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Decomposition of Ca : Cu = 1 : 1 nitrate powder: thermal analysis and structural studies

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Thermal decomposition processes in mixtures of Ca : Cu = 1 : 1 nitrate powders produced by a conventional technique and by freeze drying method have been investigated by thermal analysis and X-ray diffraction. Results have been compared with literature values and data obtained by our investigations of individual calcium and copper nitrates. Temperatures at which decomposition processes occur change with by ±30°C and depend also on the level of mixing of the nitrates. An exemption is the temperature for CuO phase formation, which was determined for the Cu-nitrate and for both 1 : 1-nitrate powders to be at 266°C. The domains of stability for different phases are shown to be variable. Also, for 1 : 1-powders, α-type and β-type $Ca(NO_3)_2 \cdot 2H_2O$ phases coexist, while in Ca-nitrate only the α-type phase was observed. © *2002 Kluwer Academic Publishers*

1. Introduction

A material useful for synthesis of high-T_c superconducting materials is the $CaCuO_2$ (Ca : Cu = 1 : 1) precursor. For the synthesis of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (2223) phase in the Bi(Pb)-Sr-Ca-Cu-O system, Dorris *et al.* [1] proposed a solid state technological route based on two-precursor powders: the first powder had the nominal composition $Bi_{1.8}Pb_{0.4}Sr_{2-y}Ca_{1+y}Cu_2O_x$ and contained the phases $(Bi,Pb)_2Sr_2CaCu_2O_8$ (2212) and Ca_2PbO_4, while the second powder had the cation ratio Ca : Cu = 1 : 1 and consisted of phases Ca_2CuO_3 and CuO. This technology was able to accelerate the phase formation processes and to avoid the growth of undesirable phases. Smith *et al.* [2] succeeded in the fabrication of 2223/Ag "powder in tube" tapes using a mixture of 2212-type powder and a powder Ca : Cu = 1 : 1 in which the phases were $Ca_{0.45}Cu_{0.55}O$ and CaO. Recently, advances in layer-by-layer pulsed laser deposition (PLD) allowed for the fabrication of $CaCuO_2$ infinite layers (IL) using targets with nominal $CaCuO_2$ stoichiometry [3], and, later on, of $(CaCuO_2)_n/(BaCuO_2)_m$ artificial superconducting superlattices with critical temperatures (T_c) up to 80 K [4], using $CaCuO_2$ and $BaCu_{0.75}O_x$ targets.

Considering the above-mentioned scientific and technological interest, in this work we investigated Ca : Cu = 1 : 1 nitrate powders by thermal analysis and X-ray diffraction. We have chosen for our studies nitrate mixtures due to the well-known fact that, when raw materials contain carbonates, residual C in Bi-2223 superconductors decreases the critical current density j_c, the critical temperature, and also enhances the formation of non-superconducting phases [5]. Also, as was shown in Ref. 6, T_c and j_c of $(CaCuO_2)_n/(BaCuO_2)_m$ superlattices produced by PLD are lower compared with related compounds obtained by the high-pressure technique [7]. This could be due not only to the inherent disorder [8], but also to carbon impurities since the targets used in the PLD were obtained by standard solid state reaction from oxides and carbonates.

2. Experimental

Ca : Cu = 1 : 1 nitrate powders were prepared by mixing Ca and Cu individual nitrates ("Ca : Cu = 1 : 1 nitrate mixture") and by the spray frozen freeze-drying (SFFD) method ("Ca : Cu = 1 : 1 nitrate freeze dried powder") [9].

Differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Differential thermogravimetric analysis (DTGA) measurements were carried out with a Derivatograph Q-1500D, in air, at a heating rate of 10°C/min. Samples of 0.31 g were weighted in alumina crucibles. For comparison, the same measurements were carried out in the same conditions on batches of individual Ca and Cu nitrates. TGA data on individual nitrates were used for calculation of the necessary weights of the individual nitrates in the "Ca : Cu = 1 : 1 nitrate mixture" preparation method.

