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Phase transformation in doped Y–Ba–Cu–O superconductors obtained by different melt processing techniques

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Abstract

In order to produce superconductors with improved properties the better understanding of the phase transformations taking place during the heat treatments in the melt processing techniques seems to be important. For the examination of the phase transformation in the Y–Ba,K–Cu–O,F superconductors a Philips PW 3710 type X-ray diffractometer equipped with a HTK 16 Anton Paar type heating chamber was used. It was established, that in the melted, Y_2O_3 particles containing materials the most part of the Y123 phase crystallizes during the heating period of the subsequent heat treatment, but in the samples presintered at lower (900 °C) temperature the formation of Y123 phase occurs mainly on cooling. The partial substitution of Ba for K influences favourably on the crystallization of Y123.

Keywords: Sintering; X-ray methods; Superconductivity; Oxide superconductors

1. Introduction

The superconducting properties of the melt textured Y–Ba–Cu–O superconductors are strongly dependent on the phase composition, the size and the distribution of the Y_2BaCuO_5 (Y211) secondary phase and the microstructural parameters such as grain size and shape, density and the presence of liquid phase.[1] These properties can mainly be affected by processing conditions and addition of different dopants.

The melt processing techniques involve the melting of the $YBa_2Cu_3O_y$ (Y123) superconducting phase above its peritectic temperature according to the following reactions:

$$YBa_2Cu_3O_y \overset{\sim 1010\,^\circ C}{\longrightarrow} Y_2BaCuO_5 + \text{liquid} \overset{\sim 1200\,^\circ C}{\longrightarrow} Y_2O_3 + \text{liquid} \quad (1)$$

Depending on the annealing temperature the Y123 grains form directly in the Y211 particles containing liquid during the slow cooling or at higher heat treating temperature (>1300 °C) the fine Y211 nuclei are formed by reaction of Y_2O_3 particles with the liquid. According to another conception the growth of Y123 is believed to be an Y-diffusion controlled process.[2,3]

The development of the microstructure depends basically on the processing parameters, such as temperature and time of the heat treating, heating and cooling rates, atmosphere, particle size and the applied substitutions. These parameters will also influence the establishment of equilibrium or metastable phase assemblages.[4]

2. Experimental procedure

Y–Ba,K–Cu–O,F based superconductors were produced by partial-melt process and Melt Powder Melt Growth (MPMG) technique from the presintered precursors of nominal compositions $YBa_{2-x}K_xCu_3O_y$, $YBa_{2-x}K_xCu_3O_yF_x$ ($x = 0$ or 0.05) and $Y_{1.8}Ba_{2.4-x}K_xCu_{3.4}O_y + zPt$, $Y_{1.8}Ba_{2.4-x}K_xCu_{3.4}O_yF_x + zPt$ ($x = 0$ or 0.06, $z = 0$ or 0.5 wt%). These compositions correspond partly to the stoichiometric composition of the $YBa_2Cu_3O_y$ (Y123) superconductive phase partly to the composition of a composite material, which contains Y_2BaCuO_5 (Y211) particles – as flux pinning centres – in the Y123 matrix. In order to inhibit the growth of the Y211 particles in these yttrium-rich nominal compositions Pt-dopant was used. We investigated the partial substitution of barium for potassium, where alkali content was added in form of KNO_3 or $KF{\cdot}2H_2O$, so the effect of incorporation of fluorine atoms beside potassium has also been studied. The samples were prepared in form of pellets (pressed under 150 MPa pressure) by solid state sintering of

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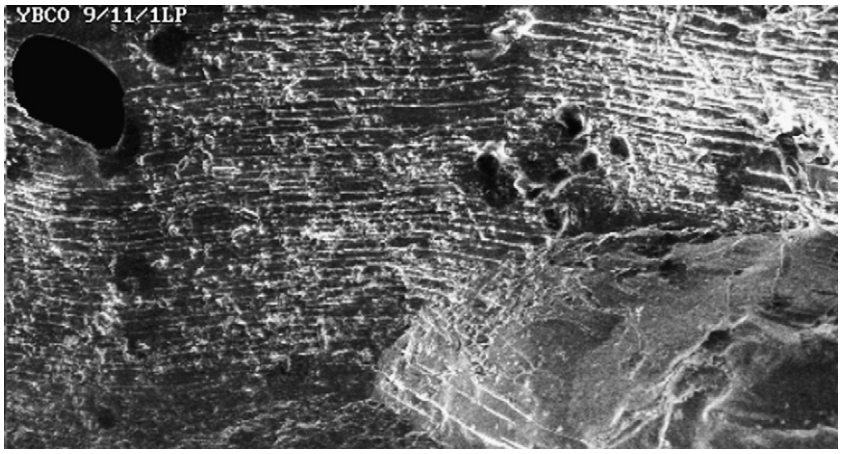

Fig. 1. SEM micrograph of the fracture surface of the sample $YBa_2Cu_3O_y$ cooled slowly from 1000 to 900 °C.

