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THERMODYNAMIC AND PSEUDO BINARY PHASE DIAGRAM OF $REBa_2Cu_3O_{7-x}$–'$Ba_2Cu_5O_7$' SYSTEMS

The effect of oxygen pressure

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Abstract

In this work the effect of oxygen pressure on the primary crystallisation fields for $REBa_2Cu_3O_{7-x}$ (*RE*=Nd, Sm, and Eu) has been studied. A DTA apparatus has been modified in order to carry out analyses under gas pressure, so the trend of temperatures of peritectic decomposition of the $REBa_2Cu_3O_{7-x}$ phases and of the eutectic equilibrium involving $REBa_2Cu_3O_{7-x}$ phases and flux mixture '$Ba_2Cu_5O_7$' have been studied at oxygen pressures of 0.21, 1, and 10 atm. This showed that primary crystallisation fields spread at the increase of the oxygen pressure and allowed us to calculate the enthalpies of reactions of $REBa_2Cu_3O_{7-x}$ phases too.

Keywords: high-T_c compounds, phase diagrams, thermodynamic properties

Introduction

In one of our previous works it has been pointed out that the field of primary crystallisation of the $REBa_2Cu_3O_{7-x}$ (RE-123) phases varies regularly as a function of the rare earth. For RE-123 phases containing light rare earths (like Pr, Nd, Sm, Eu, Gd) the temperature range between peritectic decomposition and eutectic equilibrium is larger than observed on yttrium-based 123 phase and when heavier rare earths are used. For this reason the crystallisation temperature range spreads and, at the same growing conditions, crystals can grow widely. In effect large single crystals of up to 20×15 mm^2 and thick up to 0.5 mm have been obtained [1, 2].

Nevertheless it is well known that the primary crystallisation fields (*p.c.f.*) of the RE-123 phases do not depend only on the gap of temperature between peritectic decomposition and eutectic equilibrium but also on the eutectic mixture composition and the molar ratio between flux and crystallising phase [3].

Moreover, oxygen partial pressure is another important variable affecting phase equilibria. Taking into account that solid–gas and liquid–gas transformations are also present, there is a dependence on the reaction atmosphere and the mixture cooling

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time, too; the determination of the *p.c.f. vs*. those parameters is a much debated question also for an accurately studied system like Y-123 [4, 5]. For this reason we are carefully investigating the influence of oxygen pressure on melt-growth process of RE-123, to a better determination of the *p.c.f.* for these phases. This is deduced from thermogravimetric analysis (TG) and differential thermal analysis (DTA) using a special apparatus modified in order to withstand pressures up to about 10 atm.

The stability, as the enthalpy of formation, of the Y-123 phase has been subject of many studies in different laboratories and, as one may expect, there is a great scatter among the results [6]. On the contrary few papers reported thermodynamic stability of the RE-123 phases. Consequently, the aim of this work was also to obtain, by means of TG and DTA, some results useful to discuss the stability of RE-123 phases in terms of reaction enthalpy, Gibbs energy and entropy change.

Experimental

RE-123 samples were prepared by conventional solid state reaction at 935°C using stoichiometric amounts of the high purity precursor oxides RE_2O_3, CuO and BaO_2. In case of uncompleted reaction a new thermal cycle has been required.

All samples have been structurally characterised by XRD powder diffraction performed in a Philips PW 1710 X-ray diffractometer using a CuK_α radiation and Ni filter to confirm that single phase was been obtained.

By means of DTA and TG analysis we contributed to the determination of $REBa_2Cu_3O_{7-x}$–'$Ba_2Cu_5O_7$' pseudobinary phase diagrams; the formula '$Ba_2Cu_5O_7$' indicates approximately a $BaCuO_2$+CuO mixture with the BaO/CuO ratio (28/72 mol%) which is usually employed in the crystal growth procedure. This investigation was performed in a Netzsch STA 409 apparatus. The high pressure differential thermal analysis pressure (HP-DTA) has been carried out in a Netzsch DTA 406 apparatus, modified in order to withstand pressures up to about 10 atm. A more detailed description of this equipment is reported elsewhere [7].

All the samples were studied in air (DTA and TG) and in oxygen partial pressure (HP-DTA), using allumina crucible and Y_2O_3 as a standard reference. Heating and cooling rate were 10 K min^{-1}. DTA and HP-DTA measurements were repeated several times under the same conditions for confirmations. Event temperatures, with standard uncertainties estimated as ±5°C (one standard deviation), were determined by the extrapolation of the linear section of the rising peak slope to its intersection with the baseline.

