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Chemical aspects of the preparation of high T_c superconducting Tl–Ba–Ca–Cu–O films by deposition from aerosol

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Abstract

Superconducting $Tl_2Ba_2CaCu_2O_x$ (2212) films have been prepared by annealing the precursor Ba–Ca–Cu–O thin layers in an atmosphere containing vapours of thallous oxide. The precursor films were deposited from aqueous aerosol of the corresponding nitrates onto MgO substrates. As a source of Tl_2O thallination pellets prepared by homogenizing of a mixture of Ba–Ca–Cu–O precursors with Tl_2O_3 were used. After common annealing of the film and the thallination pellet, which were in close contact, superconducting (2212) phase was obtained in the film as well in the pellet. The best T_c values of the synthesized (2212) films and pellets were 103.5 and 102 K, respectively. The chemical aspects of both thermal decomposition reactions during film growing as well as those proceeding during the thallination process, are discussed from the point of view of thermogravimetric TG, DTG and DTA measurements. © 1997 Elsevier Science B.V.

Keywords: Aerosol deposition from nitrate solutions; High T_c superconductor $Tl_2Ba_2CaCu_2O_x$ films; Powder X-ray diffraction; Thermogravimetry

1. Introduction

Today, a number of methods and their modifications are well developed and used for preparation of thin films of high-T_c (HT_c) superconducting materials [1–3]. They can be divided into two basic groups: vacuum methods such as laser ablation, sputtering, evaporation, molecular beam epitaxy, etc., and chemical deposition methods like chemical vapour deposition, sol–gel methods (spin-coating, dip-coating) and deposition from aerosol or spray pyrolysis. Usually, the vacuum methods give films with thicknesses $t < 1$ μm and the chemical methods applied at about atmospheric pressure and ambient temperatures are able to produce films with thicknesses $t > 1$ μm. Of the chemical methods mentioned above, a special attention must be paid to the method of aerosol deposition. Although, generally, the superconducting properties of synthesized films (the critical current density J_c, intergranular coupling between the film grains, crystallographic orientation) may be better in case of vacuum methods, real possibilities exist that by knowing the chemical aspects of the whole growing process more in detail, the conditions of the spray

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pyrolysis may be optimized to prepare HT_c films, the properties of which may approach those obtained by vacuum methods. From this point of view we may say, that aerosol deposition is promising, rather simple and relatively inexpensive non-vacuum method used for preparation of HT_c films on substrates of various, also non-planar shapes. Thin films of all three best known HT_c systems suitable for practical applications, i.e. Y–Ba–Cu–O (YBCO), Bi–Sr–Ca–Cu–O (BSCCO) and Tl–Ba–Ca–Cu–O (TBCCO) were already prepared by means of this method [3].

Of the group of HT_c materials mentioned above, the BSCCO and TBCCO systems are considered today as the most real candidates in high-current and high-field applications such as power transmission lines, various types of superconducting magnet systems, etc. Besides their suitable physical properties these two types of materials may eventually be fabricated also in sufficient lengths. From the point of view of critical temperature T_c values, the Tl-based system with T_c up to 127 K is superior to the BSCCO one with T_c around 110 K. Also the J_c values should be high enough not only in the absence of external magnetic field but first of all in its presence. From this respect, an important characteristic of HT_c superconductors is their irreversibility line i.e. their $B^*(T)$ dependence, which limits the extent and degree of utilization of a particular superconductor [4,5]. In this $B^*(T)$ representation the superconducting properties of the Tl-based group of superconductors are superior to those of Bi-based and this is the reason for a growing interest in the Tl-based HT_c superconductors.

Two basic configurations of processing methods are currently used to prepare TBCCO superconductors, the so called close and open approach. The close-system process is represented by the powder-in-tube (PIT) method in which the initial powder mixture of individual constituents including thallium is imbedded and sealed in a metallic sheath. In the open-system approach thallium (because of its toxicity) is introduced into the precursor (Ba–Ca–Cu–O) usually in a separate step. The precursor film is deposited on a suitable substrate by some of the methods mentioned above. Among films with best superconducting properties involve those prepared by deposition from aerosol which allows to produce this material in shape of tapes or wires in technically applicable lengths [6–17].

