Thermochimica Acta, 133 (1988) 23–26
Elsevier Science Publishers B.V., Amsterdam

USE OF EMANATION THERMAL ANALYSIS IN CHARACTERIZATION OF $YBa_2Cu_3O_x$

V. BALEK[1] and J. ŠESTÁK[2]
[1]Nuclear Research Institute, 250 68 Řež, Czechoslovakia
[2]Institute of Physics, Czechoslovak Academy of Sciences, 180 40 Prague 8, Czechoslovakia

ABSTRACT

The use of emanation thermal analysis for the study of microstructural changes occurring during the preparation of $YBa_2Cu_3O_x$ by heating in oxygen atmosphere is demonstrated. Emanation thermal analysis has been suggested as a suitable tool for qualitative testing of the intermediate products of oxide superconducting ceramics.

INTRODUCTION

Many papers on the characterization of $YBa_2Cu_3O_x$ have recently appeared. Thermogravimetry and differential thermal analysis were used [1–3] in the study of the preparation of this material making it possible to determine the temperature intervals of the phase changes in the feed mixtures as well as in the final ceramic product. Moreover, the thermogravimetry was used for characterization of oxygen non-stoichiometry changes during the heat treatment of the material.

The application of emanation thermal analysis in the investigation of the above system is described for the first time in this paper.

EXPERIMENTAL

The emanation thermal analysis, ETA [4] is based on the measurement of the radon release rate from samples previously labelled. Both the feed sample of Y, Ba, Cu coprecipitated oxalates and the oxide ceramic sample were labelled by the adsorption of trace amounts of ^{228}Th and ^{224}Ra from acetone solution. The radon atoms ^{220}Rn are formed by the radioactive decay according to the scheme

$$^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn \xrightarrow{\alpha}$$

and implanted into the solid at a max. depth of 120 nm, due to the recoil energy of the atoms of ^{224}Ra during the decay.

The ETA measurements were performed in oxygen atmosphere at the heating rate 5 K min^{-1} using NETZSCH simultaneous thermoanalyser STA 429 equipped with the ETA unit [5]. The ETA curves are plotted as temperature dependences of the radon release rate E related to the total radioactivity of the sample measured.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

RESULTS AND DISCUSSION

The ETA curve of the feed Y, Ba, Cu coprecipitated oxalate mixture is demonstrated in Fig. 1, curve 1, together with the thermogravimetry results (curve 2). It is obvious that the peaks in curves 1 and 2, Fig. 1, in the temperature range 60–300 °C correspond with the decomposition of the oxalate mixture which was already described elsewhere [2]. In the temperature range 300–750 °C no significant changes were observed in curve 2, a loss of the sample mass amounting to 8.8% of the initial sample mass was observed in the range 750–900 °C indicating probably the release of CO_2 as the result of the decomposition of the intermediate products (e.g. $BaCO_3.BaO$).

The ETA results (curve 1, Fig. 1) of the feed oxalate mixture reflect in the temperature range 300–750 °C the stepwise microstructure changes accompanying the formation of the intermediate and final oxide decomposition products. The decrease of radon release rate above 750 °C indicates apparently the formation of the perovskite phase, whereas decrease of E above 850 °C may be ascribed to the sintering of the powdered sample, possibly enhanced by partial melting of $BaCO_3.BaO$ intermediate product.

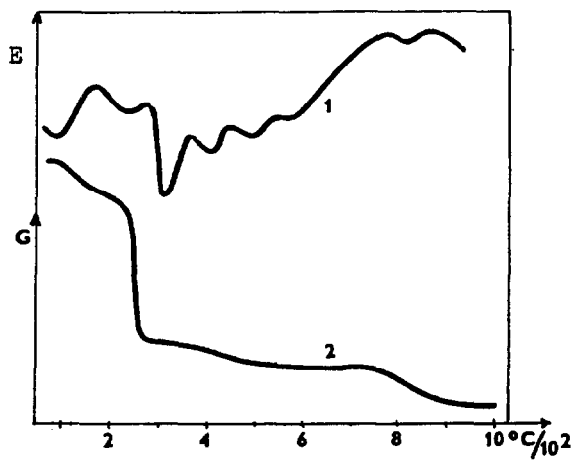

Fig. 1. Temperature dependence of the radon release rate E (curve 1) and of the sample mass loss G (curve 2) measured during heating of Y, Ba, Cu oxalate coprecipitate at the heating rate 5 k min^{-1} in the presence of oxygen. The parameters E and G are given in arbitrary units.

The ETA curve in Fig. 2, curve 1, characterizes the thermal behaviour of the oxide superconducting material. The sample was prepared by the heat treatment of the feed mixture in oxygen at 960 °C for 48 hours, and subsequent annealing during the slow cooling. The sample composition determined by chemical analysis was $YBa_2Cu_3O_{6.5}$.

