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The high-temperature thermal expansion of BiPbSrCaCuO superconductor and the oxide components (Bi_2O_3, PbO, CaO, CuO)

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The thermal expansion of superconducting $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ (BiPbSrCaCuO) and its oxide components Bi_2O_3, PbO, CaO and CuO have been studied by high-temperature dilatometric measurements (30–800 °C). The thermal expansion coefficient for the BiPbSrCaCuO superconductor in the range 150–830 °C is $\alpha = 6.4 \times 10^{-6}\ K^{-1}$. The temperature dependences of $\Delta L/L$ of pressed Bi_2O_3 reveals sharp changes of length on heating ($T_1 = 712$ °C), and on cooling ($T_2 = 637$ °C and $T_3 = 577$ °C), caused by the phase transition monoclinic–cubic (T_1) and by reverse transitions via a metastable phase (T_2 and T_3). By thermal expansion measurements of melted Bi_2O_3 it is shown that hysteresis in the forward and the reverse phase transitions may be partly caused by grain boundary effect in pressed Bi_2O_3. The thermal expansion of red PbO reveals a sharp decrease in $\Delta L/L$ on heating ($T_1 = 490$ °C), related with the phase transition of tetragonal (red, $a = 0.3962$ nm, $c = 0.5025$ nm) – orthorhombic (yellow, $a = 0.5489$ nm, $b = 0.4756$ nm, $c = 0.5895$ nm). The possible causes of irreversibility of the phase transition in PbO are discussed. In the range 50–740 °C the coefficient of thermal expansion of pressed Bi_2O_3 ($\alpha_m = 3.6 \times 10^{-6}$ and $\alpha_c = 16.6 \times 10^{-6}\ K^{-1}$ for monoclinic and cubic Bi_2O_3 respectively), the melted Bi_2O_3 ($\alpha_m = 7.6 \times 10^{-6}$ and $\alpha_c = 11.5 \times 10^{-6}\ K^{-1}$), PbO ($\alpha_t = 9.4 \times 10^{-6}$ and $\alpha_{or} = 3.3 \times 10^{-6}\ K^{-1}$ for tetragonal and orthorhombic PbO respectively), CaO ($\alpha = 6.1 \times 10^{-6}\ K^{-1}$) and CuO ($\alpha = 4.3 \times 10^{-6}\ K^{-1}$) are presented.

1. Introduction

High-temperature heat treatments of BiPbSrCaCuO samples (with heating and cooling in the temperature range 30–850 °C) are necessary and important stages in the fabrication of superconducting ceramics. During sintering, processes such as reaction diffusion, the formation of new phases, the precipitation of these phases and phase transitions may accompany the BiPbSrCaCuO growth. In this connection, temperature changes in the crystal structure and properties of the oxide components (Bi_2O_3, PbO, $SrCO_3$, CaO, CuO) used in the formation of the BiPbSrCaCuO, represents a special interest. Owing to differences in the thermal expansion coefficients of the BiPbSrCaCuO and its oxide components and because of possible phase transformations in the oxide components, deformation, dislocation and other defects may arise in growing superconductors. These distortions, in turn, can essentially influence the form and volume of sintering tablets of the superconductor. The swelling phenomenon of Ag-sheathed Bi-2223 tapes during the first sintering stage is observed in the work of Lu *et al.* [1]. It is found that the swelling of the tablets is related to the formation of SrCaCuO with a consequent volume increase. To avoid a similar phenomena during the sintering of superconductors, it is necessary to have at one's disposal data on the thermal expansion coefficients of BiPbSrCaCuO and its oxide components in a wide temperature range.

At the present time only a few thermal expansion studies of the BiPbSrCaCuO system at low (– 263–27 °C) [2, 3] and moderate temperatures (30–500 °C) [4, 5] are published. Anomalies in the thermal expansion at 30–830 °C in Ag-diffusion doped BiPbSrCaCuO superconductors have been investigated by Altunbaş *et al.* [6]. No work is reported in the literature on the values of the thermal expansion coefficients of undoped BiPbSrCaCuO and its oxide components at high temperatures.