As a source of an aerosol, usually aqueous solutions of metallic nitrate components are used. It is therefore of a primary importance to know their decomposition temperatures and intervals and temperatures of their transfer into metallic oxides. For this purpose, detailed thermogravimetric TG, DTG as well as DTA measurements must be performed in detail for each component as well as for their homogenized mixtures. Some results of these measurements we published already in our previous paper concerning the preparation of 2212 films [8]. A purpose of the following paper is to complete the information concerning the chemical aspects of the whole growing process. MgO single-crystalline substrates were used in our case to deposit precursor films from an aerosol.

2. Experimental

The spray-deposited Tl–Ba–Ca–Cu–O (TBCCO) films were prepared by the two-step process [4,8]. According to this method the Ba–Ca–Cu–O precursor films were first deposited from an aerosol onto a suitable substrate and then, the precursor films were annealed in an atmosphere containing thallous oxide vapor in oxygen.

In the first step the aerosol generated by a commercial Thomex L-2 ultrasonic inhalating equipment at frequency of 2.7 MHz in the form of droplets of mean diameter 2–3 μm, was sprayed for 5 min over the MgO single-crystalline substrate heated to about 180–200°C. The source of the aerosol was an aqueous 0.01 M solution of Ba, Ca and Cu nitrates with the molar ratio of components Ba : Ca : Cu=2 : 2.3 : 3. Three to five cycles were applied, leading to films of a total thickness of 2–3 μm. Between cycles the samples were heated to 450°C for 5 min. The samples with deposited precursors were stored in a desiccator. Immediately before the thallination step the decomposition of nitrates was completed by annealing in an oxygen stream at 800–850°C for 30 min. In this step also traces of carbonates, which may be formed in the reaction with atmospheric CO_2 during the handling, were removed.

Thallium was introduced into the films in the second step by annealing the precursor film sample together with a Tl_2O_3 containing pellet (thallination pellet) at 850°C and 30 min, both being in near contact in a closed alumina crucible and in an O_2 atmosphere.

The pellets for thallination of the films were prepared by pressing the powders obtained in two ways:

In the first, the homogenized mixture of $Ba(NO_3)_2 : Ca(NO_3)_2{\cdot}4H_2O : CuO=2 : 2.3 : 3$ was heated in a dynamic vacuum of 10^{-2} Torr at slowly increasing temperature up to 950°C. The preparation of precursor pellets from a mixture of Ba and Ca nitrates together with CuO has to be performed in dynamical vacuum at slowly increasing temperature, otherwise the highly reactive molten mixture strongly attacked the platinum crucible. The product obtained was after cooling homogenized with Tl_2O_3 to a ratio of $Tl : Cu=2 : 3$. It contained some admixture of unreacted Ba and Ca oxides, which are highly reactive toward atmospheric CO_2. The pellets were therefore stored in a desiccator.

In the second procedure the powder was prepared by homogenizing the mixture of the $Ca_2CuO_3 : BaCuO_2 : Tl_2O_3$ components in the molar ratio 1 : 2 : 1. $BaCuO_2$ and Ca_2CuO_3 were prepared by sintering a mixture of $BaCO_3$ with CuO (1 : 1) and $CaCO_3$ with CuO (2 : 1), respectively. Two annealing procedures in air at temperatures of 900 and 925°C with intermediate grinding were applied.

The dynamical thermogravimetric TG, DTG and DTA studies were performed on the Derivatograph Q 1500/MOM device in a static air atmosphere. The initial weight of powder samples was 100 mg. Measurements were performed at a heating rate of $10\ \mathrm{K\ min^{-1}}$ from room temperature to 1000°C.

The T_c values of prepared films and bulk samples were measured by means of a standard four-point DC resistive method with $1\ \mu\mathrm{V\ cm^{-1}}$ criteria.

The X-ray powder diffraction data were obtained with Ni-filtered CuKα radiation on Philips PW 1710 diffractometer at a scan angles 2τ ranging from 4° to 72°.