X-ray diffraction patterns were obtained with a DRON 2.0 diffractograph ($Cu_{K\alpha}$ radiation) on decomposed samples at different temperatures. Heat treatment for decomposition was performed in air using alumina boats. When samples attained a certain temperature (heating rate 10°/min.) they were extracted and cooled rapidly in air on a massive copper block.

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3. Results

Thermal analysis curves are presented in Fig. 1. Temperatures for the transformations and the chemical compositions at these temperatures were calculated from TGA/DTGA curves, and are presented in the following paragraphs. X-ray diffraction patterns obtained on the decomposed Ca : Cu = 1 : 1 nitrates are shown in Fig. 2, and semi-quantitative data are gathered in Table I, together with the identified phases.

3.1. Thermal decomposition of the calcium nitrate ($Ca(NO_3)_2 \cdot 4.49H_2O$)

Processes for the decomposition of $Ca(NO_3)_2 \cdot (4+m)H_2O$ are presented in Table II and can be summarize by the following scheme:

$$Ca(NO_3)_2 \cdot (4+m)H_2O \overset{\textbf{A}}{\xrightarrow[\text{incongruent melting}]{\text{34 to 122°C}}} \begin{array}{c}\alpha Ca(NO_3)_2 \cdot 2H_2O \\ Ca(NO_3)_2 \cdot 3H_2O\end{array} \overset{\textbf{B}}{\xrightarrow[\begin{array}{l}\text{steps of weight loss:}\\ \text{1. – 122 to 148°C}\\ \quad\text{– 148 to 175°C}\\ \text{2. 175 to 229°C}\end{array}]{\text{122 to 229°C}}}$$

$$Ca(NO_3)_2 \overset{\textbf{C}}{\xrightarrow[\text{no transformation}]{\text{229 to 460°C}}} Ca(NO_3)_2 \overset{\textbf{D}}{\xrightarrow[\begin{array}{l}\text{steps of weight loss:}\\ \text{1. 460 to 525°C}\\ \text{2. 525 to 568°C}\\ \text{3. 568 to 590°C}\\ \text{4. 590 to 685°C}\end{array}]{\text{460 to 685°C}}} CaO$$

Our results are quite consistent with literature data. For example, Ref. [10] described the decomposition processes of $Ca(NO_3)_2 \cdot 4H_2O$ as follows:

$$Ca(NO_3)_2 \cdot 4H_2O \xrightarrow[\text{incongruent melting}]{\text{30 to 40°C}} [Ca(NO_3)_2 \cdot 3H_2O]_{\text{l.s.}} \xrightarrow[\begin{array}{c}\text{steps of weight loss:}\\ \text{1. 40 to 70°C, fast vaporization}\\ \text{(endo-peak at 60°C)}\\ \text{2. 70 to 144°C slow vaporization}\\ \text{(no endo-peak)}\end{array}]{\text{40 to 140°C}} \begin{array}{c}\alpha Ca(NO_3)_2 \cdot 2H_2O \\ Ca(NO_3)_2 \cdot 3H_2O\end{array}$$

$$\xrightarrow[\begin{array}{c}\text{steps of weight loss:}\\ \text{1. 140 to 175°C}\\ \text{2, 3. 175 to 225°C}\end{array}]{\text{140 to 225°C}} Ca(NO_3)_2 \xrightarrow[\text{no transformation}]{\text{225 to 455°C}} Ca(NO_3)_2 \xrightarrow[\begin{array}{c}\text{decomposition steps:}\\ \text{1. 455 to 490°C}\\ \text{2. 490 to 520°C}\\ \text{3. 520 to 540°C}\\ \text{4. 540 to 645°C}\end{array}]{\text{455 to 645°C}} CaO$$