In the present work, the results of thermal expansion studies in the range of 30–800 °C on superconducting BiPbSrCaCuO ceramics and its components (Bi_2O_3, PbO, CaO, CuO) are presented. The phase transitions in Bi_2O_3 and PbO during the high-temperature heat treatments are also investigated.

2. Experimental procedure

The samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ (BiPbSrCaCuO) were prepared using a conventional solid-state

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reaction method [7]. The majority of the lines in the X-ray diffraction measurements on the BiPbSrCaCuO ceramics corresponded to the high-T_c 2223 phase with a zero-resistivity at $T_c = 110$ K [8].

Samples of the oxide components were prepared by pressing (at 300 MPa) Bi_2O_3 (99.9% purity), PbO (99.9%), CaO (99.95%) and CuO (99.99%) powders in tablets of 13 mm in diameter and 3 mm in thickness. The pressed tablets were annealed in air at temperatures between 450–800 °C for 19–24 h. For Bi_2O_3, in addition to the pressed sample, we used samples prepared by melting the pressed Bi_2O_3 at a temperature $T > 830$ °C followed by a fast cooling at a rate of about 800 °C min^{-1}.

For the high-temperature thermal expansion measurements we used an inductive Linseis-dilatometer with a sensitivity $\Delta L/L = 10^{-5}$ [6]. Samples for measurement were prepared in the form of a rectangular bar of size $10 \times 3 \times 3$ mm^3. The thermal expansion of the samples were measured from 30–800 °C in air. In these thermal expansion measurements, samples were given a three-step heat treatment: heating from the room temperature to high temperature 700–800 °C, annealing at the high permanent temperature (T_p) for 1–5 h and then cooling from T_p to room temperature. The rates of heating and cooling of the samples are 2 °C min^{-1}, 5 °C min^{-1} and 10 °C min^{-1}. A few of the thermal expansion experiments were carried out in an argon atmosphere. X-ray diffraction measurements were performed using a Rikagu D/Max-III C diffractometer with CuK_α radiation.

3. Results and discussion

We first consider the results of thermal expansion measurements on the oxide components of the superconductor.

3.1 Bismuth sesquioxide, Bi_2O_3

Samples for the thermal expansion measurements were prepared by two methods: (a) by pressing Bi_2O_3 powder into tablets and annealing at 780 °C for 24 h and (b) by melting the pressed sample.

Fig. 1 shows the change of the relative length $\Delta L/L$ as a function of temperature for heating with a rate of 5 °C min^{-1} of the pressed Bi_2O_3. It is seen that $\Delta L/L$ at a temperature $T_1 = 712$ °C is sharply increased. It will be noted that the subsequent repeated measurements of the thermal expansion on heating of this sample and other pressed samples of Bi_2O_3 revealed a jump in $\Delta L/L$ at the same temperature $T_1 = 712 \pm 3$ °C.

Data of the $\Delta L/L$ change with temperature during cooling of the pressed Bi_2O_3 are also presented in Fig. 1. Two peculiarities in the $\Delta L/L$ curve at $T_2 = 638$ °C and $T_3 = 555$ °C related with the beginning of a sharp decrease in the sample length, are observed. Temperature T_2 in the subsequent repeated measurements on this sample and also on other pressed samples of Bi_2O_3 does not change much ($T_2 = 637 \pm 5$ °C). Whereas the temperature T_3 is essentially changed varying in the range 644–555 °C.

It is to be noted that the length of the pressed Bi_2O_3 after the thermal expansion measurements (heating–cooling), when the sharp changes of T_1, T_2 and T_3 are observed, is decreased. After the thermal expansion measurements at temperatures $T_1 < 712$ °C, when the anomalies in $\Delta L/L$ are not revealed then the sample length is relatively constant. The average values of the critical temperatures (the beginning of the $\Delta L/L$ jump) and of the thermal expansion of the pressed Bi_2O_3 (three samples, six measurements each) are presented in Table 1.

