Reduction of YBCO melting temperature by simultaneous Ca substitution and Ag addition

K. BUCHKOV, E. NAZAROVA, K. GUROVA[a], A. ZAHARIEV, H. SECHENSKI[b], K. NENKOV[c,d]
Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria
[a]Prof. Assen Zlatarov University, 8010 Burgas, Bulgaria
[b]Acad. A. Balevski Institute of Metal Science, Equipment and Technologies with Hydro-aerodynamics center, Bulgarian Academy of Sciences, 1574 Sofia, Bulgaria
[c] IFW, Leibniz Institute for Solid State and Materials Research, P.O. BOX 270016, D-01171 Dresden, Germany
[d]International Laboratory of High Magnetic Fields and Low Temperatures, 53-421 Wroclaw, Poland

Series of polycrystalline samples with composition $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0.025, 0.05 and 0.20) were investigated by Differential Thermal Analysis (DTA). A systematic decrease of the melting temperature - T_m with increasing of the Ca content was established. For sample with x=0.20, small endothermic minimum is observed, which could be fingerprint of (e_1) binary eutectic reaction, due to presence of $BaCuO_2$. DTA solidification curves shows indication for easier nucleation of Y(Ca)123 phase. The simultaneous effect of Ca substitution and Ag-addition, also lead to additional reducing of T_m. The presence of (e_1) reaction is detected for all Ag-added samples. The observed decrease effects of Ca on the T_m are used for preparation of mono-filamentary Ag-sheathed tape with $Y_{0.80}Ca_{0.20}Ba_2Cu_3O_{7-\delta}$ core. The partial melting and texture is observed in superconductor, but the current transport of the tape is still insufficient.

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1. Introduction

The potential for high J_c applications of high-temperature superconductors (HTSC) is limited by the presence of weak inter-grain links and inappropriate mechanical properties. In order to overcome these obstacles, further improvement of processing techniques and optimization of sintering conditions are necessary. It is known, that chemical modifications of YBCO system strongly affect many processing parameters. For instance the Ag-addition changes morphology, texturing, phase equilibrium, grain connectivity (S-N-S type links) [1-4]. This is the main reason for usage of Ag structures as substrate, buffer layer and metal sheath in thin films and tapes, respectively. Ca-substitution and Ca-addition in $YBa_2Cu_3O_{7-\delta}$ also have significant effect on different characteristics: grain connectivity, morphology, phase equilibrium [5-9]. It is known that Ca segregates mainly at the grain boundaries, forming S-N-S type inter-grain links [5, 6].

In the present study, we investigate the influence of both Ca substitution and simultaneously Ag-addition on the thermal properties of series YBCO polycrystalline samples using DTA analysis.

2. Experimental

Two series of polycrystalline samples with nominal composition $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0,025, 0.05 and 0.20) with and without 10 wt. % Ag additions are investigated. They are prepared by standard solid state synthesis. Phase purity is checked with XRD analysis. The morphology of the samples were characterized by dual beam scanning electron/focused ion beam system (SEM/FIB LYRA I XMU, TESCAN), equipped with EDX detector (Quantax 200, Bruker). DTA analysis is performed using commercial Netzsch 449 apparatus in inert (N_2) atmosphere and temperature rate 10^0C/min. Mono-filamentary Ag-sheathed tape with $Y_{0.80}Ca_{0.20}Ba_2Cu_3O_{7-\delta}$ core is prepared by several stages of mechanical deformation and final heat treatment. The first stage is hydrostatic extrusion of Ag-tube filled with superconducting powder in order to achieve significant densification of superconducting core. The extrusion is followed by several stages of cold rolling deformation and annealing at 850 ^{o}C for 10 min after each deformation treatment. The tape thickness is in the range 170 – 230 μm. The final stage is heat treatment process: 80h re-sintering at 930^{o}C in order to achieve partial melting of the superconductor core, followed by slow cooling with rate 2^0C/min and oxygenation for 48h at 450^{o}C. Transport and DC magnetization measurements of the tape are performed using PPMS-9 and MPMS-XL.

3. Results and discussion

DTA analysis is very useful tool for investigation of materials phase diagram, melting and crystallization

processes and etc. The results of DTA analysis of series polycrystalline samples $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0,025, 0.05 and 0.20) are presented on Fig. 1.