The lattice parameters $\underline{a}$ and $\underline{c}$ for $Tl_2Ba_2CaCu_2O_x$ (2212) and $Tl_2Ba_2CuO_y$ (2201) phases were calculated in the following way, which can be used for orthorhombic and higher symmetries. The $\underline{c}$ parameter was evaluated by relation:

$$\underline{c}_{cor} = \lambda(l_2 \cos\tau_1 - l_1 \cos\tau_2)/(2\sin\delta\tau_{12}) \qquad (1)$$

The relation (1) can be easily derived from the general expression:

$$\sin\delta\tau_{12} = \sin(\tau_1 - \tau_2) = \sin\tau_1\cos\tau_2 - \sin\tau_2\cos\tau_1 \qquad (2)$$

where $\sin\tau_i = \lambda l_i/2\,\underline{c}$, l_i and τ_i represent diffractions $00l_i$ and corresponding diffraction angles τ_{00l_i}. λ is the applied wave length, $\underline{c}_{cor}$ means the value of the $\underline{c}$ parameter corrected for "zero error", where also the "absorption error" is at least partially eliminated due to application of the angular differences $(\tau_1-\tau_2)$ instead of τ_{00l_i} values, as it is the case in evaluation:

$$\underline{c} = \lambda l_i/(2\sin\tau_{00l_i})$$

The constancy of differences $\delta\tau_{12}$ of the observed (τ_{obs}) and calculated (τ_{cor}) diffraction angles of reflections $00l_i$ according to Eq. (1) is shown in Table 1. The value of $\delta\tau_{12}$ can be then applied for correction of all remaining diffraction data, which are used for the evaluation of the $\underline{a}$ parameter of 2212 as well as 2201 phase. In the Table 1 the lattice parameters of these phases for the bulk sample prepared by the sintering of $BaCuO_2$–Ca_2CuO_3–Tl_2O_3 precursors are shown.

Table 1
Comparison of the observed (τ_{obs}) and calculated (τ_{cal}) diffraction angles of the 2212 phase

h	k	l	τ_{obs}(°)	τ_{cal}(°)	$\delta\tau_{12}$(°)
0	0	2	3.0425	3.028	0.015
0	0	4	6.079	6.064	0.015
0	0	6	9.1325	9.118	0.015
0	0	8	12.2125	12.198	0.015
0	0	12	18.492	18.4775	0.015
0	0	14	21.7155	21.7005	0.015
0	0	15	28.400	28.385	0.015

[a] Lattice parameters for the bulk Tl–Ba–Ca–Cu–O phases prepared from $BaCuO_2$–Ca_2CuO_3–Tl_2O_3 precursors:
[b] 2212: $\underline{a} = 3.864(6)$ Å, $\underline{c} = 29.188(1)$ Å, V = 435.79 Å^3
[c] 2201: $\underline{a} = 3.859(8)$ Å, $\underline{c} = 23.127(4)$ Å, V = 344.40 Å^3

3. Results and discussion

The Ba–Ca–Cu–O precursor films were sprayed from the aqueous solution of corresponding nitrates onto MgO substrate. The results of TG, DTG, DTA measurements of a homogenized mixture of solid nitrates are shown in Fig. 1. The chemical reactions and the appropriate temperature intervals of the thermal decomposition are given in Table 2. It can be seen that the temperature of the substrate (180–200°C) lies below the decomposition temperature of nitrates. The light blue colour of the as deposited sample indicates

