Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 611–615

APPLICATION OF HIGH PRESSURE-DTA FOR HIGH PRESSURE-LIQUID PHASE EPITAXY OF DOPED MERCURY AND THALLIUM HTS FORMATIONS*

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Abstract

The fabrication method of superconducting thin films of compositions $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) and $Tl_2Ba_2CuO_y$ (2201) on single-crystalline $SrTiO_3$ and $LaAlO_3$ substrates is reported. The highest obtained T_c was 134 K and J_c over 10^6 A cm^{-2} at 77 K. High pressure DTA (HP-DTA) was applied to grow mercury- and thallium-based high-temperature superconducting crystals and thin films, to identify melting points of particular phases within these oxide systems and determine suitable processing conditions. The DTA system operates at the: maximum temperature of 1200°C, volume up to 5 cm^3, working pressure up to 1.5 GPa and at a working atmosphere – inert gas with up to 25% oxygen.

Keywords: HBCCO, high pressure high temperature DTA, liquid phase epitaxy, mercury-based HTS, TBCCO, thallium-based HTS

Introduction

Thallium- and mercury-based superconducting films participate in a wide range of practical applications within the modern microelectronics, because of their characteristic properties, such as high T_c (exceeding 120 K), high enough J_c and good microwave behavior. We have reported the fabrication method of thin films on $SrTiO_3$ and $LaAlO_3$ substrates with T_c up to 134 K and J_c over 10^6 A cm^{-2} at 77 K [1]. Parameters optimization and better reproducibility of the growth process were achieved due to the former investigation of the phase equilibrium during high gas pressure annealing. The high pressure DTA (HP-DTA) method was applied for this investigation.

High superconducting properties that were found within these two series of compounds cause they are of technological interest. One of them is based on mercury, i.e. $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1–6), the most interesting compound within this group, $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223), reveals the highest critical temperature T_c of 135 K at ambient pressure [2] and over 150 K under high pressure [3]. The other com-

* Paper was presented at CCTA 8, Zakopane (Poland), September, 2000

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

pound Hg-1212 in a thin film form also shows a high critical current density J_c~10^6 A cm^{-2} at 100 K in self-field [4]. The other HTS family involves thallium, its formula is $Tl_mBa_2Ca_{n-1}Cu_nO_y$ (m=1, 2 and 1≤n≤5).

Compounds of both groups reveal the unique technical and environmental problems caused by the low decomposition temperature, i.e. high volatility of HgO and Tl_2O, about 500C, and the high equilibrium pressure of O_2, Hg and Tl vapours over the liquid phase. To overcome these limitations, the high gas pressure methods were successfully applied for synthesis and growth of mercury- and thallium-based HTS polycrystalline bulks, single crystals, thin films and thick layers on various substrates at equilibrium pressures [5–8].

In this paper we describe the application of the apparatus for high pressure differential thermal analysis (HP-DTA), which was successfully used to grow Hg- and Tl-based HTS compounds, using the high pressure liquid phase epitaxy (HP-LPE) method.

Samples preparation and processing

The Hg- and Tl-free precursors with nominal compositions $Ba_2CaCu_2O_x$ and $Ba_2Ca_2Cu_3O_x$ were prepared by the modified sol-gel method, as described elsewhere [6, 9]. Precursor powders were then mixed with appropriate amounts of HgO or Tl_2O_3 in a glove-box. So obtained material was uniaxially pressed at pressure of 0.3–0.8 GPa into pellets of 17 mm in diameter and 3 mm high. The pellets were put into a crucible made either of $BaZrO_3$ or of gold, for Hg- or Tl-based compounds, respectively. The substrates used in the LPE method were placed in the support fixed on the wall of the crucible. The crucible was mounted in a furnace inserted into the high pressure gas chamber.

High pressure instruments were made at the High Pressure Research Center of the Polish Academy of Sciences. The pressure system, crucible set-up and experiment run were described elsewhere [6, 7, 10, 11].

HP-DTA system allows to perform DTA experiment with the following parameters: maximum temperature of 1200°C, maximum temperature rate of 1000°C min^{-1}, temperature resolution of 0.1°C, time resolution of 0.1 s, sample volume up to 5 cm^3, working pressure up to 1.5 GPa and at an inner environment – inert gas with up to 25% oxygen. The reducing and oxygenating atmospheres within that range may be applied as well. The system allows to keep stable partial pressures of Hg, HgO, Tl, TlO_2, O_2, $CaHgO_2$ at 100 MPa and to run at high reaction rates, fully preserving environment safety. The measuring system may record 16 points per second.

