

DILATOMETRY AND HIGH TEMPERATURE X-RAY DIFFRACTOMETRY STUDY OF LaCrO_3 PREPARED USING MICROWAVE HEATING

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The phase transitions in the LaCrO_3 were studied using bulk dilatometry and high temperature X-ray diffractometry from room temperature to 1050 and 1200°C, respectively. LaCrO_3 was prepared at 500°C from oxalate precursor employing microwave heating technique. Bulk shrinkage measurements on LaCrO_3 pellets were carried out using dilatometer designed and fabricated in our own laboratory. Dilatometric curves of LaCrO_3 showed two peaks in $\Delta L/L$ vs. temperature curves in the range 200–400 and 800–1000°C, respectively. These phase transitions have been confirmed using high temperature X-ray diffractometry. The role of simple technique like bulk dilatometry in detecting and monitoring the polymorphic transformations in solids is discussed for lanthanum chromates.

Keywords: dilatometry, LaCrO_3 , microwave heating, X-ray diffraction

Introduction

LaCrO_3 and alkaline earth substituted LaCrO_3 are thermally stable at high temperatures in both oxidizing and reducing environments. These compounds show high electrical conductivity and good refractory properties and are used as interconnect materials in high temperature solid oxide fuel cells [1–3]. In addition, LaCrO_3 has been extensively investigated for its catalytic activity [4] as well as for its potential as an oxygen sensor [5–7]. LaCrO_3 is orthorhombic at room temperature and known to undergo crystallographic transitions first to the rhombohedral (hexagonal) and then to cubic at higher temperatures [8, 9]. Several authors have reported the synthesis, characterization and physical properties of this compound [10–13]. Microwave assisted synthesis technique has been found to give good quality ceramic products within a short time [14, 15]. This technique, in addition, provides good alternative to conventional synthesis. In continuation of our recent studies on microwave assisted synthesis and characterization of mixed oxides [16–18], we report here the results obtained during the study of shrinkage behavior of LaCrO_3 . These results are compared with the shrinkage behavior of LaCoO_3 prepared by the same technique. The results obtained by bulk dilatometry are complemented by more accurate high temperature X-ray diffraction measurements.

Experimental

Preparation of LaCrO_3

LaCrO_3 , used in the present study, was synthesized from lanthanum trisoxalatochromate(III) (LTCR) precursor employing microwave heating technique. LTCR precursor calcined in microwave system yielded pure orthorhombic LaCrO_3 powder at 500°C within 1 hour. Detailed procedure for the synthesis of LaCrO_3 powder employing microwave heating technique is described elsewhere [19]. The powder formed was ground and pressed into cylindrical pellet of 10 mm diameter and 4.85 mm thickness. Shrinkage behavior of LaCrO_3 pellet was studied using push rod dilatometer fabricated from original own available components. The pellet was heated in static air at the heating rate $10^\circ\text{C min}^{-1}$ and change in its length as a function of temperature was recorded.

Fabrication of thermodilatometer

Thermodilatometer (TD) was fabricated incorporating quartz push rod and sample holder made of quartz tube. Expansion or contraction of the sample moves the push rod upward or downward. The signals resulting due to this movement were recorded electronically. The expansion or contraction of the material was converted to millivolt recordable signal with the help of displacement indicator and sensor (LVDT). The push rod used in the instrument was made of quartz and is 305 mm long and 8 mm in diameter.

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This rod was housed in one end closed 290 mm long quartz tube of 12 mm inner diameter. Displacement transducer (LVDT) used for the fabrication of TD was of Syscon make (Model SI-70T), Bangalore. It comprised of coil and a core which moves inside the coil. The primary coil of LVDT was excited with a signal at a carrier frequency of 4 kHz. The two secondary coils coupled inductively to the primary through the core were connected in series opposition, so that when the core is exactly at the center of the coil the signal output of sensor is zero. Any displacement of the core from the center of the coil (due to contraction or expansion of the pellet) resulted in an increase or decrease of the signal. Thus, the sensor output was a true representation of the amplitude and direction of the displacement. The displacement indicator used in the present study depicts resolution 0.001 mm with 0.1% accuracy. The mechanical assembly of the system consisted of a stand made up of four mild steel rods. This stand carries a stationary platform at the center of which the probe was fixed on the upward side, to measure the mechanical displacement of the rod. A silica tube containing the push rod was fixed exactly below the probe, on downward side of the platform. A precision micrometer screw located on the platform carries the coil assembly of the probe, which could be adjusted with respect to the core of LVDT. The core located on one end of the push rod was adjusted with the help of micrometer screw symmetrically with respect to the two secondary coils of LVDT to yield zero output, prior to the start of the experiment. The sample holder silica tube was provided with a small slit type hole near its closed end through which the sample pellet could be inserted and kept between the push rod and flat bottom end of the sample tube. Another slit of about 10 mm was provided at the upper level in this tube which facilitated lifting of the push rod while placing the sample pellet in position. The silica tube carrying the sample and push rod (Fig. 1) was housed in another closed end silica tube of larger diameter (25 mm I.D.) was mechanically coupled with the SS platform, using the aluminium collar and O-ring joint. The chromel–alumel thermocouple for measuring the temperature of the pellet was fixed onto the central silica tube carrying the sample and a quartz push rod. The stand carried another movable platform for mounting the furnace, which could be moved up or down with the help of a screw jack. The position of the furnace could be adjusted in such a way that the sample pellet was located in the uniform temperature zone of the furnace. The heating of furnace was programmed employing a PID temperature programmer (Max Thermo Make, Model MC-2438). The sample could be heated either at a fixed predetermined rate of heating or in a se-

