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THERMOGRAVIMETRIC AND DILATOMETRIC STUDIES OF $LaBa_2Cu_{3-y}M_yO_x$ (M = Ni, Li; $y = 0, 0.1$)

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ABSTRACT

Thermogravimetric (TG) and dilatometric studies of the pure compound $LaBa_2Cu_3O_x$ and the Ni and Li doped compounds $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and $LaBa_2Cu_{2.9}Li_{0.1}O_x$ were carried out in the temperature range $298 \leqslant T \leqslant 1173$ K. The results were analysed and compared with those obtained earlier for $YBa_2Cu_3O_x$. The values of oxygen content x for the compounds $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ were obtained from the TG data in $8\%H_2$–Ar and their behaviour compared with that of pure CuO and NiO under similar conditions. The values of average linear thermal expansion coefficients (α_l) were determined from the dilatometric data for the pure and Ni and Li doped compounds of $LaBa_2Cu_3O_x$. The dilatometric and TG results both suggest that the oxygen ions in the pure compounds $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ are more loosely bound than those in the doped compounds.

INTRODUCTION

In our previous papers [1,2], we reported lattice and bulk thermal-expansion studies of the well-established superconducting compound $YBa_2Cu_3O_7$ using high-temperature X-ray powder diffractometry [1] and dilatometry [2]. We have also reported [3] thermogravimetric (TG) studies of pure and K doped $YBa_2Cu_3O_x$ in the temperature range from ambient to 1203 K. As a continuation of these investigations, we report here the TG and dilatometric studies of pure, Ni and Li doped $LaBa_2Cu_3O_x$ in the temperature range $298 \leqslant T \leqslant 1203$ K.

EXPERIMENTAL

The pure compound $LaBa_2Cu_3O_x$ and the Ni and Li doped compounds $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and $LaBa_2Cu_{2.9}Li_{0.1}O_x$ were prepared by means of the standard ceramic technique. Appropriate amounts of La_2O_3, $BaCO_3$, Li_2CO_3, NiO and CuO powders were thoroughly mixed, uniformly ground and heated at 1175 K in air for 24 h. with intermittent grinding. The product was

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reground, pelletised and heated in flowing oxygen for 18 h at 1175 K and then slowly furnace-cooled to room temperature in oxygen.

The compounds were characterized by X-ray powder diffractometry (XRD) using Cu K_α radiation.

Thermogravimetric studies were carried out in flowing oxygen between room temperature and 1175 K during heating and cooling at a rate of 5 °C min^{-1} using a Shimadzu TG instrument, Model TGC-31 at 50 μg sensitivity. The oxygen content x of the pure compound $LaBa_2Cu_3O_x$ was determined from TG runs recorded on powdered samples in 8%H_2–Ar from ambient temperature to 1203 K at the slow heating rate of 2 °C min^{-1}.

The bulk thermal-expansion studies were carried out from ambient temperature to 1173 K in air at a heating rate of 5 °C min^{-1} using a Model LKB-3185 fused quartz pushrod-type dilatometer. The samples in the form of pressed, sintered, cylindrical pellets with ca. 65% theoretical bulk density were used.

RESULTS AND DISCUSSION

The X-ray powder diffractograms recorded for the pure compound $LaBa_2Cu_3O_x$ and for the doped compounds $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and $LaBa_2Cu_{2.9}Li_{0.1}O_x$ at room temperature are shown in Fig. 1, along with that obtained for pure $YBa_2Cu_3O_7$ [1]. The X-ray patterns of the pure, and Ni and Li doped $LaBa_2Cu_3O_x$ all show a single-phase nature and are identical. However, as compared with $YBa_2Cu_3O_7$, these patterns show a slight shift in peak positions towards lower 2θ and indicate small changes in peak intensities.

The TG data obtained in flowing oxygen for these compounds are shown in Fig. 2. As can be seen from this figure, the behaviour of these compounds is more or less similar to that of $YBa_2Cu_3O_7$. All these compounds begin to lose oxygen at around 650 K and the loss increases with increasing temperature. The oxygen lost on heating is regained during cooling. However, the percentage of oxygen lost in the Ni and Li doped compounds is comparatively less than that lost from pure $LaBa_2Cu_3O_x$ or $YBa_2Cu_3O_7$.