As can be seen, there are also differences between our data and Ref. [10]. Temperatures of the processes are shifted by ~±10 to 40°C. In our opinion, this shift is too large to be due to possible differences in calibration. Some processes in the temperature range of 30 to 140°C could not be clearly revealed, e.g., melting at 30–40°C (42°C in Ref. [11]) with formation of the $Ca(NO_3)_2 \cdot 3H_2O$ liquid solution (l.s.), and two step-vaporization; the first one (40–70°C) developing with a high rate of weight loss, and the second one slower with no observable DTA-peak (70–140°C). Changes in the rate of weight loss (with no visible DTA effect) can be observed in Fig. 1 at 134°C and 209°C, respectively. For the decomposition of $Ca(NO_3)_2$, in Ref. [10] was indicated a four-steps process, with temperatures for the maximum of the transformation rates—DTGA—and of the corresponding endothermic effects being 470, 510, 536 and 570°C. Calcium nitrate investigated by us has shown 4 steps of weight loss, two of them well defined (558 and 615°C in DTGA) and two not so well defined. In the work of Wendland [12], $Ca(NO_3)_2$ decomposes in two steps. Another interesting observation regarding the decomposition of $Ca(NO_3)_2$ and the formation of CaO, is that the last step of decomposition should be the most intensive (according to Ref. [10]), while for $Ca(NO_3)_2 \cdot 4.49H_2O$ this statement is not true, as can be seen in Fig. 1. Anyway, the decomposition of $Ca(NO_3)_2$

is a complex process. Melting, vaporization, crystallization, chemical transformations are included and are overlapping. In this situation, it is very difficult to separate and determine possible processes. Small changes in the shape of DTA/DTGA could be due to unknown processes which we tried to investigate.

From calculations from the TGA curve, for temperatures of 568 and 585–590°C, the molar weights were determined (see Table II). These values are close to the molar weights that could be ascribed to compositions $0.5Ca(NO_3)_2 + 0.5CaO_4$ and $Ca(NO_3)_2 + 0.5CaO + 0.25O_2$, respectively. In proposing the above-mentioned compositions, we were also led by small diffraction peaks which could be ascribed to the CaO_4-phase, and to the absence of diffraction peaks corresponding to CaO_2 in our experimental XRD pattern. At 644°C there was an exothermic tendency, which could be crystallization to CaO.

3.2. Thermal decomposition of the copper nitrate ($Cu(NO_3)_2 \cdot 6.87H_2O$)

Our investigations led to the following results, presented in Table III, and summarized as follow:

$$Cu(NO_3)_2 \cdot (6+n)H_2O \xrightarrow[\text{incongruent melting}]{\overset{\textbf{A}}{\text{room temp. to 108°C}}} Cu(NO_3)_2 \cdot 3H_2O \xrightarrow[\substack{\text{weight loss steps:}\\ \text{1. 108 to 165°C}\\ \text{2. 165 to 235°C}}]{\overset{\textbf{B}}{\text{108 to 235°C}}}$$

$$Cu(NO_3)_2 \cdot 3Cu(OH)_2 \xrightarrow{\overset{\textbf{C}}{\text{235 to 290°C}}} CuO$$

Considering the data presented in Refs. [13–15] for the decomposition of $Cu(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ respectively, the decomposition steps for copper-nitrate resulted to be:

$$Cu(NO_3)_2 \cdot 6H_2O \xrightarrow[\text{melting with } H_2O \text{ loss [13]}]{\text{26°C}} Cu(NO_3)_2 \cdot 3H_2O \xrightarrow[\substack{\text{melting, max. of the endo-peak}\\ \text{at 136°C [14] / 112°C [11]}}]{\text{119 to 140°C}}$$

$$[Cu(NO_3)_2 \cdot 3H_2O]_{l.s.} \xrightarrow[\substack{\text{DTA/DTG-peak}\\ \text{at 203°C [14]}}]{\text{140 to 280°C}} Cu(NO_3)_2 \cdot 3Cu(OH)_2 \xrightarrow[\substack{\text{205-315°C (DTA/DTG-}\\ \text{peak at 290°C) [15] or}\\ \text{280-345°C (DTA/DTG-}\\ \text{peak at 310°C) [14]}}]{} CuO$$

