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Bulk Thermal Expansion Studies of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$

A. C. Momin,[1] E. B. Mirza,[1] and M. D. Mathews[1]

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The compounds $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ were prepared by ceramic techniques and characterized by X-ray powder diffractometry (XRD) and microthermogravimetry (μTG) and their bulk thermal expansion measurements were carried out using dilatometry in the temperature range $298 \leqslant T \leqslant 1073$ K in air. The results have been analyzed and are compared with those obtained earlier for $YBa_2Cu_3O_7$. The XRD analysis shows that both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ are single phase in nature, having an orthorhombic symmetry. The μTG analysis carried out in oxygen, air, and nitrogen shows negligible weight loss ($\sim 0.1\%$) on heating to 1073 K, indicating that these two compounds, unlike $YBa_2Cu_3O_7$, are quite stable. The analysis of bulk thermal expansion data reveals that the average linear thermal expansion coefficient (α_l) for both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ is almost the same ($\alpha_l \approx 10.5 \times 10^{-6}\,K^{-1}$) and is found to be nearly half of that for $YBa_2Cu_3O_7$ ($\alpha_l \approx 18 \times 10^{-6}\,K^{-1}$), suggesting that the interatomic bonding in both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ is stronger as compared to $YBa_2Cu_3O_7$.

KEY WORDS: $BiCaSrCu_2O_x$; $Bi_2CaSr_2Cu_2O_x$; ceramics; dilatometry; thermal expansion.

1. INTRODUCTION

In our previous papers [1, 2], we have reported lattice thermal expansion and bulk thermal expansion studies of the well-established compound $YBa_2Cu_3O_7$ using high-temperature X-ray powder diffractometry (XRD) and dilatometry, respectively. In continuation of these investigations, we report here the bulk thermal expansion studies of the newly discovered [3] compounds $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ in the temperature range $298 \leqslant T \leqslant 1073$ K in air.

[1] Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India.

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2. EXPERIMENTAL

2.1. Preparation and Characterization

The single-phase compound $BiCaSrCu_2O_x$ could not be prepared by the usual ceramic technique. For this reason, we resorted to a two-step matrix reaction method. The matrix $CaSrCu_2O_x$ was first made by mixing thoroughly appropriate amounts of $CaCO_3$, $SrCO_3$, and CuO. The mixture was pressed into a pellet and heated at 1033 K in air for 48 h with intermittent grinding. The heated product was ground to a fine powder and mixed with a proper amount of Bi_2O_3. The mixture was uniformly ground, pressed into a pellet, and heated at 1033 K in air for 48 h with intermittent grinding till the reaction was complete. The reacted product was uniformly powdered, pressed into a pellet, and further heated at 1073 K in air for 48 h. The pellet was quickly withdrawn from the furnace for fast cooling to room temperature.

The single-phase compound $Bi_2CaSr_2Cu_2O_x$, unlike $BiCaCrCu_2O_x$, could be prepared by the usual ceramic technique in a single-step reaction. Appropriate amounts of Bi_2O_3, $CaCO_3$, $SrCO_3$, and CuO were mixed together, uniformly ground, pressed into a pellet, and heated at 1033 K for 96 h in air, with intermittent grinding. The resulting product was crushed to a fine powder, pelletized, and further heated at 1073 K for 48 h in air. The pellet was quickly withdrawn from the furnace for fast cooling to room temperature.

The compounds prepared as above were characterized by XRD using CuK_α radiation. The cell parameters were evaluated from d-spacing measurement of all observed reflections in the 2θ range of 20–55° (CuK_α). Accurate values of cell parameters were obtained using a computer program for least-squares refinement. A microthermogravimetric (μTG) analysis of the above compounds was carried out in oxygen, air, and nitrogen from ambient to 1073 K using a Shimadzu TG instrument, Model TGC-31, at 50-μg sensitivity with a heating and cooling rate of $5\ K \cdot min^{-1}$.