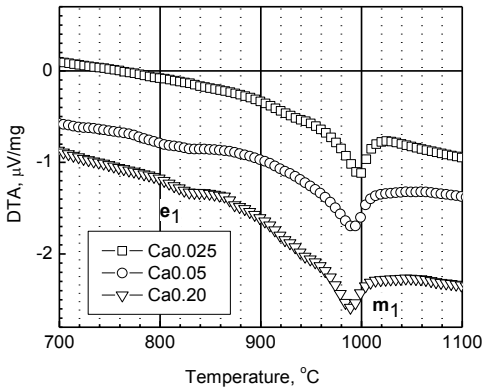

Fig. 1. DTA analysis for samples $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0,025, 0.05 and 0.20).

The endothermic minimum indicates the reaching of YBCO incongruent melting temperature T_m: related to the peritectic reaction (m_1):

$$Y(Ca)123phase \rightarrow Y(Ca)211phase + L(m_1).$$

It is seen from the figure that T_m decreases, with the increasing the amount of Ca. The values are presented in Table 1.

Table 1.

$Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$	T_m (°C)	$\Delta T=T_m- T_s$
x=0.025	1000	183
x=0.05	992	160
x=0.20	988	155
$Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ +10wt% Ag		
x=0.025	963	176
x=0.05	973	196
x=0.20	975	186

It was observed by many authors [5, 6, 10] that increasing the amount of Ca reduce the grain size. This morphology peculiarity results in depression of T_m in samples with smaller grains. On the other hand a local stoichiometric variations due to the substitution effect and presence of $BaCuO_2$ at the grain boundaries, also has its impact [11, 12].

Another characteristics of the DTA curves is the presence of small endothermic minimum around 830° C for sample (x=0.2). A binary eutectic reaction (e_1): $Y(Ca)123phase + BaCuO_2 \rightarrow L(e_1)$ probably take place. The limit for effective solubility of Ca^{2+} in YBCO phase is approximately x=0.11 [13]. The higher levels of Ca-substitution, lead to replacement of Ba and forming of small amount of $BaCuO_2$, which explains the presence of (e_1) reaction for sample x=0.20. For the same sample, small amount of $BaCuO_2$ is detected by XRD analysis. In some cases the presence of small amount $BaCuO_2$ at grain boundaries could be thermodynamically favorable [12].

The simultaneous effect of Ca-substitution and 10% wt. Ag-addition is also investigated. DTA curves are presented on Fig. 2.

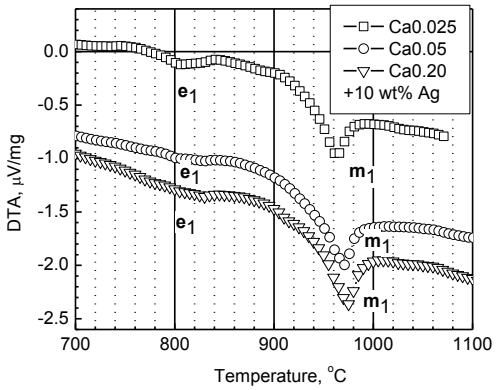

Fig. 2. DTA analysis for samples $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0,025, 0.05 and 0.20) + 10 wt. % Ag.

The endothermic minimum is related to the peritectic reaction (m_1). It is seen that there is additional effect of Ag on the lowering of T_m (Table 1). For all samples the DTA curves shows endothermic minimum approximately at 830° C, which could be explained again with occurrence of eutectic reaction [2] in quasy-ternary system – (Y(Ca)123phase-$BaCuO_2$–CuO_2)-Ag.

The TDA solidification curves are presented on Fig. 3 (a, b) for both sample series. We accepted that exothermal peak is identical to solidification temperature (T_s).