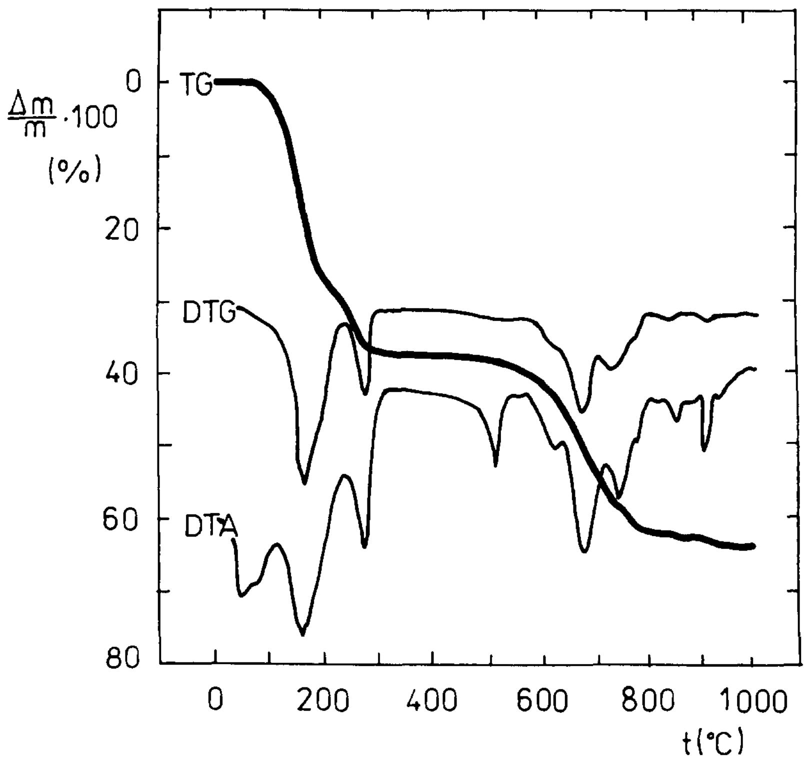

Fig. 1. Thermogravimetric TG, DTG and DTA data for the homogenized Ba, Ca and Cu nitrates (2 : 2.3 : 3) used for preparation of a solution for aerosol spray deposition.

Table 2
The reactions proceeding at the thermal decomposition of the homogenized solid mixture of $Ba(NO_3)_2 : Ca(NO_3)_2\cdot 4H_2O : Cu(NO_3)_2\cdot 3H_2O=2 : 2.3 : 3$

Proceeding reaction	Temperature interval (°C)	Mass loss (wt%) exp./calc.
$2\ Ba(NO_3)_2+2.3\ Ca(NO_3)_2\cdot 4H_2O+3\ Cu(NO_3)_2\cdot 3H_2O\rightarrow 18.2\ H_2O+3\ NO_2+0.75\ O_2$	50–210	27.8/27.4
$2\ Ba(NO_3)_2+2.3\ Ca(NO_3)_2+1.5\ Cu_2O(NO_3)_2\rightarrow 3\ NO_2+0.75\ O_2$	210–230	9.0/9.1
$2\ Ba(NO_3)_2+2.3\ Ca(NO_3)_2+3\ CuO\rightarrow 4.6\ NO_2+1.15\ O_2$	500–650	14.2/13.9
$2\ Ba(NO_3)_2+2.3\ CaO+3\ CuO\rightarrow 4\ NO_2+\ O_2$	650–900	12.5/12.1
$0.15\ BaO+1.85\ BaCuO_2+1.15\ Ca_2CuO_3$		
Sum of the released components:		
$18.2\ H_2O+14.6\ NO_2+3.65\ O_2$		63.5/62.5

the presence of undecomposed nitrates, which are deposited on the surface. At above conditions the droplets of the aerosol splash on the surface, where consequently the solvent and at least the part of the crystal water is removed.

In [3,8] four general working modes which are effective at the deposition from aerosol have been proposed (Fig. 2). The actual mode, which is a complex process, depends on many parameters: the surface temperature of the substrate and the temperature

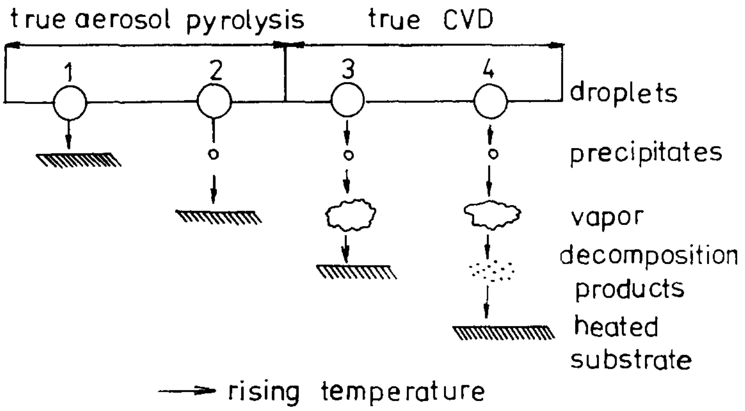

Fig. 2. Working modes that may occur during chemical deposition of an aerosol onto a heated substrate.