2.2. Dilatometric Studies

Bulk thermal expansion measurements were carried out in the temperature range 298 to 1073 K in air at a heating rate of $5\ K \cdot min^{-1}$ using a Model LKB 3185 fused quartz pushrod-type dilatometer. Samples in the form of pressed sintered cylindrical pellets with ~65% theoretical bulk density were used.

3. RESULTS AND DISCUSSION

The room-temperature XRD patterns of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ in the 2θ range of 20–55° (CuK_α) are shown in Fig. 1 along with that of $YBa_2Cu_3O_7$. The XRD patterns of both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ are almost identical and reveal a single-phase nature. All observed reflections in the XRD patterns of these two compounds could be indexed on the basis of orthorhombic unit cells, the cell parameters of

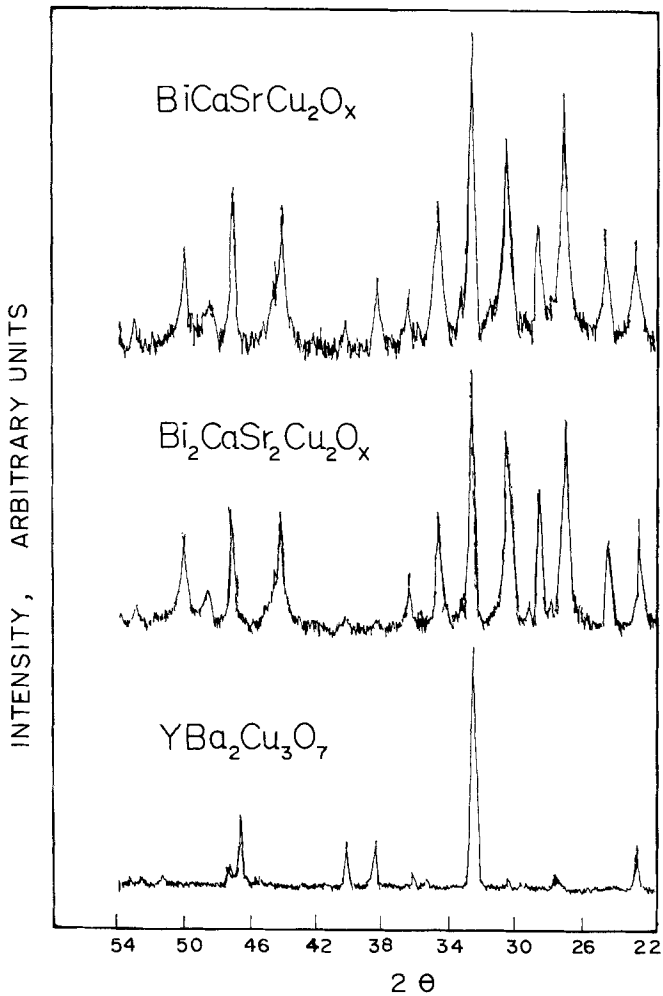

Fig. 1. Comparison of room-temperature X-ray powder diffractograms of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ (present study) and $YBa_2Cu_3O_7$ [1] in the 2θ range 20–55°, (CuK_α).

Table I. The Cell Parameter Data for the Orthorhombic Unit Cells of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ (Present Work) and $YBa_2Cu_3O_7$ [1]

Compound	Cell parameter (Å)		
	a	*b*	*c*
$BiCaSrCu_2O_x$	5.40	5.46	30.29
$Bi_2CaSr_2Cu_2O_x$	5.37	5.48	30.73
$YBa_2Cu_3O_7$	3.84	3.89	11.66

which are given in Table I together with those obtained earlier for $YBa_2Cu_3O_7$ [1].