In our experiments, H_2O-loss took place at higher temperatures (up to +30°C) and the formation of CuO occurred at lower temperatures. At 71°C there was a change in the slope of DTA-curve, and at 138°C and 150°C one can observe steps in the DTGA curve (Figs 1). These processes could not be ascribed to a certain chemical reaction and it is likely that they are related to the melting/vaporization steps during decomposition. In DTGA measurement, there was a change in slope for the curve at 267°C. We have calculated the molar weight for this temperature and have found that the composition could be ascribed to $0.25CuO + 0.75Cu(OH)_2$. It means that, between 235 and 267°C, only the copper nitrate $Cu(NO_3)_2$ present in the copper hydroxonitrate $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ decomposes into CuO, while the copper hydroxide $Cu(OH)_2$ present in the copper hydroxonitrate decomposes into CuO at higher temperatures. For this discussion, see also Table III. However, $Cu(OH)_2$ could not be detected by XRD.

It is worth mentioning that we did not performed Fourier Transform Infrared Spectroscopy (FTIR) for checking for the presence of amorphous products. Nevertheless, the shape of XRD patterns at low diffraction angles, even at room temperature, permits us to believe that the fraction of amorphous products, if any, is very small and can not change significantly our analysis.

3.3. Thermal decomposition of the Ca : Cu = 1 : 1 nitrate mixture ($CaCu(NO_3)_4 \cdot 14.11H_2O$)

The decomposition process (see Tables I and IV, and Fig. 2) of the Ca : Cu = 1 : 1 nitrate mixture is as follows:

$$\begin{array}{c} Ca(NO_3)_2\cdot(4+m)H_2O. \\ Cu(NO_3)_2\cdot(6+n)H_2O \end{array} \xrightarrow[\substack{\text{incongruent melting and} \\ H_2O \text{ loss}}]{\substack{\textbf{A} \\ \text{30 to 106°C}}} \begin{array}{c} Ca(NO_3)_2\cdot 3H_2O \\ Cu(NO_3)_2\cdot 3H_2O \\ <\mathit{Ca(NO_3)_2\cdot 4H_2O}> \\ <\mathit{\beta Ca(NO_3)_2\cdot 2H_2O}> \end{array} \xrightarrow[\substack{\text{decomposition for Cu-nitrate} \\ H_2O\text{-loss for Ca-nitrate} \\ \text{weight loss in 2 major steps:} \\ \text{1. 106 to 173°C (see Table 4)} \\ \text{2. 173 tp 234°C (see Table 4)}}]{\substack{\textbf{B} \\ \text{106 to 234°C}}}$$

$$\begin{array}{c} \alpha, \beta Ca(NO_3)_2\cdot 2H_2O \\ Cu(NO_3)_2\cdot 3Cu(OH)_2 \\ <\mathit{Ca(NO_3)_2}> \end{array} \xrightarrow[\substack{\text{steps of weight loss:} \\ \text{1. 234 to 252°C} \\ \text{2. 252 to 285°C}}]{\substack{\textbf{C} \\ \text{234 to 285°C}}} \begin{array}{c} \alpha, \beta\ Ca(NO_3)_2\cdot 2H_2O \\ Ca(NO_3)_2 \\ CuO \end{array} \xrightarrow[\text{no transformation}]{\substack{\textbf{D} \\ \text{285 to 435°C}}}$$

$$\begin{array}{c} \alpha, \beta\ Ca(NO_3)_2\cdot 2H_2O \\ Ca(NO_3)_2 \\ CuO \end{array} \xrightarrow[\substack{\text{decomposition major steps:} \\ \text{1. 435 to 525°C} \\ \text{2. 525 to 640°C}}]{\substack{\textbf{E} \\ \text{435 to 640°C}}} CaO + CuO$$

Phases in brackets are secondary phases observed by XRD. Sometimes, the concentration of these phases is high, as can be seen in Table I.

