DTA studies of formation of $\text{LaBa}_2\text{Cu}_3\text{O}_x$

K SUCHARITHA and C S SUNANDANA*

School of Physics, University of Hyderabad, Hyderabad 500 134, India

Abstract. The 1:2:3 composition in the La–Ba–Cu–O system has been investigated to understand the formation pathways of the $\text{LaBa}_2\text{Cu}_3\text{O}_x$ using the static air differential thermal analysis (DTA) as the principal probe and X-ray diffraction and EPR as supporting probes. The major endothermic events observed in DTA are attributed to $\gamma \rightleftharpoons \alpha$ type phase transition of BaCO_3 and the formation of “123” phase. It was found necessary to dry the La_2O_3 at high temperatures to make it crystalline and reactive. BaCO_3 was prepared afresh to achieve optimum reactivity. Even after four DTA runs the compound was not single phase as seen in XRD which shows the presence of BaCuO_2 as the impurity. The $\text{Ba}(\text{NO}_3)_2$ -based mixture appears to react slower than the BaCO_3 -based mixture.

Keywords. DTA; XRD; EPR.

1. Introduction

Although systematic studies of the formation pathways of “123” and other oxide superconductors eventually lead to the basic understanding of thermodynamics and kinetics, such studies have been rather rare (Ruckenstein *et al* 1989). We believe that in the 123 compound the crystallinity and reactivity of both La_2O_3 and BaCO_3 play a crucial role. We report in this paper the results of a DTA investigation supported by powder X-ray diffraction and electron paramagnetic resonance of the 123 reaction mixture employing BaCO_3 [LC] and $\text{Ba}(\text{NO}_3)_2$ [LN] as the precursors for BaO. We had earlier carried out a DTA study of Y 123 compound (Srinivasa Rao *et al* 1989).

2. Experimental

Using reagent grade La_2O_3 (IRE, 99.9%) [preheated up to 900°C], BaCO_3 [freshly prepared from $\text{Ba}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{CO}_3$], $\text{Ba}(\text{NO}_3)_2$ [Loba, 99.5%] and CuO [Loba 99%] reaction mixture for the 123 composition were prepared according to the equation $\frac{1}{2}\text{La}_2\text{O}_3 + 2\text{BaO} + 3\text{CuO}$ [$\text{X} = \text{CO}_3, (\text{NO}_3)_2$]. The DTA runs were performed on both the reaction mixtures from ambient to 930°C in static air with a heating rate of $12^\circ\text{C}/\text{min}$. The lab built DTA set-up was calibrated using $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ run with Ch–Al–Ch differential thermocouple. After the I-DTA run the set-up was furnace-cooled and II-DTA run was performed, without disturbing the set-up, under the same conditions. This programme was repeated several times to get the DTA curves. The 123 mixture taken in a separate crucible was also kept simultaneously along with the DTA set-up in the furnace to get the samples for XRD and EPR after I, II, III, and IV-DTA runs. The 123 composition was prepared by sintering the powder thrice at 920°C and by final sinterings (twice) in the pellet form at 950°C for 20 h in static air.

* For correspondence.

All the XRD patterns were recorded with SEIFERT diffractometer using $\text{CuK}\alpha$ (Ni filter) radiation. The EPR patterns were recorded with JEOL FE 3X spectrometer (~ 9 GHz, 100 kHz modulation). The resistivity of the sintered 123 sample was determined by the DC four-probe technique [semiconducting, $\rho_{RT} = 100 \text{ m}\Omega\text{cm}$].

3. Results and discussion

The DTA curves of I, II, III and IV runs and their XRD and EPR spectra are shown in figures 1 and 2. Figure 1a presents the DTA curves of La_2O_3 – BaCO_3 – CuO reaction mixture. These thermograms are similar to those for YC 123 (Srinivasa Rao *et al* 1989) except that the events are all exothermic in YC 123 whereas they are endothermic in LC 123. In the I-DTA run we got a small exothermic peak at 383°C which could be a sign of evolution of CO_2 from carbonate. This exothermic peak is not much strong as in the case of YC 123 (Srinivasa Rao *et al* 1989). The endotherm at 793°C —sharp and intense—represents the $\gamma \rightleftharpoons \alpha$ (ortho to hexa)-type phase transition in BaCO_3 , being located nearer to 820°C in the pure compound (Nishino *et al* 1972).

Figure 1. (a) DTA runs, (b) XRD patterns and (c) ESR spectra after IV-DTA run of La_2O_3 – BaCO_3 – CuO system.

Figure 2. (a) DTA runs, (b) XRD patterns and (c) ESR spectra after III-DTA run of $\text{La}_2\text{O}_3\text{-Ba}(\text{NO}_3)_2\text{-CuO}$ system

Also present is a small kink at 814°C which could be due to the decomposition of BaCO_3 . From the I-DTA run onwards the low temperature peak disappears because of the possibility of the completion of almost all CO_2 evolution in the I and II runs and we got only one endotherm at 510°C in II and III-DTA runs and at 537°C in IV-DTA run, whose intensity increases with the consecutive DTA runs, in contrast to YC 123 where the peak is exothermic (at 570°C) and becomes smaller in the IV-DTA run (Srinivasa Rao *et al* 1989). This peak could represent the formation of 123 phase.