The TG data obtained in 8%H_2–Ar for pure $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ are shown in Fig. 3 along with that obtained for pure CuO. TG data were also obtained for pure NiO in order to compare its behaviour with that of CuO and are shown in the same figure. As can be seen from Fig. 3, the weight loss for pure CuO commences at 463 K and is complete at 523 K, while for NiO it commences at a slightly higher temperature (498 K) and is complete at 633 K. However, for the compounds $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$, although the weight loss commences at around the same temperature, it is complete at much higher temperatures as compared with that for pure CuO and NiO. Besides, the weight loss observed in both CuO

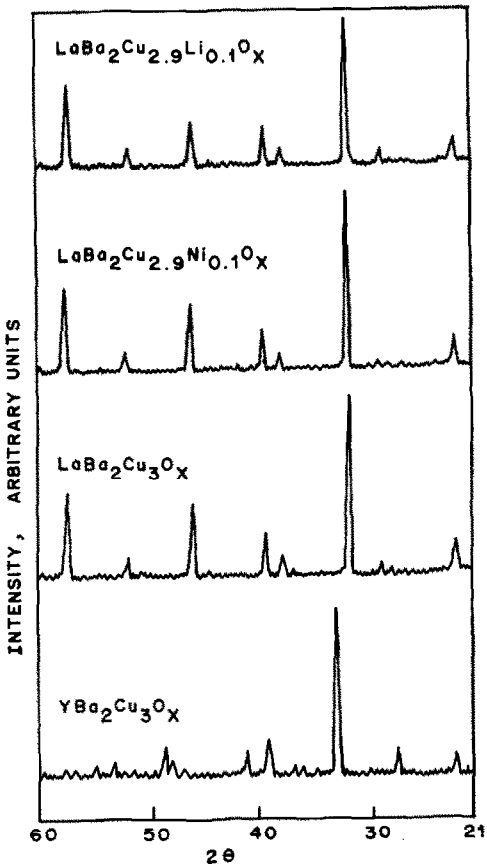

Fig. 1. Comparison of room temperature X-ray powder diffractograms of $LaBa_2Cu_3O_x$, $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and $LaBa_2Cu_{2.9}Li_{0.1}O_x$ (present study) and $YBa_2Cu_3O_x$ [1] in the 2θ range 20–60° (CuK_α).

and NiO is a single-step process of reduction of oxides to the respective metal, while in $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ there are intermediate steps which are attributed [4] to the hydroxide formation and subsequent decomposition into the constituent oxides, and for CuO a reduction to metallic copper, according to the following overall reactions:

$$CuO + H_2 \rightarrow Cu + H_2O\uparrow \quad (1)$$

$$NiO + H_2 \rightarrow Ni + H_2O\uparrow \quad (2)$$

$$2LaBa_2Cu_3O_x + (2x-7)H_2 \rightarrow La_2O_3 + 4BaO + 6Cu + (2x-7)H_2O\uparrow \quad (3)$$

$$2YBa_2Cu_3O_x + (2x-7)H_2 \rightarrow Y_2O_3 + 4BaO + 6Cu + (2x-7)H_2O\uparrow \quad (4)$$

The values of oxygen content x calculated from the total weight loss observed (Fig. 3) were 6.99 ± 0.05 and 7.00 ± 0.05 for $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$, respectively. The total weight loss observed for CuO and NiO