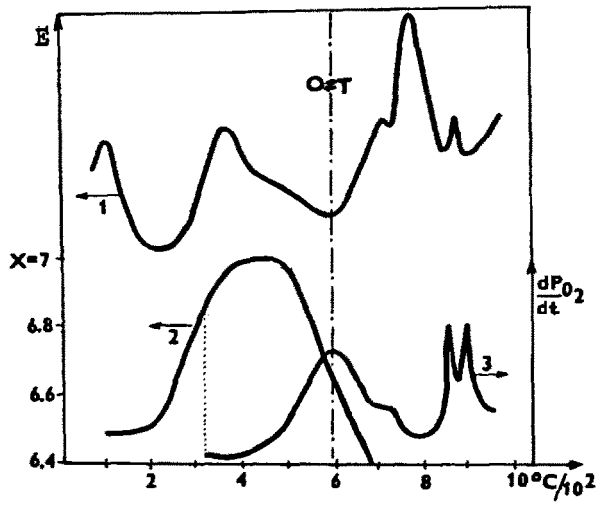

Fig. 2. Temperature dependences of the radon release rate E (curve 1) measured during heating in oxygen atmosphere of $YBa_2Cu_3O_{6.5}$ as compared with the oxygen stoichiometry X (curve 2) and the rate of oxygen partial pressure dP_{O_2}/dt (curve 3).

In curve 2, Fig. 2, the changes of the oxygen stoichiometry X of the material of this composition are demonstrated, as reported in [1,2]. As follows from the comparison of the curves 1 and 2 in Fig. 2, in the course of the oxygen in-take by the sample, in the temperature range 220–400 °C, an increase of the radon release rate E was observed in curve 1. This may be explained by the fact that the oxygen vacant sites are maintained ordered in the temperature range 200–400 °C [2] which makes easier the radon release from the sample.

It is interesting to note that the maximum radon release rate observed at 380 °C corresponds to the maximal possible content of oxygen X = 7. At this oxidation stage the most favourable conditions for superconducting properties of the sample exist. During heating above 450 °C the oxygen desorption from the orthorhombic structure takes place [6] and the oxygen stoichiometry falls down (see curve 2, Fig. 2). In this temperature interval the decrease of the radon release rate was observed, indicating that the oxygen vacant sites randomization is connected with distortion of the paths of radon atoms to escape and/or by trapping of radon atoms by the defect sites formed in this temperature interval. Supposing that the interatomic space in c-axis of the perovskite structure of this material is approx. 3.9 Å, the radon atoms of the size 1.9 Å serve here as the probe of the microstructure changes in situ.

As indicated by X-ray patterns, the measurement of electrical properties and other methods [7,8], the orthorhombic structure of the perovskite phase changes into tetragonal structure at approx. 600 °C. At this temperature the radon release rate E starts to increase, indicating the microstructure changes in the solid.

In curve 3, Fig. 2, the results of the oxygen pressure rate dP_{O_2}/dt above the sample of the composition $YBa_2Cu_3O_{6.85}$ during heating in oxygen are demonstrated, as reported in [6]. Interestingly, the increase of the oxygen pressure rate above the sample, shown in curve 3, corresponds to the decrease of radon release rate from the sample, caused probably by trapping radon atoms on the structure defects. The maximum change of the oxygen pressure rate takes place at 600 °C which corresponds to the orthorhombic tetragonal transition. On oxygen heating of the sample above 750 °C, the changes in the microstructure of the sintered ceramics were indicated in curve 1 as well as in curve 3, Fig. 2. The interpretation of the ETA effects related to these microstructure changes is under investigation.

CONCLUSION

The emanation thermal analysis is demonstrated as a suitable tool for detecting microstructure changes in $YBa_2Cu_3O_x$ ceramics during heating. This method enabled us to reveal processes taking place during the thermal treatment of the oxide ceramics which were not detectable by other methods. The ETA may be recommended for quality testing of the intermediate products during preparation of the oxide ceramic superconductors.

REFERENCES

1. P. Strobel et al., Letters to Nature, 327 (1987) 306.
2. T. Ozawa et al., Thermochim. Acta, 124 (1988) 147.
3. J. Šesták et al., J. Therm. Anal., in print.
4. V. Balek, Thermochim. Acta, 22 (1978) 1 and 110 (1987) 147.
5. W.D. Emmerich, V. Balek, High Temp.-High Press., 5 (1973) 67.
6. H. Strauven et al., Sol. State Comm., 65 (1988) 293.
7. H.M. O'Bryan, P.K. Gallagher, Advanced Ceram. Mat., Vol. 2 (1987) 648.
8. Z. Strnad, J. Šesták, Sklář a keramik, 20 (1988) 50 (a review in Czech).