The μTG curves obtained for $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ during heating and cooling between room temperature and 1073 K in oxygen are shown in Fig. 2. The μTG curve obtained for $YBa_2Cu_3O_7$ under identical conditions is also shown in this figure for comparison. As can be seen from Fig. 2, the weight loss observed on heating to 1073 K for

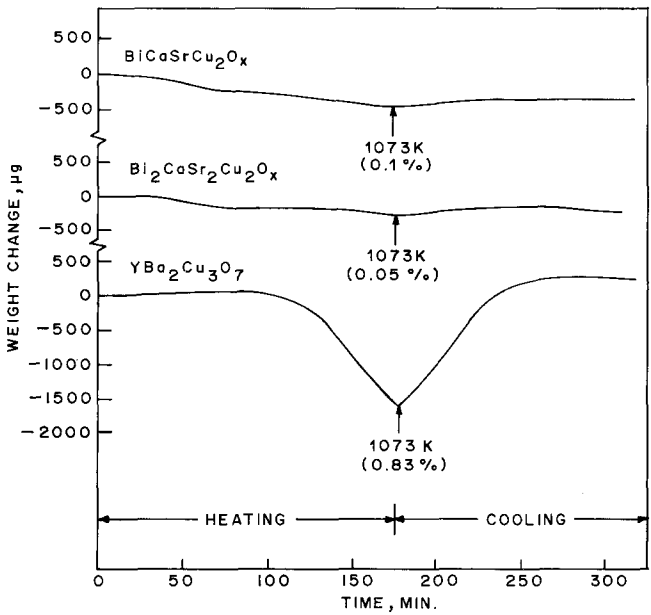

Fig. 2. μTG data for $BiCaSrCu_2O_x$, $Bi_2CaSr_2Cu_2O_x$, and $YBa_2Cu_3O_7$ in flowing oxygen in the temperature range 298–1073 K (sample weight, 200 mg) at the heating/cooling rate of 5 K · min^{-1}. The figures in parentheses show the percentage weight loss at 1073 K.

both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ is negligibly small, ~0.05–0.1 %. The initial weight loss observed below 573 K is attributed to moisture loss. However, in the case of $YBa_2Cu_3O_7$, the weight loss observed on heating to 1073 K is much higher (0.83 %). The μTG curves obtained in air and nitrogen for these compounds also showed similar trends during heating.

The dilatometric data are shown in Fig. 3, wherein the percentage linear thermal expansion is plotted as a function of temperature from ambient to 1073 K in air for $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$. The dilatometric results obtained earlier [2] for $YBa_2Cu_3O_7$ under identical conditions are also shown in Fig. 3 for comparison.

The temperature variation of percentage linear thermal expansion $100(\Delta L/L)$ can be expressed by the following equations obtained by the least-squares method valid in the range 298–1073 K in air.

For $BiCaSrCu_2O_x$

$$100(\Delta L/L) = 4.84 \times 10^{-4}(T-298) + 2.88 \times 10^{-6}(T-298)^2 - 2.71 \times 10^{-9}(T-298)^3 \quad (1)$$