3.4. Thermal decomposition of the Ca : Cu = 1 : 1 nitrate freeze-dried powder ($CaCu(NO_3)_4\cdot 9.4H_2O$)

Thermal analysis (Fig. 1, Table V) and XRD data (Fig. 2, Table I) suggest the following sequence of processes during heat treatment:

$$\begin{array}{c} Ca(NO_3)_2\cdot(4+m)H_2O\cdot \\ Cu(NO_3)_2\cdot(3+n)H_2O \end{array} \xrightarrow[\substack{\text{1. 41 to 89°C} \\ \text{2. 89 to 147°C}}]{\substack{\textbf{A} \\ \text{room temp. to 147°C}}} \begin{array}{c} Ca(NO_3)_2\cdot 3H_2O \\ Cu(NO_3)_2\cdot 3H_2O \\ <\mathit{\beta Ca(NO_3)_2\cdot 2H_2O}> \end{array} \xrightarrow[\substack{\text{decomposition for Cu-nitrate} \\ H_2O\text{-loss for Ca-nitrate weight loss steps:} \\ \text{1. 147 to 176°C} \\ \text{176 to 191°C} \\ \text{2. 191 to 234°C}}]{\substack{\textbf{B} \\ \text{147 to 234°C}}}$$

$$\begin{array}{c} \alpha, \beta\ Ca(NO_3)_2\cdot 2H_2O \\ Cu(NO_3)_2\cdot 3Cu(OH)_2 \end{array} \xrightarrow[\substack{\text{steps of weight loss:} \\ \text{1. 234 to 253°C (see Table V)} \\ \text{2. 253 to 280°C (see Table V)}}]{\substack{\textbf{C} \\ \text{234 to 280°C}}} \begin{array}{c} \alpha, \beta\ Ca(NO_3)_2\cdot 2H_2O \\ CuO \\ <\mathit{Ca(NO_3)_2}> \end{array} \xrightarrow[\text{no transformation}]{\substack{\textbf{D} \\ \text{280 to 400°C}}}$$

$$\begin{array}{c} \alpha, \beta\ Ca(NO_3)_2\cdot 2H_2O \\ CuO \\ <\mathit{Ca(NO_3)_2}> \end{array} \xrightarrow[\substack{\text{decomposition major steps:} \\ \text{1. 400 to 553°C } (H_2O \text{ loss and decomposition} \\ \text{of } Ca(NO_3)_2 \text{ (see DTA, Table 5)} \\ \text{2. 553 to 625°C (decomposition of } Ca(NO_3)_2)}]{\substack{\textbf{E} \\ \text{400 to 625°C}}} CaO + CuO$$

$$\xrightarrow[\text{exo-peak in DTA at 710°C (see Table V, Fig. 1)}]{\substack{\textbf{F} \\ \text{700 to 740°C}}} \begin{array}{c} <\mathit{Ca_{0.45}Cu_{0.55}O}> \\ CaO \\ CuO \end{array}$$

Details on the decomposition processes for both 1 : 1-nitrate powders, and comparative analysis of the results follows.

4. Discussion

The initial decomposition process (**A**) for the two Ca : Cu = 1 : 1 powders is different since the initial phase composition was different. For the freeze-dried powder (paragraph 3.4), two steps occurred. In the first one, the main process was the decomposition and melting of $Ca(NO_3)_2\cdot 4H_2O$ with the formation of $Ca(NO_3)_2\cdot 3H_2O$. In the second step, melting of $Cu(NO_3)_2\cdot 3H_2O$ occurred. There is no strict separation between the two processes, as deduced from the overlapping of XRD data. Sometimes, for temperatures corresponding to the **A**-process (up to 147°C), $Cu(NO_3)_2\cdot 6H_2O$ was detected in XRD patterns. A possible explanation could be the absorption of water