The observed jumps on the $\Delta L/L$ versus temperature curve of the pressed Bi_2O_3 may be caused by the phase transitions monoclinic–cubic ($T_1 = 712$ °C) on heating and on cooling by the reverse phase transition through the cubic–metastable tetragonal ($T_2 = 637$ °C) and metastable tetragonal–monoclinic ($T_3 = 577$ °C) as is listed in Table 1 [9, 10]. The results of our studies of the phase transitions in the pressed Bi_2O_3 by thermal expansion measurements confirm the data reported earlier on DTA measurements on Bi_2O_3 [9]. The decrease in $\Delta L/L$ on the heating of the sample at

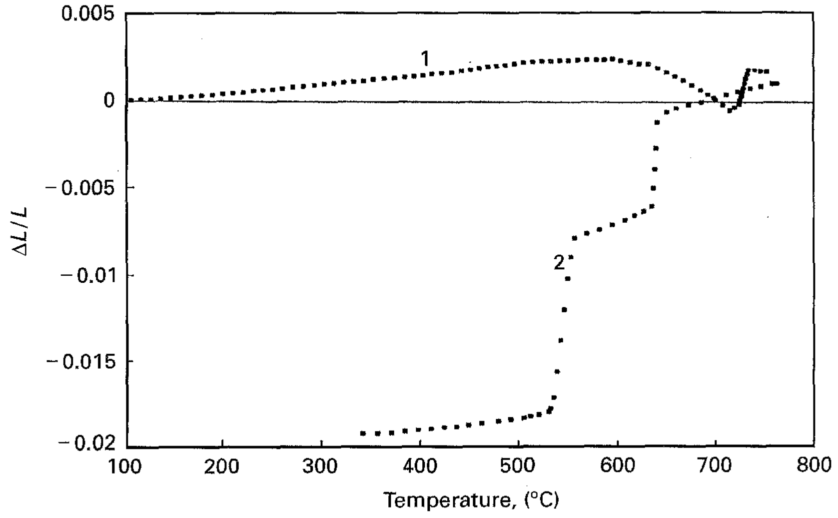

Figure 1 Curves of $\Delta L/L$ versus temperature of pressed Bi_2O_3 for (1) heating and (2) cooling.

TABLE 1. The thermal expansion data of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ and its components (Bi_2O_3, PbO, CaO and CuO)

Sample	The crystal structure	$\alpha(\times 10^6)$ (K^{-1})	The temperature range (°C)	The phase transition	Temperature of phase transition.	
					heating (°C)	cooling (°C)
BiPbSrCaCuO	Orthorhombic	6.4	150–830			
Bi_2O_3 (pressed)	Monoclinic	3.6	100–600	Monoclinic–Cubic	712	
Bi_2O_3 (pressed)	Cubic	16.6	780–637	Cubic–Metastable		637
Bi_2O_3 (pressed)	Metastable	20.6	637–577	Metastable–Monoclinic		577
Bi_2O_3 (melted)	Monoclinic	7.6	70–600	Monoclinic–Cubic	712	
Bi_2O_3 (melted)	Cubic	11.5	760–630	Cubic–Monoclinic		630
PbO (red)	Tetragounal	9.4	50–480	Tetragonal–orthorhombic	490	
PbO (yellow)	Orthorhombic	3.3	500–700			
CaO	Cubic	6.1	420–740			
CuO	Monoclinic	4.3	70–650			

temperatures between 580–710 °C (before the jump of $\Delta L/L$ at 712 °C) may be caused by the processes of reconstruction of the crystal lattice before the monoclinic–cubic phase transition.