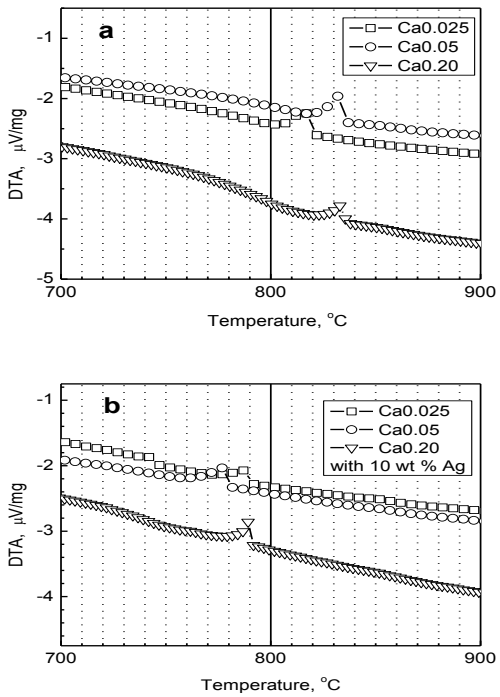

Fig. 3. DTA solidification analysis for samples: without (a) and with (b) Ag-addition respectively.

For the Ca-substituted samples, a decrease of $\Delta T=T_m-T_s$ is observed, with increasing the of Ca content. This is an implication for easier Y(Ca)123 phase nucleation, as it is observed for similar MTG samples [8]. Ag addition does not have any systematical effect on the nucleation process.

We have to note that measured temperature values for (e_1) and (m_1) reactions are lower than reported in the literature [14], which is a result of the fact that our DTA analysis is performed in inert (N_2) atmosphere.

It is well known that OPIT technology is not applicable for preparation of Ag-sheathed YBCO tapes. The main obstacles are the limitations of the solid state synthesis and T_m incompatibility, between YBCO and Ag-sheath [14, 15], and does not allow texturing. In order to apply the observed decrease effects of Ca-substitution on the T_m, we have prepared Ag-sheathed mono-filamentary tape with $Y_{0.80}Ca_{0.20}Ba_2Cu_3O_{7-\delta}$ core. The selection of the superconducting core and final heat treatment process of our tape is performed accordingly to the results from DTA analysis at 930°C.

On Fig. 4 it is shown SEM image of the cross section of $Y_{0.80}Ca_{0.20}Ba_2Cu_3O_{7-\delta}$ core.

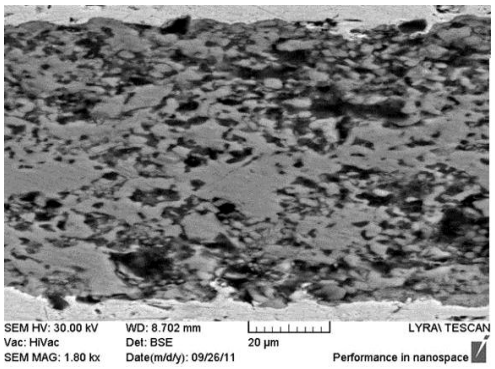

Fig. 4. SEM image of the cross-section of the superconducting core.

Partial melting of superconducting core is observed. The EDX analysis shows insignificant Ag diffusion into the core.

In consistency with this, partial texture is detected by XRD analysis (Φ-scan shown in inset) on Fig. 5.

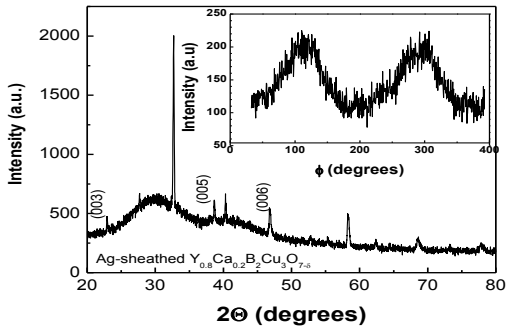

Fig. 5. XRD analysis of the Ag-sheathed tape.

For clarity, only texture related (00l) peaks are indicated in the figure. Critical temperature of the tape determined by the temperature dependence of DC magnetization is 80 K. However the J_c transport of the tape is still very low (500 A/cm^2 at 20 K).

4. Conclusions

In conclusion we demonstrate that systematic increase of Ca substitution in polycrystalline YBCO samples reduced T_m temperature up to 988ºC. Further lowering of melting temperature with approximately 20ºC is achieved with Ag addition. Partial melting and texturing is observed in Ag-sheathed superconducting tape with $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ core, but it was not sufficient for obtaining high enough J_c.

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*Corresponding author: buchkov@issp.bas.bg