TABLE I XRD data showing the evolution of the identified phases with temperature during decomposition of 1 : 1-nitrate powders (+-traces, ++-well detectable, +++-maximum content)

Phase	$Ca(NO_3)_2 \cdot 4H_2O$	$Cu(NO_3)_2 \cdot 3H_2O$	$Cu(NO_3)_2 \cdot 6H_2O$	$Ca(NO_3)_2 \cdot 3H_2O$	$Cu_2(OH)_3NO_3$	$\alpha Ca(NO_3)_2 \cdot 2H_2O$	$\beta Ca(NO_3)_2 \cdot 2H_2O$	$Ca(NO_3)_2$	CuO	CaO	$Ca_{0.45}Cu_{0.55}O$	Ca_2CuO_3
PDF	26-1406	21-0296	24-0370	19-0255	15-0014	20-0229	27-0087	07-0204	41-0254	43-1001	[17]	34-0282
Phase notation	1	2	3	4	5	6	6′	7	8	9	∗	z
Ca-nitrate (18°C)	+++	-	-	-	-		-	-	-	-	-	-
Cu-nitrate (18°C)	-	+	+++	-	-	-	-	-	-	-	-	-
1 : 1-SFFD (18°C)	+++	+++	-	-	-	-	-	-	-	-	-	-
1 : 1-mixt. (105°C)	++	+++	-	+	-	-	+	-	-	-	-	-
1 : 1-mixt. (170°C)	+	-	-	+	+++	-	++	++	-	-	-	-
1 : 1-mixt. (240°C)	+	-	-	-	+++	++	+	++	-	-	-	-
1 : 1-mixt. (310°C)	+	-	-	-	-	+	+	+	+	-	-	-
1 : 1-mixt. (365°C)	+	-	-	-	-	+++	+++	+++	+++	-	-	-
1 : 1-SFFD (365°C)	-	-	-	-	-	+++	+++	+	+++	-	-	-
1 : 1-mixt. (480°C)	-	-	-	-	-	-	++	+++	+++	-	-	-
1 : 1-mixt. (590°C)	-	-	-	-	-	-		+	+++	+	-	-
1 : 1-mixt. (655°C)	-	-	-	-	-	-		+	+++	+++	++	-
1 : 1-SFFD (710°C)	-	-	-	-	-	-		-	+++	+++	+++	-
1 : 1-SFFD (840°C)	-	-	-	-	-	-		-	+++	++	-	+++

Together with the identified phases, the corresponding Powder Diffraction Data File (PDF) is presented.

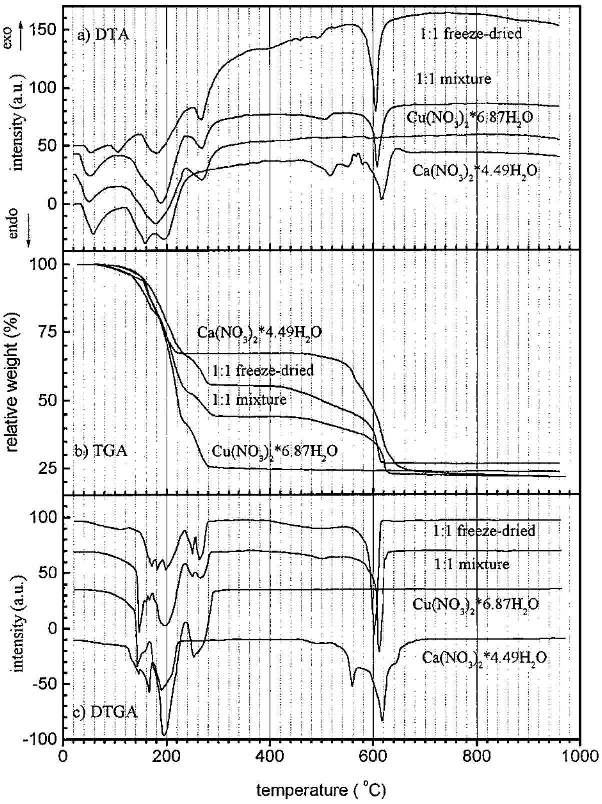

Figure 1 Thermal analysis measurements: (a) DTA curves; (b) TGA curves; and (c) DTGA curves.

from atmosphere. In Fig. 3 are presented the XRD patterns of Ca : Cu = 1 : 1 nitrate freeze-dried powder before the decomposition, measured at 18°C (winter) and 28°C (summer).