Figure 1b presents the characteristic XRD features of BaCO_3 -based reaction mixture. One of the features is a strong peak at $2\theta = 32.5^\circ$ and a cluster of peaks around $2\theta = 23^\circ$ to 26° whose intensity decreases systematically with each run. The multiple peaks over the range $2\theta = 27^\circ$ to 29° and 33° to 35° are due to the impurity phase BaCuO_2 (Nevriva *et al* 1988). In LC 123 the crystallinity and reactivity of La_2O_3 and BaCO_3 play a major role in the formation of 123 as could be seen from the XRD after the I-DTA run. The major 123 phase is already formed just by the

completion of I-DTA run itself. In the XRD patterns all the lines are indexable to 123 phase (tetragonal) and BaCuO_2 phase. There is not much variation in the intensities of the most prominent line in the 123 phase and the % of impurity phase BaCuO_2 (by roughly comparing the intensities) with DTA run. The impurity (BaCuO_2) phase persists even after the IV-DTA run.

The DTA curves and the XRD patterns of $\text{La}_2\text{O}_3\text{--Ba(NO}_3)_2\text{--CuO}$ reaction mixture are shown in figure 2. These clearly reflect the slower formation of the 123 phase with $\text{Ba(NO}_3)_2$ than with BaCO_3 as the starting material in contrast to that of Y 123 where $\text{Ba(NO}_3)_2$ -based mixture reacts faster than the BaCO_3 mixture (Srinivasa Rao *et al* 1989). The DTA curves are very much similar than that of the BaCO_3 reaction mixture. The sharp endotherm at 783°C represents the evolution of the NO_2 gas similar to that obtained for YN 123 (Srinivasa Rao *et al* 1989).

XRD pattern after I-DTA run shows the presence of starting material—mainly CuO, the 123 phase slowly started forming and the impurity phase BaCuO_2 . One of the features is a strong peak at $2\theta = 32.5^\circ$ and multiple peaks around 30° to 35° whose intensity and position seem to change systematically with each run. The cluster of peaks between 40° and 45° disappears after the I-DTA run. The prominent peaks of the 123 phase slowly start separating from the multiple peaks and increasing in intensity from the II-DTA run onwards. The diminution of the multiple peaks is slowly achieved due to heat treatment during the successive DTA runs. The impurity phase BaCuO_2 is present even after the IV-DTA run as in the case of LC 123.

Figures 1(c) and 2(c) show the EPR spectra of LC 123 after IV-DTA run and LN 123 after III-DTA run respectively. There is a significant difference between the EPR signals for CO_3 and NO_3 -based mixture after the I-DTA run (not shown). The EPR signal for BaCO_3 -based mixtures after I, II, III (not shown) and IV-DTA runs are very much similar to each other with constant g values of $g_1 = 2.2171$, $g_2 = 2.1277$ and $g_3 = 2.0612$ whereas the EPR signal for NO_3 -based mixture after I-DTA run shows a signal which could be due to CuO—confirmed from the XRD. The CuO signal becomes broader after the II-DTA run implying the disappearance of CuO which is also seen from XRD and signal due to major phase slowly built-up after II and III-DTA runs. The g values of EPR signal after III-DTA run are found to be same as that of BaCO_3 -based mixture. These g values are exactly the same as that got for sintered LC 123 pellet implying that the observed EPR signal could be characteristic of the non-superconducting 123 phase (major phase) assuming that it is not antiferromagnetic.

4. Conclusions

- (i) Our DTA studies suggest CO_2/NO_2 evolution, BaCO_3 phase transition ($\gamma \rightleftharpoons \alpha$) and its decomposition and BaCuO_2 formation as the important steps in the formation of La 123 (semiconducting) oxide.
- (ii) The $\text{Ba(NO}_3)_2$ -based reaction mixture reacts slowly compared to that of BaCO_3 -based reaction mixture as evidenced by XRD results. In either case it is necessary to preheat La_2O_3 to achieve maximum crystallinity and reactivity.
- (iii) The impurity phase BaCuO_2 is present even after the IV-DTA run implying that a larger number of heat treatments are necessary to get a single phase 123 compound.
- (iv) The strong, identical EPR signal observed in *both* nitrate and carbonate reactions

is tentatively attributed to the major (semiconducting) 123 phase, assuming it to be paramagnetic but *not* antiferromagnetic. Careful quantitative measurements are necessary to confirm this assignment.

(v) The asymmetry of the DTA peaks is very interesting and a quantitative DTA study to determine enthalpies would lead to the thermodynamics of the formation of these oxides.

Acknowledgement

One of us (KS) thanks Programme Management Board on superconductivity for financial support.

References

- Nevriva M, Pollert M, Sestak J and Triska A 1988 *Thermochim. Acta* **127** 395
Nishino T and Nishiyama S 1972 in *Reactivity of solids* (eds) T S Anderson *et al* (London: Chapman and Hall) p. 766
Ruckenstein E, Narain S and Wu N L 1989 *J. Mater. Res.* **4** 267
Srinivasa Rao Y and Sunandana C S 1989 in *Advances in ferrites* (eds) C M Srivastava and M J Patni (New Delhi: Oxford & IBH) Vol. II p 763