Y_2O_3, $Ba(OH)_2{\cdot}8H_2O$, CuO, KNO_3 or $KF{\cdot}2H_2O$ and $PtCl_4$ powders at 900 °C for 25 h in oxygen atmosphere.[5]

In the partial-melt process the presintered specimens are heat treated on ZrO_2 base plate at 1100 °C for 20 min in oxygen stream (60 dm^3 O_2/h), then cooled to 1000 °C at 300 °C/h, from 1000 to 950 °C or to 900 °C at 2 °C/h, and at this temperature the samples are held for 1 h and subsequently cooled to room temperature at 300 °C/h.

In the MPMG technique the presintered pellets are melted in Pt-crucible at 1345 °C for 2 h and then rapidly cooled down to room temperature. This material is ground, pressed into pellets and then heat treated at 1100 °C according to the above given schedule.

In our study the effects of different parameters, such as substitutions, method of the processing and the cooling rate below the peritectic temperature on the phase composition were investigated. The phase transformations occurring during the heat treatment were examined directly by a HTK16 Anton Paar type heating chamber equipped to a Philips PW 3710 type X-ray diffractometer. This dynamic X-ray diffraction method used a relative fast heating and cooling was employed to study the effect of nominal composition and K or K and F additives on the rate of phase transformations by reason of characteristic peak intensities.

3. Results and discussion

The magnetic properties of partial-melt processed samples with different compositions were degraded in spite of their oriented microstructure, when a slow cooling (2 °C/h) was employed from 1000 to 900 °C after the melting at 1100 °C for 20 min in oxygen atmosphere (Fig. 1).

In order to improve the magnetic properties the specimens have to be cooled slowly only in the temperature range 1000–950 °C. This means that the slow cooling has to be finished above the eutectic temperature ($T_E \sim 890$ °C). In this case the magnetic levitation force was 6–14 times higher than that of the starting presintered samples.[6,7]

In order to study closely this effect X-ray diffraction heating chamber investigations of the powdered (<25 μm) presintered

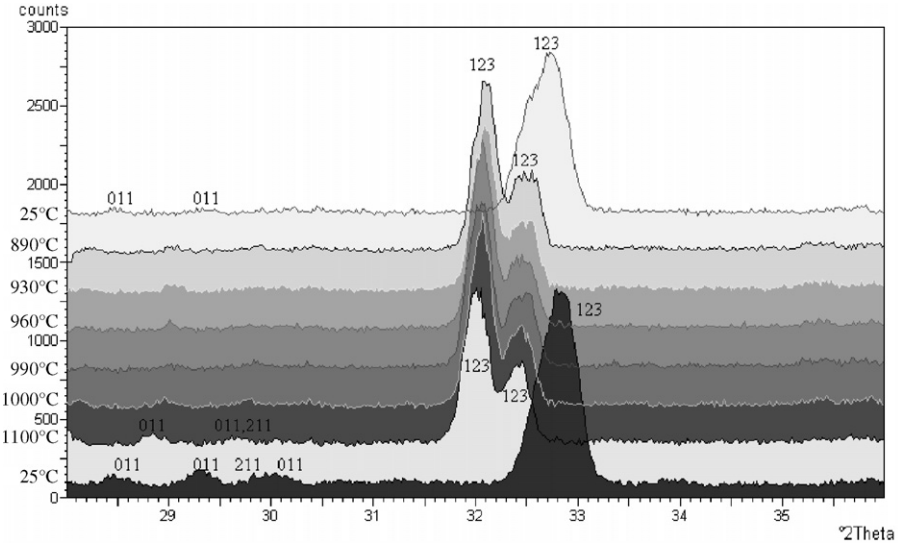

Fig. 2. XRD heating chamber pattern of $YBa_2Cu_3O_y$ specimen presintered at 900 °C.