Based on these patterns, the following mechanism can be proposed: $Cu(NO_3)_2 \cdot 3H_2O$ absorbs water and could transform into $Cu(NO_3)_2 \cdot 6H_2O$ and/or dissolve in the self-contained water. Some water will become chemically bound by the new copper compound. Less physically bound water and a different concentration of $Cu(NO_3)_2 \cdot 3H_2O$ could change the local equilibrium; and for a certain domain of temperatures $Ca(NO_3)_2 \cdot 4H_2O$ will improve its level of crystallization (shape and mean grain size). The diffraction lines belonging to $Ca(NO_3)_2 \cdot 4H_2O$ increase and become narrow. The rate of absorption enhances with temperature and in summer the rate of water absorption is higher. As can be seen in Fig. 3, we repeated the XRD measurement at 28°C, for 2θ between 35 and 45 degrees, using fresh powder. From the intensity of the peaks compared with the first measurement at 28°C, it is clear that at higher temperatures, the quantity of absorbed water is quite high even during the relatively short time of measurement.

Some peaks in the XRD pattern were not identified. Peaks identification is difficult but, according to Krishnaraj *et al.* [11], it is possible that calcium $Ca(NO_3)_2 \cdot xH_2O$ and copper $Cu(NO_3)_2 \cdot yH_2O$ nitrates have a variable amount (x, y) of crystallization water in freeze-dried materials.

In the case of Ca : Cu = 1 : 1 nitrate mixture, the domains of stability for some phases change compared with individual nitrate powders. For example, a relatively high content of $Ca(NO_3)_2 \cdot 4H_2O$ was identified by XRD in a "Ca : Cu = 1 : 1-mixture" heat treated at 105°C (Fig. 2, Table I). Also, traces of $\beta Ca(NO_3)_2 \cdot 2H_2O$ were first detected at 105°C, with phase stability up to 480°C. Nirsha *et al.* [10] reported a small quantity of low-temperature $\beta Ca(NO_3)_2 \cdot 2H_2O$ phase in addition to the majority phase $\alpha Ca(NO_3)_2 \cdot 2H_2O$, in a $Ca(NO_3)_2 \cdot 4H_2O$ sample heated at 160°C for 4 hr.

Above a certain temperature (225°C in Ref. [10] or 229°C in our measurements), the decomposed Ca-nitrate consists of only $Ca(NO_3)_2$, while in both 1 : 1-powders (mixture and SFFD) high content of $\beta Ca(NO_3)_2 \cdot 2H_2O$ phase was observed at high temperatures. Also, compared with individual Ca-nitrate, the domain of stability for the $\alpha Ca(NO_3)_2 \cdot 2H_2O$ phase in 1 : 1 powders is larger and shifted to higher temperatures: from ∼170 up to $365 \div 480$°C. It is interesting that in 1 : 1-powders, β-type of $Ca(NO_3)_2 \cdot 2H_2O$ phase seems to be more stable than α. Not only the domain of stability for β nitrate is larger but, at higher

TABLE II Ca-nitrate decomposition, including the temperatures of transformations determined from DTA and TGA/DTGA curves, the calculated molar weight considering TGA/DTGA data, the ascriebed chemical composition, and the decomposition processes