surrounding the sample during the deposition, as well as on the volatility of the solvent and of the precursors, respectively. The flowing conditions near the surface also play an important role. In the first mode (1) at low temperatures of substrate and for solvents with relatively low volatility, the aerosol droplets splash on the surface of the heated substrate, where the solvent evaporates and an amorphous as deposited film is formed. This mode is effective for deposition process of nitrates at conditions described above. The crystalline film is formed in subsequent thermal decomposition and recrystallisation of deposited precipitates at a temperature, which is higher than the deposition one. In the second mode (2), which is effective at elevated substrate temperatures the solvent is evaporated before the droplets arrive at the heated surface. The microcrystalline precipitates of the precursors are directly deposited on the substrate. These two modes can be designated as true deposition from aerosol. If the temperature of the substrate is further raised, and as well as the solvent as the precursors are volatile, the modes (3) and (4) are effective. Deposition occurs directly from the vaporized precursors (3) and their decomposition products, respectively (4). The mechanism of modes (3) and (4) is related to the classical CVD. Generally the films deposited by true CVD show higher density and better texture than those deposited by true aerosol pyrolysis.

The increase of the deposition temperature above 200° led to a proportional increase in the copper oxide content. From the sprayed precursors only copper nitrate has covalent character. Therefore, it is able to vaporize and at elevated temperatures it is deposited in the form of a highly homogenous films by modes probably near to (3) and (4). The more ionic barium and calcium nitrates are deposited at such conditions by mode (2). It should be mentioned here that the overall rate of the deposition process decreases with increasing temperature of the substrate, probably as a consequence of more turbulent streaming conditions in the surrounding of the surface. The kinetics of the formation of nucleation centers on the surface may also play a role.

The partial decomposition of the as-deposited film of amorphous nitrates was performed at intermediate heating to 450°C between individual cycles. In this step, the water of crystallization is fully released and Cu nitrate decomposes to black CuO. This increases the originally very weak adhesion of the as deposited film to the substrate. The complete decomposition of the fixed nitrate, however, is performed in the final heating at 850°C.

The films deposited from aerosol at low substrate temperatures show high rates of growth, however, the density and texture of the resulting superconducting films cannot be fully optimized [3]. Probably the gaseous decomposition products evolved in the final decomposition of the precursors, together with the fact that the microstructure of the film is formed in relatively thick layers, produce a relatively porous superconducting film and the texture is not perfect.

A bulk pellet containing Ba–Ca–Cu–O precursors and an admixture of thallium oxide was used as a source of Tl for the thallination reaction. The deposited film and the bulk Tl_2O_3-containing pellet, which were in close contact, were heated in a closed crucible to a temperature necessary to obtain a sufficient pressure of thallium oxide on the surface of the film for the formation of TBCCO superconducting phase. This simple arrangement, which is widely used for keeping a relatively constant vapour pressure of thallium oxide over the precursor film has the advantage of low losses of the toxic Tl from the relatively open system. In this method in addition to the TBCCO film a bulk pellet of superconducting TBCCO film a bulk pellet of superconducting TBCCO, which can be used as a source of polycrystalline material e.g. for a powder to tube (PIT) method, was produced.

The results of the TG, DTG and DTA measurements of the bulk thallination pellet prepared from the Ba and Ca nitrates and CuO in the ratio 2 : 2.3 : 3 are shown in Fig. 3. From the course of the TG curve it can be seen that in the range of 400–450°C a partial reduction of Tl_2O_3 takes place as it has been described in [19]:

$$Tl_2O_3 \rightarrow 0.5Tl_4O_3 + 0.75O_2 \tag{4}$$

A weight loss of 0.6% corresponding to the above equation indicates that this reaction does not proceed quantitatively under the dynamical experimental conditions (heating rate 10 K min^{-1}). Above 600°C Tl_2O develops according to the reactions:

$$0.5Tl_4O_3 \rightarrow Tl_2O + 0.25O_2$$

$$Tl_2O_3 \rightarrow Tl_2O + O_2 \tag{5}$$

Because of the volatility of Tl_2O and its high partial pressure, it partly sublimes from the pellet. The released thallous oxide is then introduced into the precursor film and reacted to TBCCO. In the particular case of the pellet annealed at 850°C for 30 min, the total loss was slightly less than 10%, which is in good agreement with the TG curve obtained at dynamical