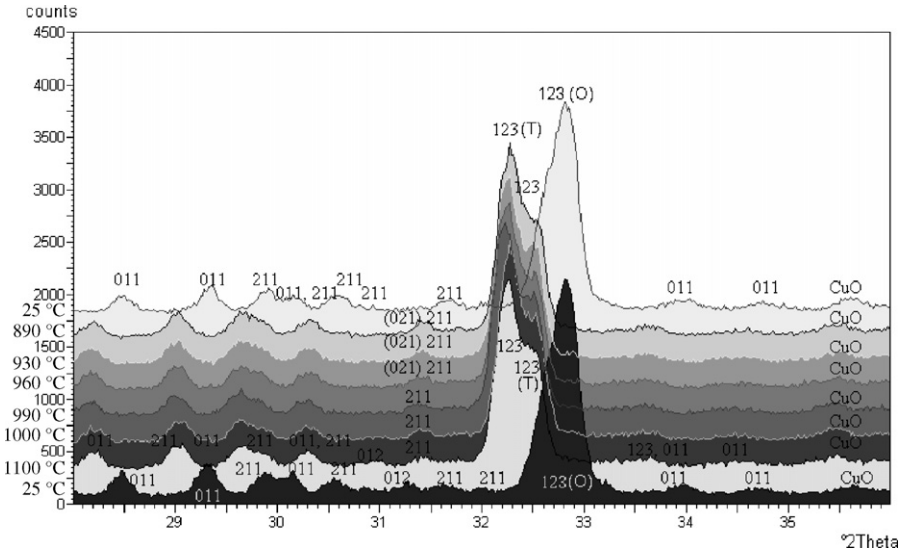

Fig. 3. XRD heating chamber pattern of $YBa_{1.95}K_{0.05}Cu_3O_y$ specimen presintered at 900 °C.

(at 900 °C for 25 h) samples of about 20 mg mass were carried out, where the X-ray diffraction patterns were measured in air at 25, 1100 °C, then during the cooling at 1000, 990, 960, 930, 890 and 25 °C using 50 °C/min heating and cooling rate and Pt-plate substrate. Before the measuring of XRD pattern at the given temperature a soaking period for 1 min was used and then the effective measure of the pattern in the range of $2\theta = 28–36°$ indicated an additional soaking for 12.5 min.

The presintered samples used for XRD heating chamber investigations contained $BaCuO_2$ (011) (JCPDS 38-1402), Y_2BaCuO_5 (211) (38-1434) and CuO second phases beside the orthorhombic Y123 phase (38-1433). The non-doped sample with the Y123 stoichiometric composition contained the smallest amount of second phases (Fig. 2), while in the case of K^+ or K^+ and F^- additives the peak intensities of the superconducting Y123 phase have increased because of the more crystallization.

According to these XRD patterns in the samples heated to 1100 °C with a relatively rapid heating rate (3000 °C/h) the incongruent melting of the Y123 and the congruent melting of the $BaCuO_2$ (011) was not completed and some tetragonal Y123 (39-1496) remained and small amount of 011 was also detected (Figs. 2–4).

Investigated the 011 peak intensities it can be stated, that on cooling from 1000 to 990 °C a small amount of 011 crystallized and its quantity did not change significantly during the fairly rapid cooling to 890 °C. On the other hand in our previous studies[6,7] the samples with stoichiometric Y123 composition and K^+ or K^+ and F^- additives contained 011 phase in considerably smaller amount after slow heating and cooling. As a consequence, the 011 phase melted congruently on slow heating to 1100 °C and in this case its crystallization from the melt was insignificant during the cooling.