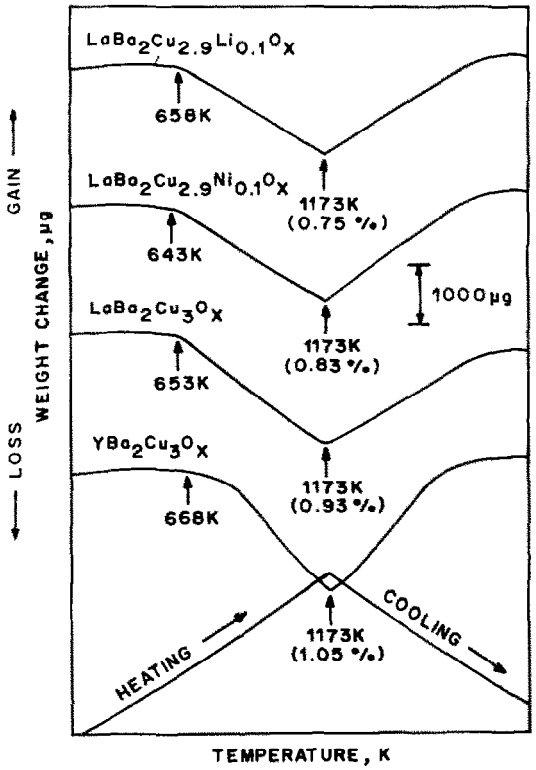

Fig. 2. TG data for $LaBa_2Cu_3O_x$, $LaBa_2Cu_{2.9}Ni_{0.1}O_x$, $LaBa_2Cu_{2.9}Li_{0.1}O_x$ and $YBa_2Cu_3O_x$ in flowing oxygen at a heating and cooling rate of 5 °C min^{-1} (sample weight = 200 mg). Figures in brackets show the percentage weight loss at 1173 K.

on reduction conform to the theoretical weight loss based on eqns. (1) and (2).

The dilatometric data obtained for the bulk thermal expansion of the pure and Ni and Li doped compounds of $LaBa_2Cu_3O_x$ are shown in Fig. 4. The dilatometric data obtained earlier [2] for $Yba_2Cu_3O_7$ under identical conditions are also shown in the same figure 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; the equations are valid in the range 298–1173 K in air.

For $LaBa_2Cu_{2.9}Ni_{0.1}O_x$

$$100(\Delta L/L) = 1.21 \times 10^{-4}(T-298) + 4.04 \times 10^{-6}(T-298)^2 - 3.09 \times 10^{-9}(T-298)^3 \quad (5)$$

For $LaBa_2Cu_{2.9}Li_{0.1}O_x$

$$100(\Delta L/L) = 5.83 \times 10^{-4}(T-298) + 2.42 \times 10^{-6}(T-298)^2 - 1.87 \times 10^{-9}(T-298)^3 \quad (6)$$

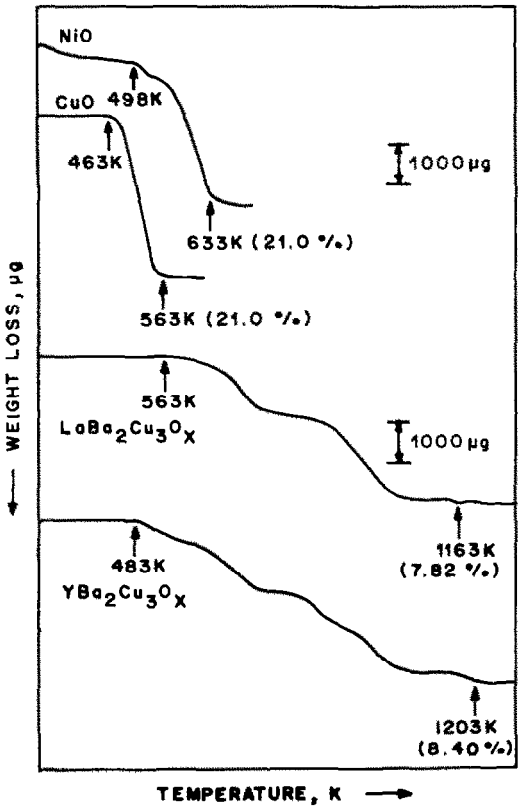

Fig. 3. TG data in 8%H_2–Ar for pure CuO and NiO (sample weight = 20 mg) and for $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ (sample weight = 50 mg) at a heating rate of 2°C min^{-1}. Figures in brackets show the percentage weight loss at the indicated temperature.

For $LaBa_2Cu_3O_x$

$$100(\Delta L/L) = 8.47 \times 10^{-4}(T-298) + 1.61 \times 10^{-6}(T-298)^2 - 0.93 \times 10^{-9}(T-298)^3 \quad (7)$$

For $YBa_2Cu_3O_7$

$$100(\Delta L/L) = 4.40 \times 10^{-4}(T-298) + 4.03 \times 10^{-6}(T-298)^2 - 2.91 \times 10^{-9}(T-298)^3 \quad (8)$$

The temperature dependence of the coefficient of average linear thermal expansion, $\alpha_l = (1/L)\Delta L/\Delta T$, derived from eqns. (5) to (8) is represented by eqns. (9) to (12).