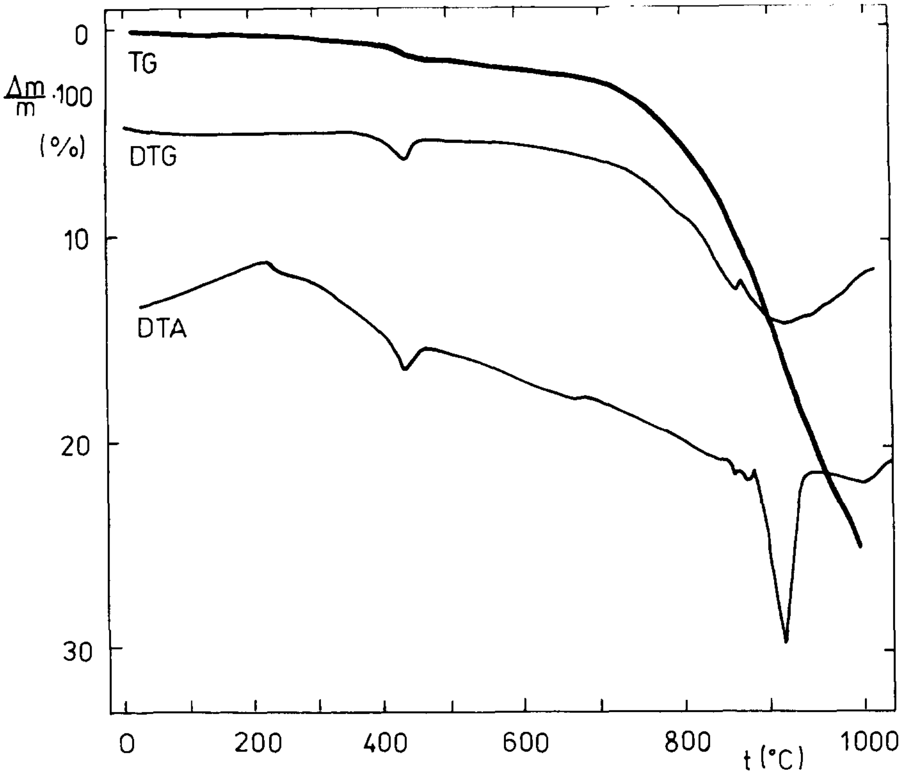

Fig. 3. Thermogravimetric TG, DTG and DTA data for the thallination pellet prepared from the mixture of Ba, Ca nitrates and CuO with an admixture of Tl_2O_3 in such a way that Tl : Ba : Ca.

conditions. The traces of Tl_2O_3 found in the pellet by powder X-ray diffractometry indicate that the unreacted Tl(I) is reoxidized at the lower temperature.

The observed decomposition and sublimation temperatures for thallium oxide found in this study are slightly lower than those reported for pure Tl_2O_3 [19]. This is in agreement with our previous studies on $YBa_2Cu_3O_7$, where we found that the reaction temperatures of the mixture of ingredients are lower than those of the individual components [18].

In the films obtained by thallination reaction more than 95 vol.% of the 2212 phase was found by X-ray powder diffractography. Besides this superconducting phase a low content of impurities (CuO, Ca_2CuO_3, $BaCuO_2$) was identified. In contrast to YBCO films prepared previously by aerosol deposition, which showed orientation with c axis perpendicular to the substrate surface [18], the prepared TBCCO samples did not exhibit any preferential orientation. We assume that it is caused by the fact that the final film is formed in a relatively fast reaction of thallium oxide with a comparatively thick Ba–Ca–Cu–O precursor coating at conditions, which are not sufficient for a formation of a distinct texture. However, the TBCCO superconductors show good intergranular coupling and even in such samples the J_c values are relatively high. The J_c values of the above samples have already been reported to be in the range $2.4 \cdot 10^3$–$6.0 \cdot 10^3$ A cm^{-2} [8], and the T_c values lie in the interval 100.0–103.5 K.