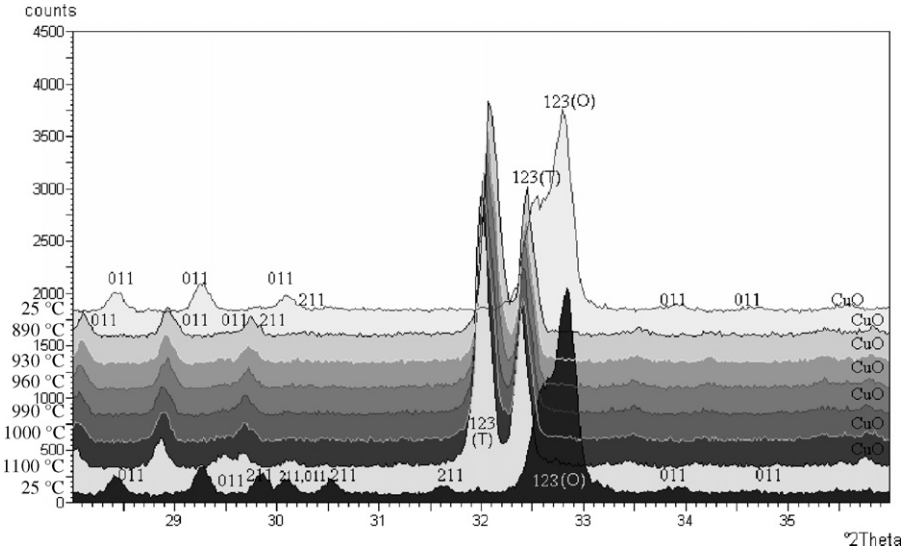

Fig. 4. XRD heating chamber pattern of $YBa_{1.95}K_{0.05}Cu_3O_yF_{0.05}$ specimen presintered at 900 °C.

Table 1
The change of peak intensities of the presintered samples measured by XRD heating chamber

Nominal composition	The change of peak intensities (%)		
	Y123 (d = 0.272 nm) 25–1100 °C	Y211 (d = 0.299 nm) 25–1100 °C	CuO (d = 0.252 nm) 25–1100 °C
$YBa_2Cu_3O_y$	−59.8	−44.3	0
$YBa_{1.95}K_{0.05}Cu_3O_y$	−37.8	−7.0	+24.1
$YBa_{1.95}K_{0.05}Cu_3O_yF_{0.05}$	−22.5	−23.1	+254.2
$Y_{1.8}Ba_{2.4}Cu_{3.4}O_y$	−60.2	−30.2	+254.2
$Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_y$	−50.4	−67.3	+29.7
$Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_yF_{0.06}$	−52.9	−17.6	0–110
$Y_{1.8}Ba_{2.4}Cu_{3.4}O_y$ + 0.5% Pt	−48.2	−1.1	0–56
$Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_y$ + 0.5% Pt	−90.2	+68.8	0–104
$Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_yF_{0.06}$ + 0.5% Pt	−84.7	+146.5	0–52

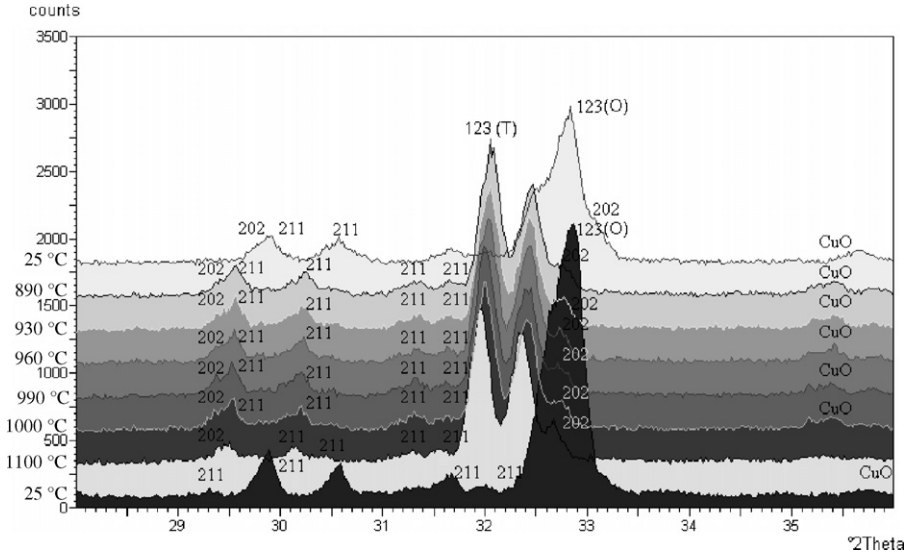

Fig. 5. XRD heating chamber pattern of $Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_y$ specimen presintered at 900 °C.