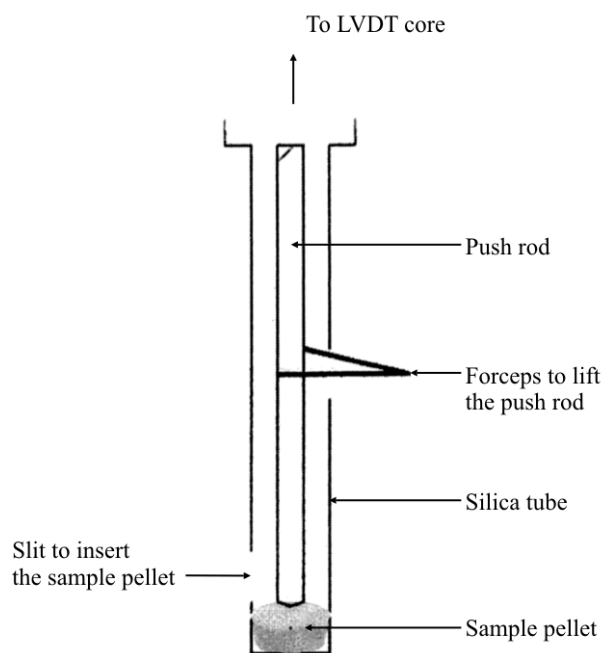


Fig. 1 Schematic diagram of silica tube carrying the sample and push rod in dilatometer

quence of heating and cooling cycles. Sixteen program segments involving heat–hold–cool routines are provided in temperature programmer. The temperature programmer used a chromel–alumel thermocouple as temperature sensor. The temperature is displayed during the reaction on a digital voltmeter provided in the unit.

The high temperature XRD patterns for LaCrO_3 were recorded at an interval of 200°C in the temperature range ambient to 1200°C employing STOE High Temperature X-Ray Diffractometer.

Results and discussion

Dilatometric study of LaCrO_3

The plot of relative change in the length ($\Delta L/L$) of pellet as a function of temperature plotted for LaCrO_3 and LaCoO_3 pellets are presented in Figs 2a–c. Figures 2a and b show two apparent peaks. First peak was located in the temperature range 200 to 400°C and the second peak started at ~ 800 and terminated at $\sim 1000^\circ\text{C}$. These peaks have resulted from the combination of the contraction due to sintering and the expansion of the lattice involving the phase transitions in LaCrO_3 . The contraction in LaCrO_3 would have been continuous (if there was only shrinkage) had there been no phase transitions in LaCrO_3 in these temperature ranges. On the contrary, shrinkage behavior of LaCoO_3 pellet (Fig. 2c) studied using the same method does not show any peak up to 1000°C .

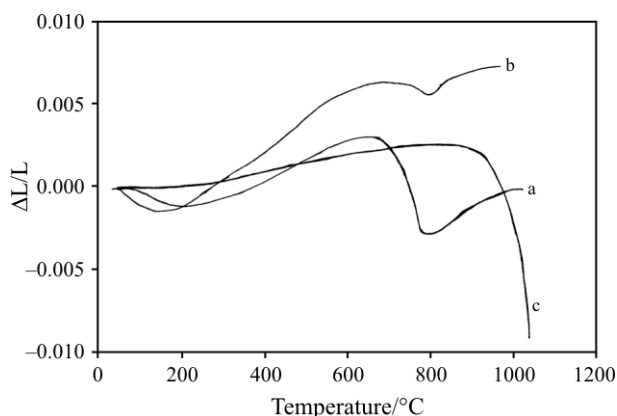


Fig. 2 Dilatometric curves of a – 1st heating cycle, b – 2nd heating cycle LaCrO₃ and c – LaCoO₃

Above 1000°C, LaCoO₃ shrinks rapidly. The two peaks observed in $\Delta L/L$ vs. temperature plots for LaCrO₃ suggest that LaCrO₃ undergoes phase transitions in the corresponding temperature ranges. These phase transitions were confirmed by the high temperature X-ray diffractometry studies.