Results and discussion

High pressure differential thermal analysis within the TBCCO system

Figure 1 shows the DTA of superconducting phase formation within the Tl system. Eutectic melting of the systems Tl_2O_3 and BaO, comprising about 70% of Tl_2O_3, oc-

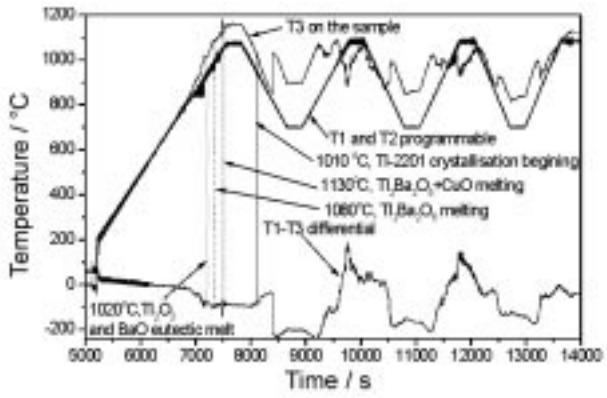

Fig. 1 HP-DTA of phase formation within the TBCCO system

curs at a temperature of 1020°C. At a temperature of 1080°C $Tl_2Ba_2O_5$ phase melts, and at a temperature of 1130°C the whole $Tl_2Ba_2O_5$+CuO system is transformed into the gas phase.

During rapid cooling at a temperature of 1010°C, a wide peak of the Tl-2201 phase crystallization is observed. The exact thallium content in this phase depends on the oxidation degree of the pressure medium. Under these experiment conditions, the oxygen content in argon was below 0.1%.

The melting process, repeated from this stage, between 700 to 1100°C, presents only two peaks, instead of three as observed during the primary melting. The recorded peaks correspond to temperatures of 1060 and 1080°C. They resemble rapid evaporation from the eutectic batch containing $Tl_2Ba_2CuO_6$+CuO and melting of the superconducting phase $Tl_2Ba_2CuO_{6+x}$.

Figure 2 shows DTA of the Tl-2201 phase. Crystallization of this phase occurs in the temperature range of 910–920°C. No phase transition is visible down to temperature 820°C, where the final crystallization of the melt $BaCuO_2$ completes.

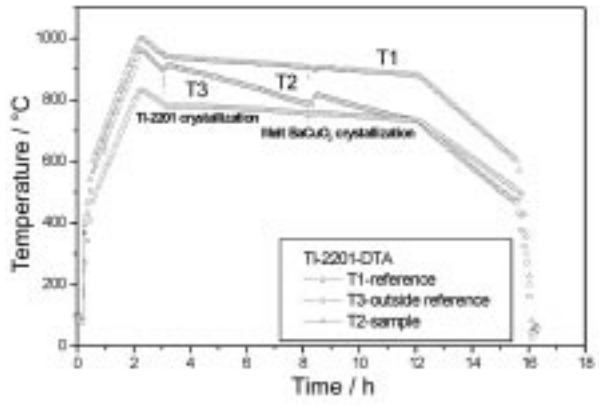

Fig. 2 HP-DTA of the Tl-2201 compound

High pressure differential thermal analysis within the HBCCO system

Figure 3 illustrates the DTA behavior of the nominal Hg 1223 compound during melting and growth performed at p=1 GPa at the rates of 15 and 8°C min^{-1}, respectively. In one batch, there arise several various compounds; the melting temperatures of which are very close to each other.

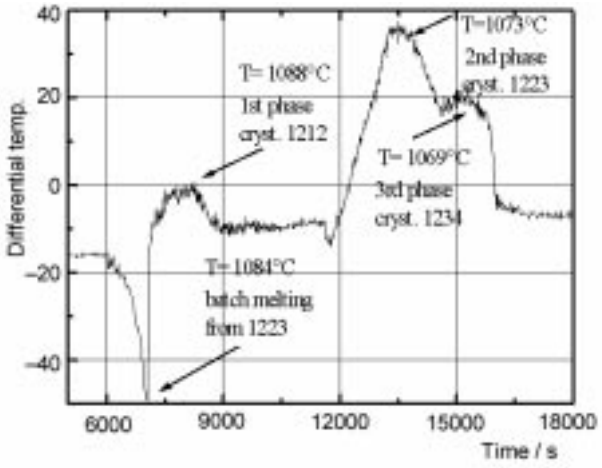

Fig. 3 HP-DTA of phase formation within the HBCCO system

The transition begins at 840, reaches its maximum at 1095, and then falls to 1040°C. The first minimum peak corresponds to the precursor melting at 1084°C. The peak at 1088°C represents crystallization of the 1212 phase. The next one at 1073°C resembles solidification of the 1223 phase. The following peak at 1069°C corresponds to the 1234 phase crystallization. The small middle peak between 1088 and 1073°C is probably correlated to remelting the earlier solidified 1212 phase.

Conclusions

The high pressure DTA method used in this investigation allowed to grow the mercury- and thallium-based HTS crystals and films under determined process conditions and to record thermal properties of these HTS compounds. It enabled the identification of melting points and determination of some thermodynamic data in conditions corresponding to the crystallization process. In HP-DTA system used oxygen partial pressure may be controlled at the assumed level. Due to the special crucible set-up applied in the HP-DTA apparatus, operation with mercury and thallium the system is free from health hazard.

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This work was supported by the Polish State Committee for Scientific Research under grant no. 7 T08A 028 17.

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