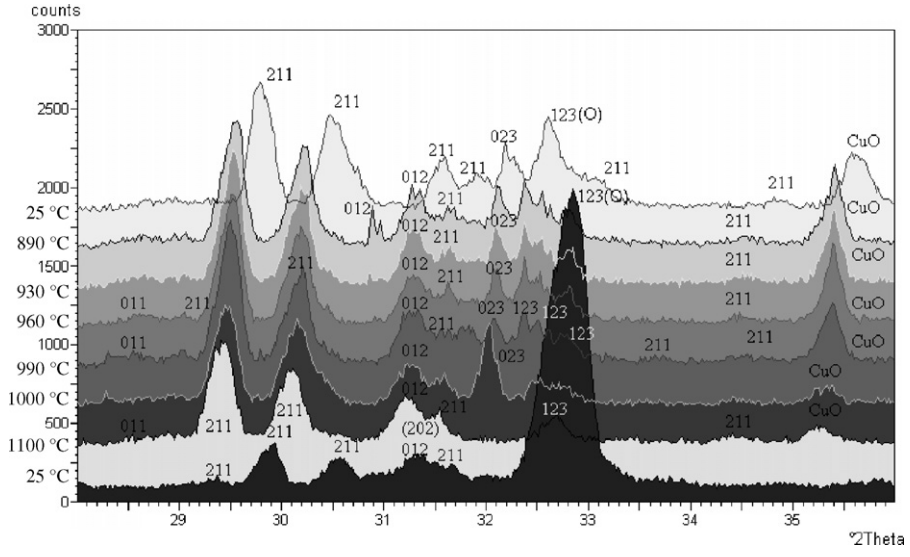

Fig. 6. XRD heating chamber pattern of $Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_y$ + 0.5% Pt specimen presintered at 900 °C.

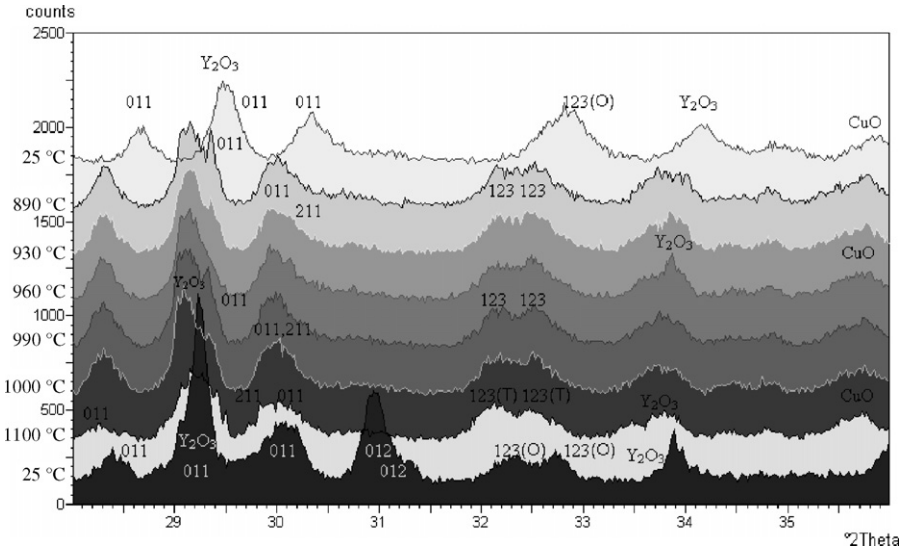

Fig. 7. XRD heating chamber pattern of $YBa_2Cu_3O_y$ specimen melted at 1345 °C.

The rapid heating rate and the short soaking time used in heating chamber investigations did not result in complete peritectic decomposition of the Y123 phase and it remained in metastable tetragonal form This tetragonal Y123 was present with nearly constant peak intensity during the cooling period until the investigated temperature (890 °C), while at room temperature again the orthorhombic structure can be observed. In the case of presintered samples with stoichiometric Y123 composition with or without K and F substitution the phase composition of the cooled sample is very similar to that of the starting material.