The average values of the thermal expansion coefficients of the pressed Bi_2O_3 samples are presented in Table 1. The thermal expansion coefficients of monoclinic, cubic and metastable (tetragonal) phases of the pressed Bi_2O_3 samples are $\alpha_m = 3.6 \times 10^{-6}$, $\alpha_c = 16.6 \times 10^{-6}$ and $\alpha_{ms} = 20.6 \times 10^{-6}\ K^{-1}$ respectively.

Factors such as the rate of heating or cooling, grain sizes and impurities [9], may affect the hysteresis of the phase transition in the forward and reverse transformations of Bi_2O_3. For this purpose, some additional experiments were carried out in order to reveal the influence of the rate of heating or cooling on the critical temperatures T_1, T_2 and T_3. The thermal expansion measurements on the pressed Bi_2O_3 sample made successively at heating or cooling rates of 10 °C min^{-1} and 5 °C min^{-1} did not reveal any change in the phase transition temperatures T_1 and T_2. However the changes in T_3 observed in these experiments are not correlated with the rate of cooling. Several runs of the thermal expansion experiments in an argon atmosphere did not reveal any change in the critical temperatures.

It was supposed that the reverse two-step transition (cubic–metastable tetragonal–monoclinic) on the cooling cycle may be related with grain boundary effects in polycrystalline Bi_2O_3 samples prepared by pressing. To check this supposition the thermal expansion of the Bi_2O_3 samples prepared by melting was measured. The density of the melted sample ($\rho = 8.5$ g cm^{-3}) exceeds the density of the pressed Bi_2O_3 sample ($\rho = 7.2$ g cm^{-3}) . The increase of the density of the melted samples may be caused by the increase of the grain sizes of the Bi_2O_3 samples.

The temperature dependences of $\Delta L/L$ of the melted Bi_2O_3 on heating and cooling are presented in Fig. 2. The $\Delta L/L$ curve of the melted sample on heating (Fig. 2, curve 1), as in the case of the pressed sample (Fig. 1, curve 1), reveals the monoclinic–cubic phase transition at a temperature $T_1 = 712$ °C. In the melted sample on cooling (Fig. 2, curve 2), as distinguished from the pressed sample (Fig. 1, curve 2), the reverse cubic–monoclinic phase transition is observed to occur in one step thus avoiding the metastable phase at $T_2 = 630$ °C. Moreover, the length of the melted sample after the thermal expansion measurements is decreased but this change is less than that of the pressed Bi_2O_3 sample. A change of heating (or cooling) rate from 10 °C min^{-1} to 2 °C min^{-1} did not effect the phase transitions temperatures T_1 and T_2 of the melted sample.

The average values of the phase transition temperatures: monoclinic–cubic on heating ($T_1 = 712$ °C) and cubic–monoclinic on cooling ($T_2 = 630$ °C) and also the thermal expansion coefficients of the monoclinic and cubic phases of the melted Bi_2O_3 samples are given Table 1.

Thus the direct cubic–monoclinic transition on cooling of the melted samples may be attributed to the increase of grain sizes, that is the decrease of the effect of the grain boundaries on the reverse phase transition. The higher values of the thermal expansion coefficients of the melted Bi_2O_3 sample ($\alpha_m = 7.6 \times 10^{-6}\ K^{-1}$) in comparison with that of the pressed sample ($3.6 \times 10^{-6}\ K^{-1}$) may also be an indication of the decrease of the grain boundary role in the reverse phase transition in the melted sample.

3.2 Lead Oxide, PbO

The samples of red PbO for the thermal expansion measurements were prepared by pressing the powder into tablets and annealing at 450 °C for 24 h in air. The colour of the sample after the annealing remained red. The majority of the X-ray diffraction peaks of the red lead oxide showed a tetragonal symmetry with $a = 0.3962$ nm and $c = 0.5025$ nm however, a few peaks were observed that correspond to PbO_2 and Pb_3O_4.