For $LaBa_2Cu_{2.9}Ni_{0.1}O_x$

$$\alpha_l = 1.21 \times 10^{-6} + 4.04 \times 10^{-8}(T-298) - 3.09 \times 10^{-11}(T-298)^2 \quad (9)$$

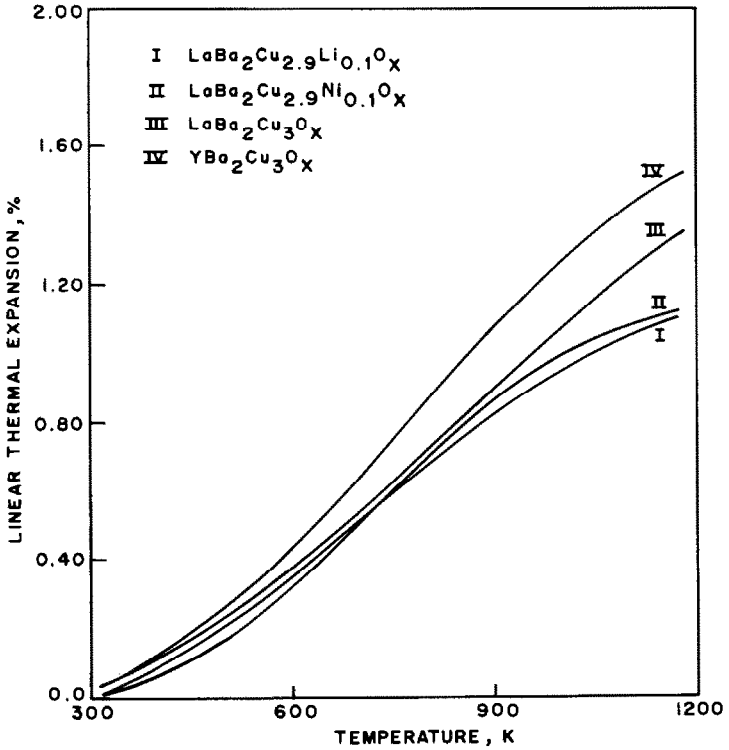

Fig. 4. Variation in the percentage linear thermal expansion as a function of temperature in the range 298–1173 K in air for $LaBa_2Cu_3O_x$, $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and $LaBa_2Cu_{2.9}Li_{0.1}O_x$ (present study) and for $YBa_2Cu_3O_x$ [2].

For $LaBa_2Cu_{2.9}Li_{0.1}O_x$

$$\alpha_l = 5.83 \times 10^{-6} + 2.42 \times 10^{-8}(T - 298) - 1.87 \times 10^{-11}(T - 298)^2 \quad (10)$$

For $LaBa_2Cu_3O_x$

$$\alpha_l = 8.47 \times 10^{-6} + 1.61 \times 10^{-8}(T - 298) - 0.93 \times 10^{-11}(T - 298)^2 \quad (11)$$

For $YBa_2Cu_3O_7$

$$\alpha_l = 4.40 \times 10^{-6} + 4.03 \times 10^{-8}(T - 298) - 2.91 \times 10^{-11}(T - 298)^2 \quad (12)$$

The values of α_l calculated from the above equations for Li and Ni doped compounds were found to be almost the same (12.81×10^{-6} K^{-1} for $LaBa_2Cu_{2.9}Ni_{0.1}O_x$ and 12.69×10^{-6} K^{-1} for $LaBa_2Cu_{2.9}Li_{0.1}O_x$). However, the α_l of both these compounds is comparatively smaller than that obtained for pure $LaBa_2Cu_3O_x$ (15.52×10^{-6} K^{-1}) or for $YBa_2Cu_3O_7$ (17.40×10^{-6} K^{-1}).

The lower values of α_l obtained for the Ni and Li doped compounds indicate that the interatomic bonding in these compounds is stronger as compared with that in the pure compounds, $LaBa_2Cu_3O_x$ or $YBa_2Cu_3O_x$.

CONCLUSION

The TG and dilatometric results obtained in the present study suggest that the oxygen ions in the pure compounds $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ are more loosely bound as compared with those in the Ni and Li doped compounds of $LaBa_2Cu_3O_x$; and, between the pure compounds, $LaBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$, the oxygen ions are more strongly bound in the former than in the latter.

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