Results and discussion

The most interesting results have been obtained carrying out differential thermal analysis under oxygen pressure. Figure 1a shows the HP-DTA curves of Nd-, Sm-, and Eu-123 in the temperature range between 850 and 1250°C at $p(O_2)$=10 atm. Instead Fig. 1b summarises the thermal events of the $NdBa_2Cu_3O_{7-x}$, $SmBa_2Cu_3O_{7-x}$ and

EuBa$_2$Cu$_3$O$_{7-x}$ phases at 0.21, 1 and 10 atm p(O$_2$). The initial thermal event (eutectic equilibrium) of Nd-123, Sm-123 and Eu-123 samples was found to occur at about the same temperature of 950°C. On the contrary it is apparent that the peritectic decomposition temperature increased as the oxygen partial pressure increased. For Nd-123 phase, the peritectic decomposition temperature increased from 1108°C at 0.21 atm, to 1122°C at 1 atm and 1150°C at 10 atm. Similarly, the melting temperature of Sm-123 increased from 1095 to 1110 and 1142°C at the same oxygen pressures. In the case of Eu-123 the melting temperature was found 1085°C at 0.21 atm, 1103°C at 1 atm and 1118°C at 10 atm. We can conclude that the eutectic temperature in the above pseudobinary phase diagrams is almost independent from the increasing pressure and can be considered nearly constant varying both RE element and the reacting

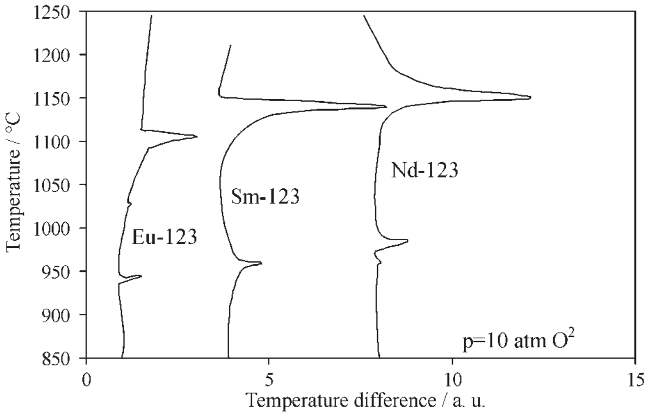

Fig. 1a HT-DTA curves of Nd-123, Sm-123 and Eu-123 at 10 atm p(O$_2$)

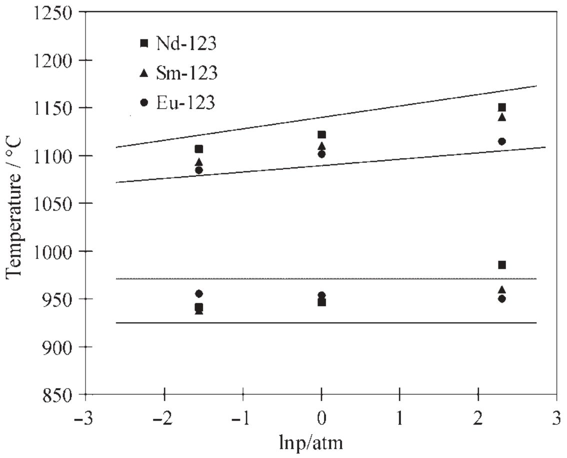

Fig. 1b Eutectic and peritectic decomposition temperatures for Nd-123, Sm-123 and Eu-123, under different oxygen pressure. The area comprised between these temperatures can be assumed as the primary crystallisation field

atmosphere. Only in the case of neodymium compounds we can observe an increasing in the eutectic temperature at $p(O_2)=10$ atm. Nevertheless, this anomaly can be explained taking into account that a $Nd_{1+y}Ba_{2-y}Cu_3O_{7-x}$ solid solution is promoted by an oxidising atmosphere [8–10], then the eutectic mixture composition could be changed in this case. The RE-123 peritectic decomposition temperature instead increase following the oxygen pressure. The total result is that the *p.c.f.* spreads working under oxygen pressure suggesting that crystal growth could be improved obtaining larger crystals.

Another significant result is summarised in Fig. 2. Plotting the RE-123 peritectic temperature equilibria in a ln*p*/atm *vs.* *T*/°C graph it is easily remarked that experimental points are well connected by a straight line represented by the equation $\ln p=mT+q$: for the Nd-123 phases $m=-17.208\pm0.122$ K, $q=134.79\pm0.43$, $R^2=0.9961$; for the Sm-123 phases $m=-15.97\pm0.11$ K, $q=126.47\pm0.41$, $R^2=0.997$; for the Eu-123 phases $m=-23.711\pm0.105$ K, $q=184.39\pm0.13$, $R^2=0.9621$.

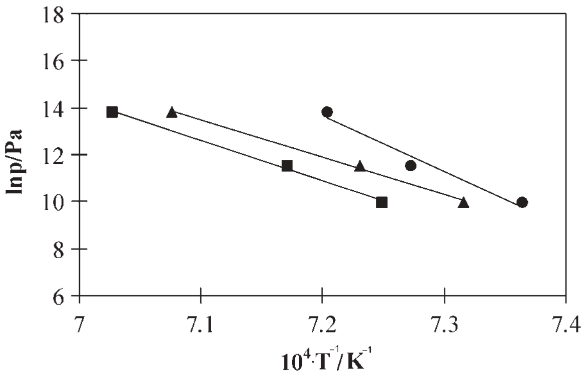

Fig. 2 Logaritmic plot of inverse peritectic decomposition temperature for RE-123 (■ – Nd, ● – Eu, and ▲ – Sm), under different oxygen pressure

Applying to these processes the equation derived from van't Hoff law $\ln K_p=(-\Delta H/RT)+c$, considering that $K_p=P_{O_2}^{\nu}$ for 1 mole of O_2, it follows: $\ln P=(-\Delta H/RT)+c$. In fact the peritectic reaction considered is:

$$REBa_2Cu_3O_{6+\delta} \rightarrow \frac{1}{2}RE_2BaCuO_5+\frac{3}{2}BaCuO_2+(1-x)CuO+\frac{x}{2}Cu_2O+\nu O_2$$

were the only gaseous phase involved is oxygen.

