

Dilatometric study of phase transitions in ferroelastic materials of the La_2CuO_4 type

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Test samples of La_2CuO_4 , in which La^{3+} ions were replaced by Sr^{2+} , Ce^{4+} , and Nd^{3+} ions, have been studied by a dilatometric method. The length of the test samples exhibits an anomalous behavior as a function of the temperature and the duration of a hold at a constant temperature in the temperature interval 990–1050 °C. It is suggested that this anomalous behavior is attributable to a structural phase transition.

Compounds based on La_2CuO_4 have attracted large interest because of the discovery of a high- T_c superconductivity in them. Despite the large number of publications on these compounds, their properties at high temperatures ($T > 900$ °C) have received very little attention. In this letter we are reporting a study of several compounds based on La_2CuO_4 by a dilatometric method in the temperature range 20–1050 °C.

The compounds $\text{La}_{1-x}^{3+}\text{Sr}_x^{2+}\text{CuO}_{4-\delta}$ ($x = 0, 0.05, 0.16, \text{ and } 0.30$), $\text{La}_{1.7}^{3+}\text{Nd}_{0.3}^{3+}\text{Cu}_{4-\delta}$, $\text{Nd}_2\text{CuO}_{4-\delta}$, and $\text{La}_{1.97}^{3+}\text{Ce}_{0.03}^{4+}\text{CuO}_{4-\delta}$ were produced by the standard ceramic technologies from “extremely pure” basic oxides. An annealing was carried out in air at $T = 1100$ °C for 1 h. An x-ray diffraction analysis was carried out on a DRON-3 diffractometer in $\text{Cr } K\alpha$ radiation in order to identify the phases present. All the samples containing La had a K_2NiF_4 structure, while all the Nd_2CuO_4 samples had a T' structure. The lattice constants agreed with those found in Refs. 1 and 2. No traces of foreign phases were found on the x-ray diffraction patterns. The porosity of the samples with the K_2NiF_4 structure was less than 6%. The dilatometric study was carried out on an ADAMEL LHOMARGY DI-24 dilatometer. The test samples were cylinders 12–15 mm long and 8 mm in diameter. The heating and cooling rates were 2–3 deg/min; the medium was air. The preliminary load on a sample was 0.1 N. The dilatometer was calibrated by means of periodic measurements of the thermal-expansion coefficients of SiO_2 , Al_2O_3 , and ZrO_2 samples, with standard $\Delta l/l(T)$ curves.

The length of a La_2CuO_4 sample was measured in the following sequence of operations. A first cycle consisted of a heating to 1050 °C, followed by cooling. A second cycle consisted of a heating to 1050 °C, a hold there for 1 h, and then a cooling. A third cycle consisted of a heating to 1050 °C, a hold there for 4 h, and a cooling. A fourth cycle consisted of a heating to 1025 °C, a hold there for 4 h, and a cooling. A fifth cycle consisted of a heating to 1030 °C, a hold there for 2 h, and a cooling. The phase composition of a sample did not change after the dilatometric measurements, according to the x-ray structural studies. Figure 1a shows the results of the measurements in the first cycle. In the course of the heating, we see a change in the slope of the $\Delta l/l(T)$ curve at 23 °C. This point coincides well with the temperature of the transition from an ortho-

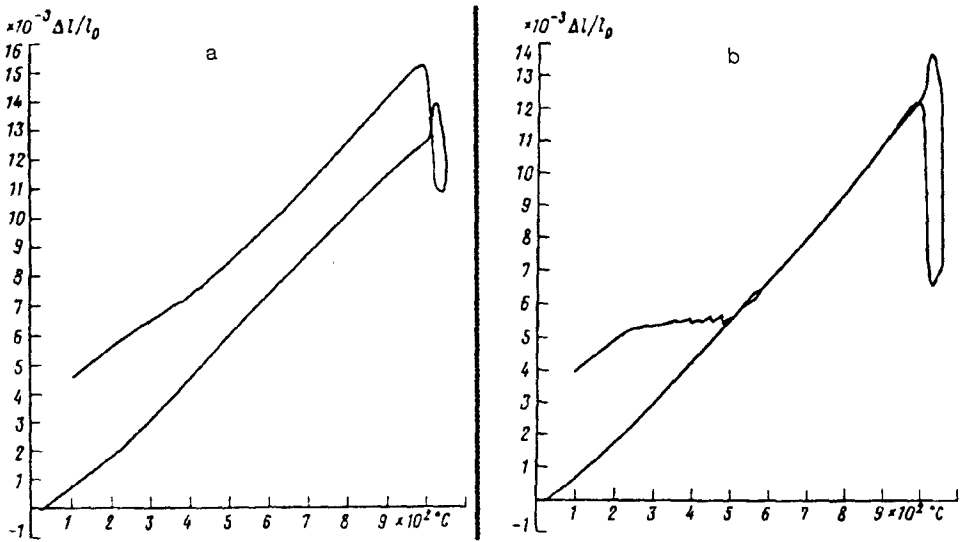


FIG. 1. Change in the length of a $\text{La}_2\text{CuO}_{4-\delta}$ sample. a—During heating to 1050°C followed by cooling; b—during heating to 1050°C , a hold there for 1 h, and then a cooling.

rhombic unit cell to a tetragonal one. At 1005°C the thermal-expansion coefficient increases sharply; it goes negative above 1025°C . During cooling, a sharp increase in the length of the sample is observed in the temperature interval $1037\text{--}998^\circ\text{C}$. During subsequent cooling, slope changes are observed on the curve of $\Delta l/l(T)$ near 450 and 230°C .