In the thallination pellet the superconducting 2212 phase was formed in about 90 vol.%. It exhibited a T_c value of 102 K. Besides the superconductor, small amounts of unreacted Tl_2O_3 and CuO, $BaCuO_2$, Ca_2CuO_3 were found in the pellet by powder X-ray diffraction measurements.

For an alternative preparation of thallination pellets a mixture of stable precursors: $BaCuO_2$, Ca_2CuO_3 and Tl_2O_3 in the molar ratio 2 : 1 : 1 was used. The TG curve (Fig. 4) of this mixture showed a mass decrease

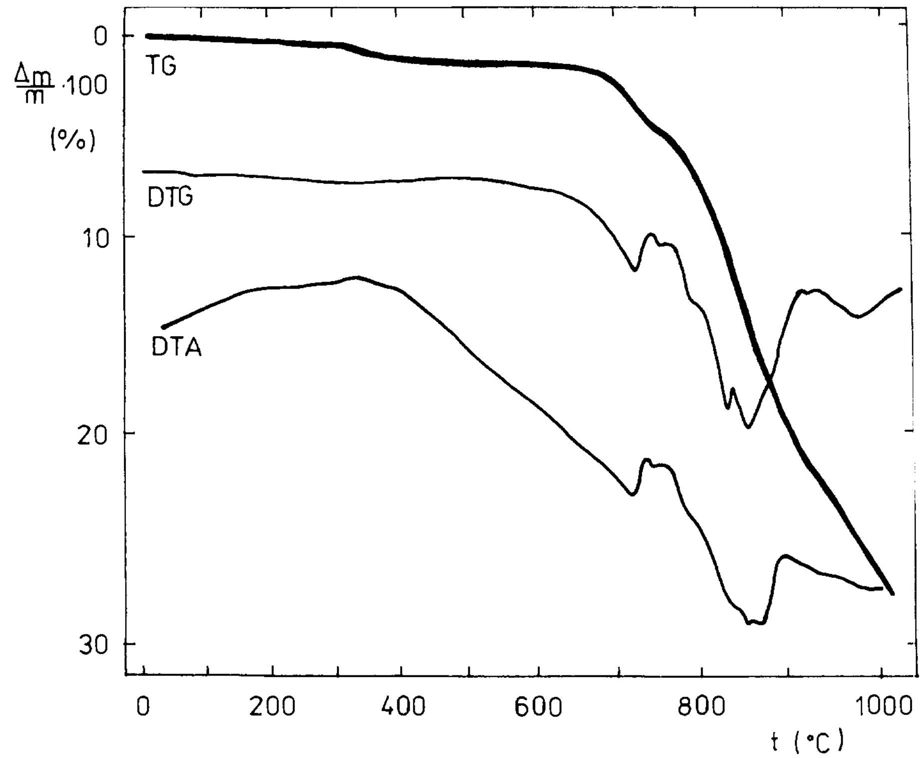

Fig. 4. Thermogravimetric TG, DTG and DTA data for the thallination pellet prepared from the mixture of $BaCuO_2$, Ca_2CuO_3 and Tl_2O_3 in a molar ratio 2 : 1 : 1.