High temperature X-ray diffraction study of LaCrO₃

XRD patterns of LaCrO₃ powder were recorded in the temperature range 200 to 1200°C and the changes in the characteristics of the most prominent peak ($\sim 2\theta = 32.59^\circ$) were followed and are presented in Fig. 3. XRD pattern of LaCrO₃ powder recorded at 200°C shows only a single peak in the region $2\theta = 32\text{--}33^\circ$. This peak

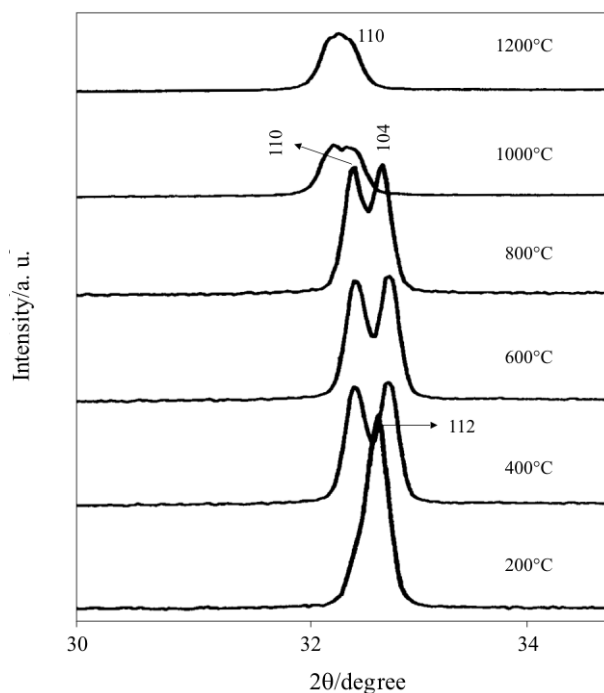


Fig. 3 XRD patterns of LaCrO₃ recorded at various temperatures

recorded at 400°C shows splitting indicating transformation from orthorhombic to rhombohedral phase between 200 and 400°C. XRD pattern of LaCrO₃ recorded upto 800°C showed no change in this doublet, but the pattern recorded at 1000°C exhibits definite change in this doublet, indicative of a second phase transition around this temperature. XRD pattern at 1200°C shows only a single peak at lower angle ($\sim 2\theta = 32.2^\circ$) indicating that LaCrO₃ was transformed from rhombohedral to cubic phase at this temperature. These phase transitions observed in LaCrO₃ in the present study are in good agreement with those reported by earlier workers [8, 9].

Conclusions

From the results presented in this paper we conclude that simple technique like therm dilatometry can be used to get the preliminary information about the phase transitions during shrinkage study, particularly in the case of materials with poor sinterability, where a clear demarcation is possible in the dimensional changes occurring due to shrinkage of material and its polymorphic transformations. LaCrO₃ has poor sinterability and is the most appropriate candidate in which the polymorphic transformation could be followed conveniently by bulk dilatometry. In fact it sinters to only 64% to theoretical density when it heated to 1700°C [20]. The transitions detected by bulk dilatometry can be confirmed and studied more accurately and extensively with the help of high temperature XRD.

The therm dilatometric pattern of LaCoO₃ (Fig. 2 c) indicates that the polymorphic transformation observed by X-ray diffraction can be totally missed if this occurs in the temperature range where rapid sintering takes place. Any polymorphic transformation occurring in LaCoO₃ above 950°C will therefore be missed in bulk dilatometric measurement but registered in high temperature X-ray diffraction pattern. Raccach and Goodenough [21] and Bhide and coinvestigator [22] reported two transitions in LaCoO₃, the first occurring around 375°C involved localized to collective electron (high spin to low spin) transition and the second first order transition occurred around 937°C which involves insulator to metal transition accompanied by crystallographic change. Since the high spin–low spin transition is not accompanied by a significant change in the structure of LaCoO₃ it is not expected to be detected by bulk dilatometry or X-ray diffraction technique. It is however clear that the crystallographic transition occurring $\sim 937^\circ\text{C}$ is superimposed on the rapid shrinkage of the sample caused by sintering in this temperature region (Fig. 2c) and therefore totally missed. The di-

mensional change in the sample occurring in bulk shrinkage of the sample far exceeds the change in the unit cell dimension of LaCoO₃ accompanying the crystallographic transition.

The thermodilatometric pattern of LaCoO₃ once again indicates that such polymorphic transformation can be totally missed if these occur in the temperature range where rapid sintering takes place. Any polymorphic transformation in LaCoO₃ occurring above ~950°C were therefore be missed in bulk dilatometric measurements.

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