The thermal expansion measurements for PbO were repeatedly carried out between 30–710 °C using a heating rate of 5 °C min^{-1}. The red PbO sample after the first thermal expansion measurement is transformed into yellow PbO and this colour at subsequent measurements remains relatively constant. The X-ray

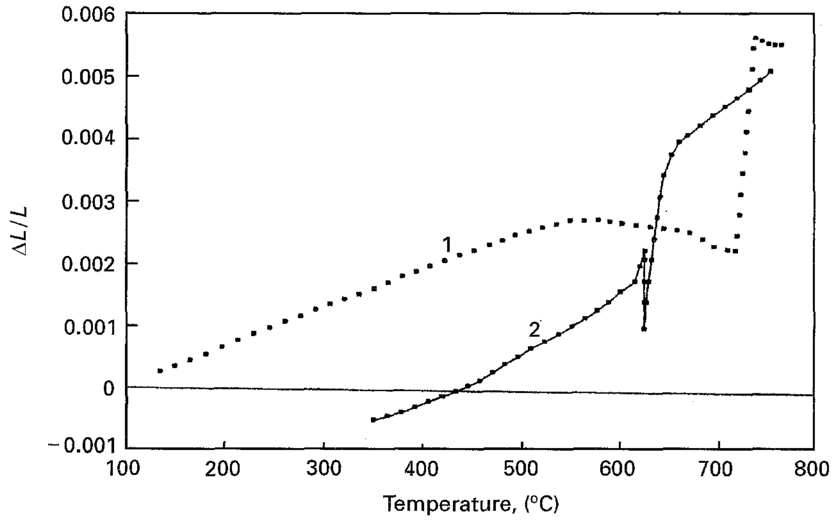

Figure 2 Curves of $\Delta L/L$ versus temperature of melted Bi_2O_3 for (1) heating and (2) cooling.

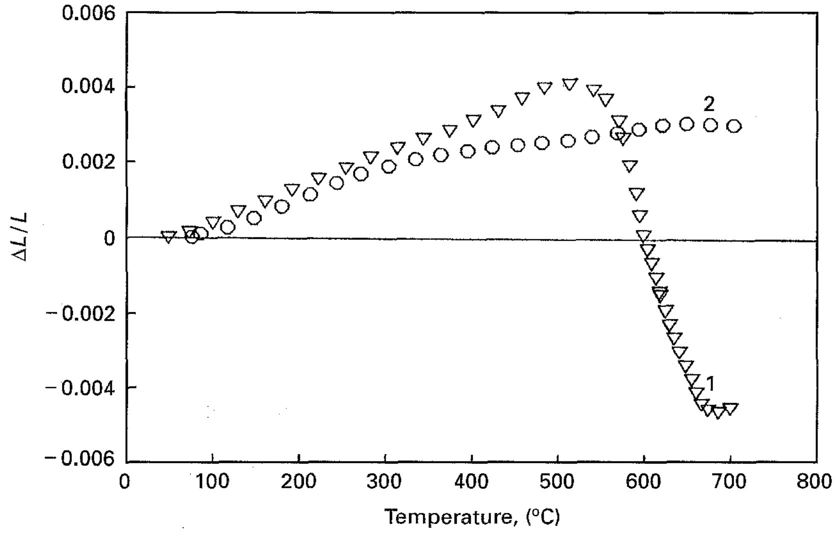

Figure 3 Curves of $\Delta L/L$ versus temperature of heating of PbO at (1): (▽): the first and (2): (○): the second cycle.

diffraction peaks observed for the yellow sample, correspond to the orthorhombic symmetry of PbO with $a = 0.5489$ nm, $b = 0.4756$ nm and $c = 0.5895$ nm.

Curves of $\Delta L/L$ versus temperature on heating the PbO sample after the first and second runs are given in Fig. 3. On the first measurement, the $\Delta L/L$ curve on heating at temperatures $T > 490$ °C reveals a sharp decrease in length (Fig. 3, curve 1). On the first cooling cycle, no peculiarities in the $\Delta L/L$ curve were observed. The second heating cycle of this yellow coloured sample did not reveal any sharp change in $\Delta L/L$ (Fig. 3, curve 2).