From this modified relation it is possible to find the value of ΔH_ρ for the peritectic reaction. Calculated values are $\Delta H_\rho=1430.8\pm85.0$ kJ mol^{-1} (O_2), $\Delta H_\rho=1327.8\pm79.6$ kJ mol^{-1} (O_2), $\Delta H_\rho=1977.8\pm118.6$ kJ mol^{-1} (O_2), for Nd-, Sm- and Eu-123, respectively.

It is significant to note that the coefficient of molecular oxygen evolving from the system (ν) depends on the decomposition reaction of RE-123 (i.e. δ) as well on the reduction of CuO (i.e. x): $\nu=(2\delta+x-1)/4$.

This latter value could not be easily determined directly from the thermodynamic data of the Cu–O system, because it strongly depends on the reaction temperature and oxygen pressure.

Of course, the total amount of evolved oxygen can be determine by TG analysis; values are: ν=2.66 10^{-1} mol O_2/mol 'Nd-123', ν=2.10 10^{-1} mol O_2/mol 'Sm-123', ν=2.50 10^{-1} mol O_2/mol 'Eu-123'. In this case the reaction enthalpy values found by DTA under pressure measurements (i.e. ΔH_ρ^0 for mole of O_2) could be correlated with ΔH_ρ^0 for mole of RE-123, by the simple relationship $\Delta H_\rho^0 = \Delta H_\rho^{DTA}\nu$:

$$\Delta H_\rho^0 = 380.6 \pm 22.6 \text{ kJ mol}^{-1} \ (NdBa_2Cu_3O_{7-x})$$

$$\Delta H_\rho^0 = 279.0 \pm 16.7 \text{ kJ mol}^{-1} \ (SmBa_2Cu_3O_{7-x})$$

$$\Delta H_\rho^0 = 493.9 \pm 29.6 \text{ kJ mol}^{-1} \ (EuBa_2Cu_3O_{7-x})$$

These data are in agreement if compared with the results reported in literature for Y-123 [6, 11, 12].

By usual relationships as $\Delta G_\rho^0 = -RT\nu\ln P_{O_2}$ and $\Delta S_\rho^0 = (\Delta H_\rho^0 - \Delta G_\rho^0)/T_\rho$ it is also possible to calculate the Gibbs free energy and the entropy change of reaction:

$$\Delta G_\rho^0 = -30.40 \pm 0.13 \text{ kJ mol}^{-1} \ (123)$$
$$\text{and } \Delta S_\rho^0 = 297.92 \pm 1.52 \text{ J K}^{-1} \text{ mol}^{-1} \ (123) \text{ for Nd-123}$$

$$\Delta G_\rho^0 = -23.80 \pm 0.1 \text{ kJ mol}^{-1} \ (123)$$
$$\text{and } \Delta S_\rho^0 = 221.53 \pm 1.10 \text{ J K}^{-1} \text{ mol}^{-1} \ (123) \text{ for Sm-123}$$

$$\Delta G_\rho^0 = -28.10 \pm 0.13 \text{ kJ mol}^{-1} \ (123)$$
$$\text{and } \Delta S_\rho^0 = 384.40 \pm 1.91 \text{ J K}^{-1} \text{ mol}^{-1} \ (123) \text{ for Eu-123}$$

These preliminary results provide as a basis for future investigation on thermodynamic aspects of the 123-cuprate compounds. In particular some more information about thermodynamic stability of RE-123 phases, as enthalpy of formation and Gibbs energy change could be correlated with thermal stability of oxygen deficient phases, structural defects and related Gibbs energy, as well as the rare earth ions size.

Conclusions

An influence of a pressure on the melt-growth process was studied for RE-123. The primary crystallisation fields, the eutectic equilibrium and peritectic melting equilibria of the RE-123 phase have been studied at oxygen pressures of 0.21, 1, and 10 atm. It was found that the incongruent melting of $NdBa_2Cu_3O_{7-x}$ takes place at 1108, 1122, and 1150°C at p=0.21, 1, and 10 atm, respectively. Similarly, the melting temperature of $SmBa_2Cu_3O_{7-x}$ increased from 1095°C at 0.21 atm to 1110 and 1142°C at 1 and 10 atm, respectively. The temperature range of the $EuBa_2Cu_3O_{7-x}$ primary crystallisation field was found to increase from ~129°C at p=0.21 atm to ~168°C at p=10 atm. These data provide useful information on the RE-123 phase diagram studies.

Moreover high-temperature thermal behaviour of RE-123 as a function of oxygen pressure has been used to determine thermodynamic properties as enthalpy, Gibbs energy and entropy of peritectic decomposition reaction.

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