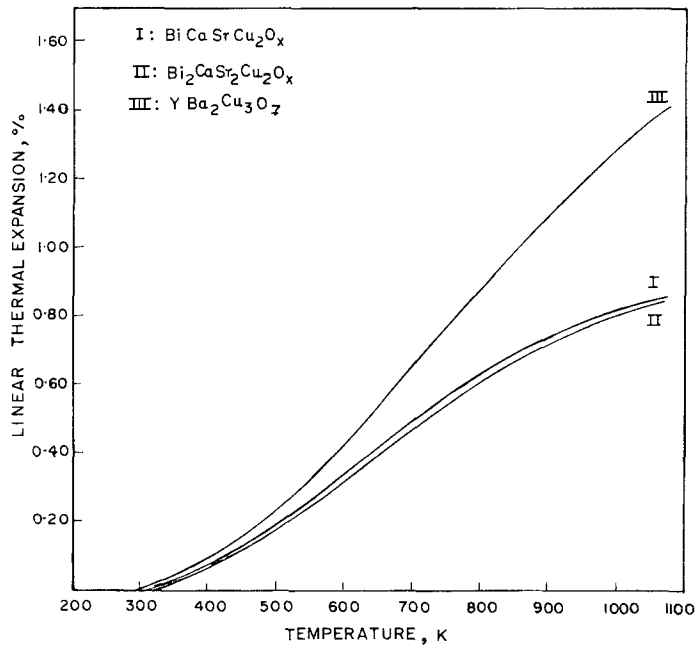

Fig. 3. Variation of percentage linear thermal expansion as a function of temperature in the range 298–1073 K in air for $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ (present work) and $YBa_2Cu_3O_7$ [2].

For $Bi_2CaSr_2Cu_2O_x$

$$100(\Delta L/L) = 2.83 \times 10^{-4}(T-298) + 3.35 \times 10^{-6}(T-298)^2 - 2.99 \times 10^{-9}(T-298)^3 \quad (2)$$

For $YBa_2Cu_3O_7$

$$100(\Delta L/L) = 4.40 \times 10^{-4}(T-298) + 4.03 \times 10^{-6}(T-298)^2 - 2.91 \times 10^{-9}(T-298)^3 \quad (3)$$

The temperature dependence of the coefficient of average linear thermal expansion, $\alpha_l = (1/L)(\Delta L/\Delta T)$, derived from Eqs. (1), (2), and (3) is represented by the following expressions.

For $BiCaSrCu_2O_x$

$$\alpha_l = 4.84 \times 10^{-6} + 2.88 \times 10^{-8}(T-298) - 2.71 \times 10^{-11}(T-298)^2 \quad (4)$$

For $Bi_2CaSr_2Cu_2O_x$

$$\alpha_l = 2.83 \times 10^{-6} + 3.35 \times 10^{-8}(T-298) - 2.99 \times 10^{-11}(T-298)^2 \quad (5)$$

For $YBa_2Cu_3O_7$

$$\alpha_l = 4.40 \times 10^{-6} + 4.03 \times 10^{-8}(T-298) - 2.91 \times 10^{-11}(T-298)^2 \quad (6)$$

The α_l values calculated from the above equations are found to be 10.59×10^{-6} and $10.47 \times 10^{-6}\ K^{-1}$ for $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$, respectively, in the temperature range 298–1073 K, while for $YBa_2Cu_3O_7$ the value obtained is $18 \times 10^{-6}\ K^{-1}$. The α_l values of both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ are thus found to be almost the same, but these values are nearly half of that of $YBa_2Cu_3O_7$. The low α_l values of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ indicate that the interatomic bonding in these two compounds is stronger as compared to $YBa_2Cu_3O_7$. This is also evident from the μTG data (Fig. 2), wherein it is observed that the oxygen loss on heating is negligibly small for both $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ as compared to that for $YBa_2Cu_3O_7$. The evolution of oxygen on heating $YBa_2Cu_3O_7$ increases the void space along the grain boundaries, which in turn contributes to the increase in bulk volume, resulting in the high value of α_l for $YBa_2Cu_3O_7$. In case of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$, the evolution of oxygen on heating is negligibly small and hence its contribution to the expansion coefficient is absent in these two compounds.

The lattice thermal expansion data obtained earlier [1] for $YBa_2Cu_3O_7$ revealed that α_l along the crystallographic axes a and b of

an orthorhombic unit cell of $YBa_2Cu_3O_7$ is almost the same ($\alpha_l \approx 7.5 \times 10^{-6}\,K^{-1}$), while that along axis c is nearly twice ($\alpha_l \approx 15 \times 10^{-6}\,K^{-1}$) that of a or b. It remains to be seen how the expansion coefficients along the crystallographic axes a, b, and c of the orthorhombic unit cells of $BiCaSrCu_2O_x$ and $Bi_2CaSr_2Cu_2O_x$ behave. It would be particularly interesting to know the behavior along the c axis. This aspect is therefore being studied using high-temperature X-ray powder diffractometry.

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