The thermal expansion data presented in Fig. 3 may be explained on the basis of known structural phase transitions in PbO [10]. The sharp decrease in $\Delta L/L$ on the first heating cycle at $T > 490$ °C and the transformation of the red PbO into the yellow colour after the first complete cycle may be due to the tetragonal–orthorhombic phase transition. The observed irreversibility of the phase transition in PbO may be related with the difference in stability of the PbO polymorphs, as is observed in the cases of TiO_2 and $CaCO_3$ [9]. We expect the orthorhombic (yellow) PbO to be more stable than the tetragonal (red) sample under a specified condition. In the presence of vacancies and changes in stoichiometry, formed in the first heating cycle, the orthorhombic phase of PbO becomes more stable relative to the tetragonal phase. The thermal expansion coefficients of the tetragonal PbO ($\alpha_t = 9.4 \times 10^{-6}$ K^{-1}) and the orthorhombic PbO ($\alpha_{or} = 3.3 \times 10^{-6}$ K^{-1}) are given Table 1.

3.3 Calcium Oxide, CaO

The pressed tablets of CaO are annealed at 800 °C for 19 h in air and then the thermal expansion measurements are carried out. The curve of the relative change of length as a function of temperature is given in Fig. 4. The temperature dependence of $\Delta L/L$ in the range 420–740 °C is approximately linear with a thermal expansion coefficient $\alpha = 6.1 \times 10^{-6}$ K^{-1}.

3.4 Copper Oxide, CuO

The pressed tablets of CuO are annealed at 750 °C for 24 h. The $\Delta L/L$ curves and the temperature profile of

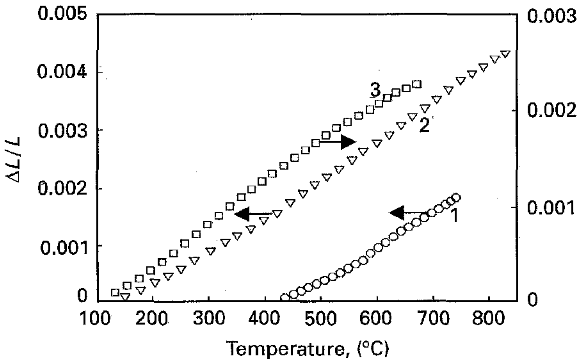

Figure 4 Curves of $\Delta L/L$ versus temperature of (1) : (○): CaO, (2): (▽): BiPbSrCaCuO and (3): (□): CuO.

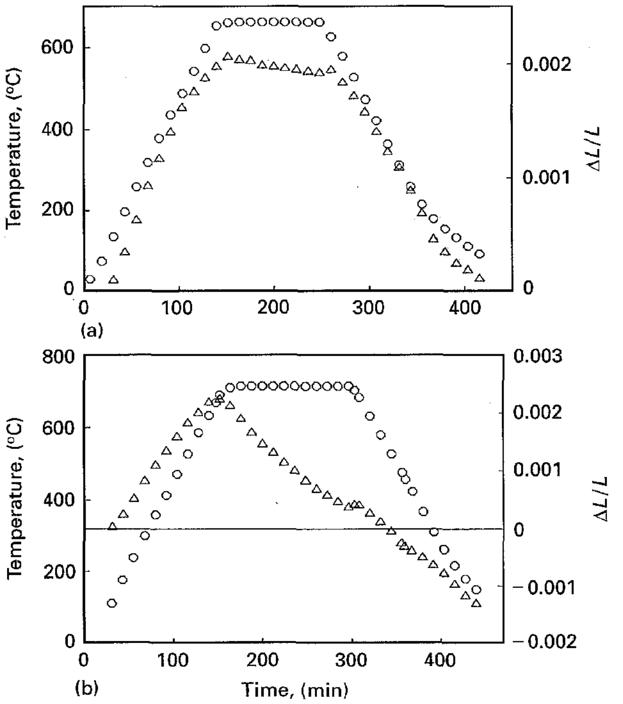

Figure 5 Curves of $\Delta L/L$, represented by (△) and temperature of CuO, represented by (○) versus time of the thermal expansion measurement. (a) $T_p = 665\,°C$ and (b) $T_p = 714\,°C$