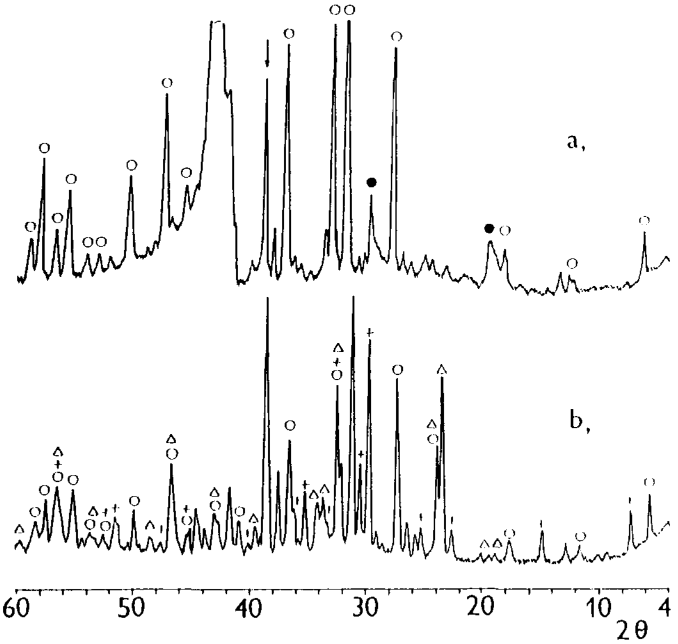

Fig. 5. Powder diffraction pattern of TBCCO film on the MgO monocrystalline substrate (a); and a bulk pellet prepared from $BaCuO_2$–Ca_2CuO_3–Tl_2O_3 mixture (b); which were prepared by annealing at 850°C 30 min^{-1} in close contact. The present phases are marked as follows: ○ 2212; • $BaCuO_2$; ↓ CuO; △ $BaCO_3$; + 2201. The main peak at $2\tau=43°$ is the MgO substrate.

of about 0.7% at 400°C, which corresponds to a partial reduction of Tl(III) described by Eq. (4). Part of thallous oxide, necessary for the thallination of the film, was removed from the pellet above 600°C in the reactions (5). The remaining thallium oxide reacted in the bulk with the $BaCuO_2$ and Ca_2CuO_3 precursors. The X-ray diffraction pattern of the pellet showed that besides the superconducting 2212 phase there was some admixtures of 2201 and $BaCO_3$ (Fig. 5b). The lattice parameters of the 2212 and 2201 superconducting phases are given in Table 1. The pellet showed a T_c value of 100.8 K. The preparation of thallination pellets by this way is more convenient than the first one since the precursors are easier to prepare and they are stable in air. Preparation of various bulk superconducting TBCCO phases from the precursor system $BaCuO_2$–Ca_2CuO_3–Tl_2O_3 has been already reported [20,21]. The formation of a particular superconducting phase depends more on the reaction conditions than on the molar ratio of the precursors in the reaction system.

The film obtained by the thallination reaction exhibited a T_c value of 100.8 K and consists of 2212 superconducting phase with a rather low orientation (Fig. 5 a). Besides it, traces of $BaCuO_2$ could be identified by X-ray powder diffractography.

We have already established the dependence of the T_c value on the unit cell parameter $\underline{c}$ and the interdependence of $\underline{c}$ and x in $Tl_2Ba_2CaCu^{III}_{2-x}Cu^{II}_xO_{8+0.5x}$ [8]. The T_c value increases with decreasing value of $\underline{c}$ (non-linear dependence) and increasing value of x (linear dependence characterized by the equation $T_c = 91 + kx$, where $k=137$). From the additional data obtained in this study the general increase of T_c with decreasing $\underline{c}$ can again be recognized. Moreover, the influence of sample size (bulk sample or deposited film) and the quality of the film substrate (ceramic single crystals or textured Ag-metal with its particular orientation) was observed. This problem will be the subject of our further interest and will be discussed in detail in a forthcoming paper.

In conclusion, some aspects of chemical reactions proceeding in a two step process leading to Tl–Ba–Ca–Cu–O superconducting films as well as to bulk phase of an analogical composition, are discussed from the point of view of results of thermoanalytical measurements. In the first step of film preparation, in the spray deposition of aqueous solution of Ba, Ca, Cu nitrates at low temperature (180–200 °C) a coating of the undecomposed nitrates is fixed on the surface. In an annealing process at 850°C they are decomposed to the corresponding oxides. To such a Ba–Ca–Cu–O precursor film Tl was introduced in the second step. As a source of highly volatile Tl_2O a thallination pellet containing a mixture of Ba–Ca–Cu–O precursors mixed with Tl_2O_3 was applied. The use of a Tl_2O_3–$BaCuO_2$–Ca_2CuO_3 mixture is highly advantageous. The film and a pellet were heated (850°C, 30 min) in close contact. The thallium oxide, which did not volatize from the pellet, formed a TBCCO bulk superconductor with Ca_2CuO_3 and $BaCuO_2$. Three experimental conditions in the film and in the bulk, a majority of the 2212 phase was formed.

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