The change of the characteristic peak intensities on heating from 25 to 1100 °C shows (Table 1), that the incongruent melting of Y123 phase is the most intensive process in the samples with the ratio Y:Ba:Cu = 1.8:2.4:3.4 and with K^+, F^- and Pt additives. This indicates that Pt addition in K^+ or K^+ and F^- containing samples promotes the peritectic decomposition of Y123 because of the modification of the viscosity of the melt and the interfacial energy and this leads to the increasing of the amounts of Y211, 012 (42-414) and CuO phases (Figs. 5 and 6). The fast cooling from 1100 to 1000 °C resulted in crystallization of $Ba_2Cu_3O_{5+x}$ (023) (40-313), while the peak intensities of the other phases do not change significantly. On the subsequent cooling to 890 °C the intensity of the Y211, the 023 and the CuO peaks increased, while that of Y123 decreased. At room temperature the reflections of the 023 and 012 phases disappeared, at the same time the intensity of the Y123 peaks increased. This indicates, that the crystallization of Y123 takes place by means of 023 phase. On the other hand these samples cooled to room temperature contained smaller amount of Y123 and larger amount of Y211

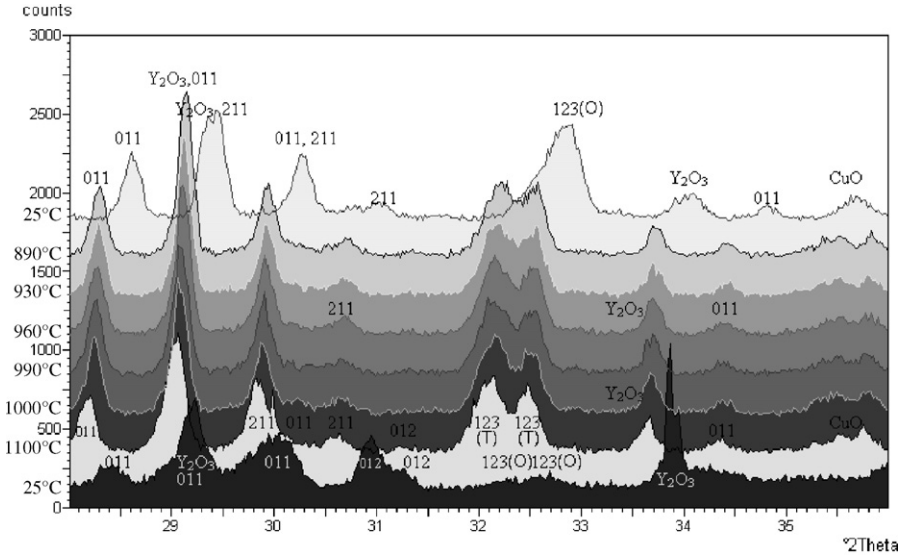

Fig. 8. XRD heating chamber pattern of $YBa_{1.95}K_{0.05}Cu_3O_y$ specimen melted at 1345 °C.

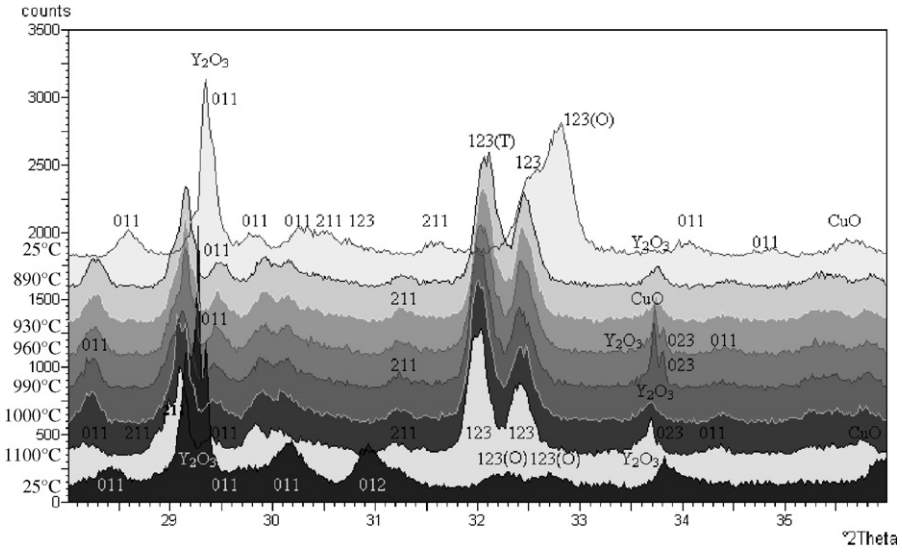

Fig. 9. XRD heating chamber pattern of $Y_{1.8}Ba_{2.34}K_{0.06}Cu_{3.4}O_y$ specimen melted at 1345 °C.

and CuO phases compared to the starting materials. These results emphasise, that the peritectic recombination was incomplete and the crystallization of the Y123 phase is restricted by the fast cooling.