CuO with respect to time are shown in Fig. 5. The measurements when the maximum permanent temperatures are $T_{p1} = 665\,°C$ and $T_{p2} = 714\,°C$ are designated case a and b respectively. For case a the form of the $\Delta L/L$ curve mimics the curve of temperature change with time. However for case b, when the sample is heated to a higher temperature of $T_{p2} = 714\,°C$, the $\Delta L/L$ curve at temperatures $T > 670\,°C$ does not mimic the temperature profile. In this case as is seen from Fig. 5b, $\Delta L/L$ decreases on heating to $T > 670\,°C$ and then keeping the sample at a constant temperature of 714 °C. This anomaly is increased with the raising of the temperature to $T_p = 760\,°C$. This unusual relative length change with temperature may be attributed to oxygen redistribution resulting in composition changes in CuO. The thermal expansion coefficient of CuO ($\alpha = 4.3 \times 10^{-6}\,K^{-1}$) for the temperature range 70–650 °C (Fig. 4, curve 3) is given in Table 1.

3.5 BiPbSrCaCuO superconductor

The thermal expansion curve, $\Delta L/L$, of a superconducting $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ sample in the temperature range 150–830 °C is presented in Fig. 4 curve 2. The thermal expansion coefficient of BiPbSrCaCuO at the above temperature range is $\alpha = 6.4 \times 10^{-6}\,K^{-1}$.

Data on the thermal expansion coefficients of the BiPbSrCaCuO superconductor and its oxide components are presented in Table 1. The thermal expansion of the pressed $SrCO_3$ can not be measured because of the fast disintegration of the annealed samples in air. The thermal expansion coefficients of BiPbSrCaCuO and its oxide components as can be seen from Table 1, are significantly different (2–3 times). Moreover Bi_2O_3 and PbO reveal phase transitions with a sharp change of the sample length. In this connection we suggest that the differences in the thermal expansion coefficients of the BiPbSrCaCuO and its oxide components may be responsible for creating strains and structural defects in the superconductors. These factors may be one of the causes of swelling of the Ag-sheathed Bi-2223 tapes [1].

4. Conclusions

The thermal expansion of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ superconductor and its oxide components Bi_2O_3, PbO, CaO and CuO are studied by high-temperature (30–800 °C) dilatometer measurements. The thermal expansion coefficient for the high-T_cBi-2223 superconductor is $\alpha = 6.4 \times 10^{-6}\ K^{-1}$.

Anomalies in the length changes versus temperature in a pressed Bi_2O_3 sample, observed on heating ($T_1 = 712\,°C$) and on cooling ($T_2 = 637\,°C$ and $T_3 = 577\,°C$), are attributed to the forward phase transition monoclinic–cubic (T_1), and the reverse transitions cubic–metastable tetragonal (T_2) and metastable tetragonal–monoclinic (T_3). It is shown that the hysteresis in the phase transitions in Bi_2O_3 on heating and cooling may be partly caused by grain boundary effects in the pressed samples.

The thermal expansion curve of PbO versus temperature reveals a sharp change on heating ($T > 490\,°C$) related with the phase transition tetragonal (red)–orthorhombic (yellow) PbO. However a length change in PbO on cooling was not observed. The possible cause of the irreversibility of the phase transition may be attributed to the difference in stability of the PbO polymorphs. The anomalies in relative length changes in CuO on heating at $T > 670\,°C$ were attributed to redistribution oxygen.

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