivalent positions of oxygen ions (Fig. 1): O(4) in plane (BaO), O(2) and O(3) in plane (CuO_2), O(1) and O(5) (vacancy) in plane (CuO). According to [20, 22] at heating of $YBa_2Cu_3O_{7-\delta}$-type phases oxygen leaves the positions O(1), and after liberation approximately a half of the above positions it causes raising a symmetry of phases from orthorhombic to tetragonal one. When cooling of $YBa_2Cu_3O_{7-\delta}$-phases an oxygen can occupy with equal probability both positions O(1) and O(5), that leads to a local distortion of crystal structure. Further ions of oxygen diffuse from the positions O(5) to the positions O(1) and arrange along b-axis of the forming orthorhombic modification of $YBa_2Cu_3O_{7-\delta}$-type phases. Two last processes, proceeding to a considerable extent unequilibriumly even at small cooling rates equal to 1–2 K/min, cause a significant difference between $YBa_2Cu_3O_{7-\delta}$-type phases LTEC values, obtained from data for heating and cooling processes.

4. Conclusions

Thermal expansion of HTSC solid solutions $YBa_{2-x}Me_xCu_3O_{7-\delta}$ (Me = Sr, Ca) was studied by dilatometry in air at 293–1123 K. LTEC values of the above phases were calculated and they were about $(1.2 - 1.4) \times 10^{-5}$ K^{-1}, $(1.8 - 2.4) \times 10^{-5}$ K^{-1} and $(1.6 - 1.8) \times 10^{-5}$ K^{-1} for 293–593, 593–893 and 893–1123 K temperature intervals respectively. For all samples studied two phase transitions were observed: orthorhombic phase I to orthorhombic phase II and orthorhombic phase II to tetragonal phase at temperatures 673–768 and 868–903 K respectively. It is found that substitution of barium by strontium or calcium in the crystal structure of $YBa_2Cu_3O_{7-\delta}$-type phases leads to decrease of the lattice parameters of the unit cell, temperatures of phase transitions and LTEC values with the increase of strontium or calcium content in the solid solutions studied. The results obtained are discussed by means of models of ordering of alkaline-earth and oxygen ions in the crystal lattice of the samples.

References

1. V. P. GLAZKOV, A. V. IRODOVA, G. V. LASKOVA and V. A. SOMENKOV, *Sverkhprovodim.: Fiz., Khim., Techn.* **1** (1988) 5.
2. S. F. PASHIN, E. V. ANTIPOV and L. M. KOVBA, *ibid.* **3** (1990) 2386.
3. T. WADA, T. SAKURAI, N. SUZUKI, S. KORIYAMA, H. YAMAUCHI and S. TANAKA, *Phys. Rev.* B. **41** (1990) 11209.
4. G. V. BAZUEV, N. A. KIRSANOV, V. G. ZUBKOV and O. V. MAKAROVA, *Izvest. Akad. Na uk. SSSR, Russ. Inorg. Mater.* (Reports of the Soviet Academy of Sciences) **25** (1989) 2042.
5. R. WOERDENWEBER, K. HEINEMANN and H. C. FREYHARDT, *Physica* C. **153–155** (1988) 870.
6. S. JIN, T. H. TIEFEL, G. W. KAMMLOTT and J. E. GRAEBNER, *ibid.* **173** (1991) 75.
7. T. M. GUER and R. A. HIGGINS, *J. Electrochem. Soc.* **140** (1993) 1990.
8. S. V. MASSYUCK, A. I. CLYNDYUCK, A. V. BOROVTSOV, G. S. PETROV and L. A. BASHKIROV, in Proceedings of the International Conference on Electronic Ceramics & Applications, ElectroCeramics V, Aveiro, Portugal, September 1996, Book 2, edited by J. L. Baptista, J. A. Labrincha and P. M. Vilarinho (University of Aveiro, 1996) p. 325.
9. S. HANSEN, J. OTAMURI, J.-O. BOVIN and A. ANDERSSON, *Nature* **334** (1988) 143.
10. A. M. BOL'SHAKOV, L. V. KHMELEVSKAYA, K. S. GAVRICHEV and A. G. REBEKO, *Russ. J. Inorg. Chem.* **43** (1998) 746.
11. A. S. ALEXANDROV, P. E. KORNILOVICH, A. D. SHEVCHENKO and A. A. SHULZHENKO, *Russ. Solid State Physics* **32** (1990) 303.
12. O. V. BASARGIN, L. A. RUDNITSKY, V. V. MOSHCHALKOV, A. R. KAUL, I. E. GRABOY and YU. D. TRET'YAKOV, *ibid.* **30** (1998) 877.
13. A. SZYTULA and G. MAVRODIEV, *Acta Phys. Pol.* A **73** (1988) 785.
14. J. MIZUSAKI, H. TAGAWA, K. HAYAKAWA and K. HIRANO, *J. Amer. Ceram. Soc.* **78** (1995) 1781.
15. G. S. PETROV, A. I. CLYNDYUCK, S. V. MASSYUCK, A. I. AKIMOV and L. A. BASHKIROV, *High Temp.-High Press.* **30** (1998) 483.
16. N. F. ZAKHARCHUK, T. P. FEDINA and N. S. BORISOVA, *Sverkhprovodim.: Fiz., Khim., Techn.* **4** (1991) 1391.
17. A. I. AKIMOV, L. A. BLIZNYUCK and A. L. KARPEI, *Vestsi Akad. Navuk Belarusi. Ser. Phys.-Math.* (Reports of the Belarus Academy of Sciences) **1** (1994) 81.
18. A. I. CLYNDYUCK, G. S. PETROV, A. F. POLUYAN and L. A. BASHKIROV, *Russ. Inorg. Mater.* **35** (1999), in press.
19. R. D. SHANNON and C. T. PREWITT, *Acta Cryst.* **25** B (1969) 925.
20. G. P. SHVEJKIN, V. A. GUBANOV, A. A. FOTIEV, G. V. BAZYEV and A. A. EVDOKIMOV, in "Elektronnaya Struktura i Fiziko-Khimicheskie Svojstva Vysokotemperaturnykh Sverkhprovodnikov" (Electronic Structure and Physico-Chemical Properties of High-Temperature Superconductors) (Nauka, Moscow, 1990) p. 110, 116.
21. A. I. CLYNDYUCK, G. S. PETROV and L. A. BASHKIROV, in Abstracts of the 1995 Fall Meeting of Materials Research Society, Boston, USA, November, December 1995, p. 195.
22. P. K. GALLAGHER, *Thermochim. Acta* **148** (1989) 229.
23. O. V. FRANK-KAMENETSKAYA, S. K. FILATOV, S. V. MOSHKIN, T. N. KAMINSKAYA, M. I. DOMNINA, M. A. KUZ'MINA, V. B. TROFIMOV and A. V. NARDOV, in "Vysokotemperaturnaya Sverkhprovodimost. Aktual'nye problemy" (High-Temperature Superconductivity. Actual Problems), edited by A. A. Kiselev (Leningrad University, Leningrad, 1989) Vol. 1, p. 6.