Bulk superconductors with the above given nominal compositions were produced also by MPMG technique. In this case the phase transformations were investigated in the samples melted from the presintered pellets at 1345 °C for 2 h in Pt-crucible and then rapidly quenched to room temperature. These premelted specimens contained nearly spherical Y_2O_3 particles (50–100 μm in diameter) in great quantity and small amounts of tetragonal Y123, 011 and 012 grains in the amorphous matrix (Fig. 7).

According to the XRD patterns measured by heating chamber the amount of Y_2O_3 decreased to about half of its original value on increasing the temperature to 1100 °C. At the same time the peak intensities of Y123 became 6–8 times higher than the starting values especially in the K-containing samples (Fig. 8). On the subsequent cooling to 890 °C or from 890 °C to room temperature the intensities of Y123 peaks showed only 1.2–1.4 and 1.4–1.8-fold increasing, respectively. This indicates, that the significant crystallization of Y123 phase takes place during the subsequent heating of the melted and quenched sample above the peritectic temperature. On the following rapid cooling to 890 °C the characteristic peak intensities did not change considerably, which means a less intensive crystallization. During the heating chamber investigation in the premelted samples, likewise to the presintered samples, tetragonal Y123 phase is present apart from the samples at room temperature. In these rapidly cooled samples a fairly large amount of Y_2O_3 always remains due to the incomplete reaction. In addition these samples contain 011 and CuO phases and in the specimens with K^+ additive also Y211 particles can be found. The partial substitution of Ba for K promotes the crystallization of Y123, especially in the samples with the ratio of Y:Ba:Cu = 1.8:2.4:3.4 (Figs. 9 and 10). For F^- doping beside K^+ the Y123 con-

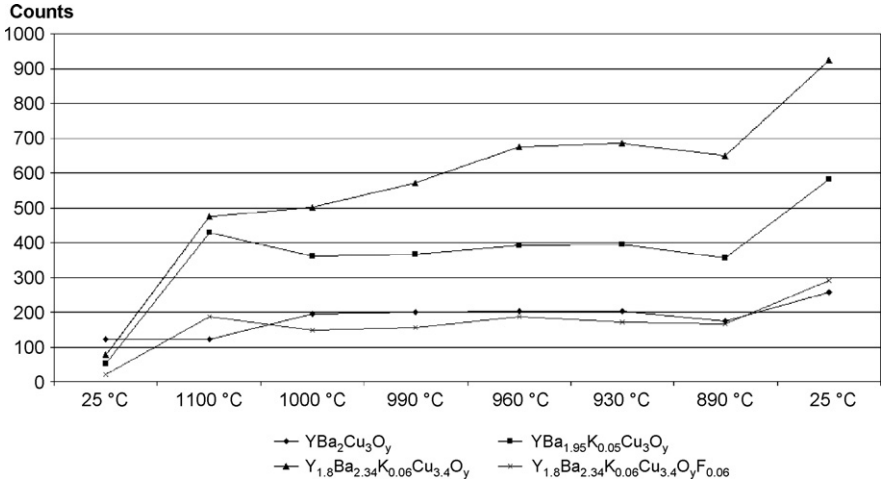

Fig. 10. The change of peak intensities of Y123 during the investigation of premelted samples by XRD heating chamber.

tent is not significantly modified compared to the undoped samples.

4. Conclusion

X-ray diffraction heating chamber was used to investigate the phase transformations during the production of Y–Ba,K–Cu–O,F (+Pt) based superconductors by partial-melt and MPMG techniques. As a result of the used fast heating and cooling the well-known phase transformations either did not occur or took place incompletely. In this way the obtained results first of all can be used to study the effect of the nominal composition and additives on the rate of the phase transformations.

In conclusion this work has shown that the addition of Pt dopant promotes the incongruent melting of the Y123 phase in the presintered samples containing K^+ or K^+ and F^- additives. This means that the Pt-dopant not only inhibit the growth of Y211 particles, but it can influence the crystallization of Y123 phase.

For the samples produced by melting (MPMG) process the reheating period of the premelted and quenched samples above the incongruent melting temperature plays an important role because of the intensive crystallization of Y123.

The partial substitution of Ba for K has a favourable effect on the crystallization of Y123 especially in the yttrium-rich nominal compositions.

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