Figure 1b shows the results of the $\Delta l/l(T)$ measurements in the second cycle. There is essentially no change in the temperature intervals of the anomalous behavior at high temperatures. Below 500°C , however, several small abrupt changes in the length of the sample are observed during cooling. The magnitude of these changes is far greater than the error of the measurement instrument. Similar results were found in the third cycle. In this cycle, the increase in the length of the sample during cooling in the temperature interval $1037\text{--}998^\circ\text{C}$ is nearly 0.7% . During holds at 1025 and 1030°C in the measurements in the fourth and fifth cycles, the sample increases in length. This behavior is shown in Fig. 2. In the fifth measurement cycle, the length of the sample continues to rise to 1004°C during the cooling. An anomalous behavior is also observed in the samples doped with Sr^{2+} . Fig. 3 shows the results found on $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$. In the range $20\text{--}900^\circ\text{C}$ the expansion of the sample is linear; at 980°C the length of the sample begins to decrease. During an isothermal hold for 10 min at $T=1050^\circ\text{C}$, the length of the sample decreases and then begins to increase (Fig. 2). The sample continues to increase in length during cooling to 940°C .

The curve of $\Delta l/l(T)$ for $\text{La}_{1.97}\text{Ce}_{0.03}\text{CuO}_4$ is similar to the curves for La_2CuO_4 , but the anomalous behavior is even more pronounced. A high-temperature transition is also observed in $\text{La}_{1.7}\text{Nd}_{0.3}\text{CuO}_4$, although the plasticity of the transition is slightly different

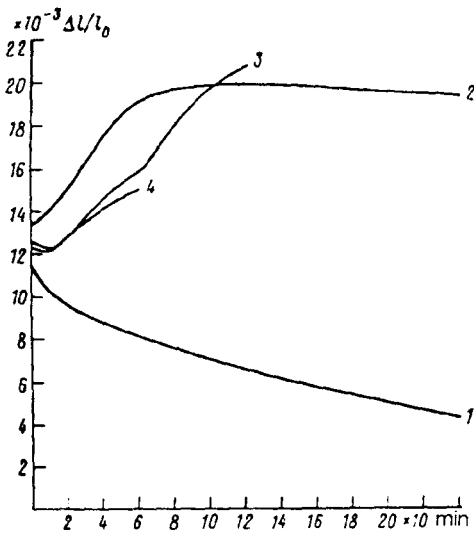


FIG. 2. Time evolution of the length of a La_2CuO_4 sample at $T=1050^\circ\text{C}$ (1), 1025°C (2), and 1030°C (3) and of a $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ sample at 1050°C (4).

in this sample. In Nd_2CuO_4 we do not observe an anomalous behavior of the curves during cooling from 1050°C .

The anomalous properties of the samples containing La can be explained under the assumption that a martensitic-type structural phase transition occurs near $T=1000^\circ\text{C}$. This transition destabilizes the domain structure of the ferroelastic material. In the $\text{La}_2\text{CuO}_{4-\delta}$ and also in the samples doped with cerium, it appears that two types of thermodynamically favored domain structures exist in the vicinity of the phase transition. The first type of domain structure corresponds to the temperature interval $1000\text{--}1035^\circ\text{C}$, and

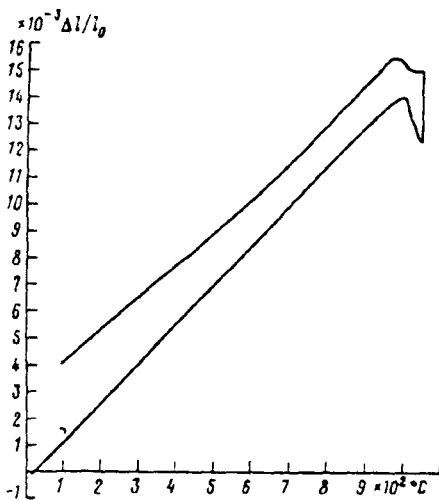


FIG. 3. Change in the length of a $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ sample in the course of a heating to 1050°C , a hold there for 1 h, and a cooling.

the second to the interval above 1035 °C. Below 1035 °C, the domain restructuring leads to an increase in the length of the sample, while above 1035 °C it leads to a decrease in the length of the sample in the direction of the external stress field. Under isothermal conditions, the rate of the restructuring of the domain structure is negligible (Fig. 2). The length may first decrease and then increase. A possible explanation is that the samples consist of two phases in the vicinity of the phase transition.

During cooling, the length of the sample is restored. The hysteresis at the transition is very slight (Fig. 1b). Since the length is restored, one might suggest that the phase transition is incomplete at 1050 °C, and that the deformation at 1050 °C is reversible. The restoration of the sample's length is usually linked with a shape memory during martensitic transitions.³

During cooling below 1000 °C, we observe several anomalies, not present under heating conditions. These anomalies are most likely attributable to a switching of the domain structure in certain parts of the ferroelastic material due to internal stress in the sample. This stress occurs as a result of the temperature cycling in the vicinity of the phase transition during compression of the sample. A switching of domains may occur abruptly after the formation of a nucleation center of the new phase if the driving force of the transition is very high. Phase transitions of an explosive nature in the ZrO₂-CeO₂ system were studied in detail in Ref. 4.

We are currently carrying out an x-ray structural study in order to determine the nature of the high-temperature phase transition.

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Translated by D. Parsons