				The calculated from TGA/DTGA		The proposed		
T_{DTA} [°C]	Obs. DTA	$T_{TG/DTG}$ [°C]	Obs. DTGA	Chem. comp.	Molar weight (g/mol)	Chem. comp.	Molar weight (g/mol)	Process
r. t.		r. t.		$Ca(NO_3)_2 \cdot 4.49\,H_2O$	245.06	$Ca(NO_3)_2 \cdot (4+m)\,H_2O$	-	
34								**A)** 34–122°C incongruent melting and loss of water
57	Endo-peak max.							
122		***122***		$Ca(NO_3)_2 \cdot 3.95\,H_2O$	235.06		-	
		134	Change in slope					**B)** 122–175°C loss of H_2O main steps:
		145	Max.					
		148		$Ca(NO_3)_2 \cdot 3.08\,H_2O$	219.57	-	-	**1.** 122 to 148°C
156	Endo-peak max.							148–175°C
175		***175***		$Ca(NO_3)_2 \cdot 2.01\,H_2O$	200.35		-	
		189	Max.					**2.** 175–229°C
194	Endo-peak max.							
		209	Change in slope					
229		***229***			164.71	$Ca(NO_3)_2$	164.09	**C)** 229–460°C
460		***460***			164.71	$Ca(NO_3)_2$	164.09	no transformation
500	Endo-peak max.	514	Max.					**D)** 460–685°C
532		***525***						decomposition of
548								$Ca(NO_3)_2$ 4 main
		558	Max.					steps of weight loss
559								460–525°C
565								525–568°C
568		***568***			134.87	$0.5\,Ca(NO_3)_2 + 0.5\,CaO_4$	134.08	568–590°C
577		Endo-peak max.						590–685°C
585		***590***			117.20	$0.5\,Ca(NO_3)_2 + 0.5\,CaO + 0.25\,O_2$	118.08	
615	Endo-peak max.	615	Max.					
644	Exo-peak max.	644	Step					
>***690***		>***685***			56.08	CaO	56.08	**E)** No transformations

Temperature values in bold italics represent the end of certain phase transformations, while temperature values in italics represent the end of intermediate steps of phase transformations.

temperatures, the quantity of β nitrate is at least equal with α nitrate, as can be deduced from the intensities of XRD peaks of the two phases (Fig. 2, Table I), while in the individual nitrate, β-type is less stable and can easily transform into α form [11].

$Ca(NO_3)_2$ phase was detected in 1 : 1 powders at temperatures where the individual Ca-nitrate is still in the decomposition process. The main differences between the 1 : 1 powders and individual Ca-nitrate can be summarize as follow:

(i) The temperature for which the decomposition process ends is lower for 1 : 1 powders and decreasing with the mixing level, (see Fig. 1);

(ii) Thermal analysis curves are smoothed down for Ca : Cu = 1 : 1, having also two decomposition peaks compared with the four peaks (sometimes not very well resolved) of individual nitrate;

(iii) The length of the decomposition step at lower temperatures (~400 to 580°C) is smallest for Ca-nitrate and largest for SFFD 1 : 1-powder. As resulted from our XRD and thermal analysis, and from literature data [10] for the individual Ca-nitrate, the melting of $Ca(NO_3)_2$ occurs in this temperature range. In addition elimination of H_2O from the α, $\beta Ca(NO_3)_2 \cdot 2H_2O$ in 1 : 1-powders was observed. Overlapping of the two processes in the 1 : 1-powders might be the explanation for the increase of the temperature domain of decomposition;

(iv) The most intensive peak in DTA and the corresponding one in DTGA related to the decomposition of $Ca(NO_3)_2$ is lower than the peaks corresponding to

TABLE III Cu-nitrate decomposition, including the temperatures of transformations determined from DTA and TGA/DTGA curves, the calculated molar weight considering TGA/DTGA data, the ascriebed chemical composition, and the decomposition processes

				The calculated from TGA/DTGA		The proposed		
T_{DTA} [°C]	Obs. DTA	$T_{TGA/DTGA}$ [°C]	Obs. DTGA	Chem. comp.	Molar weight (g/mol)	Chem. comp.	Molar weight (g/mol)	Process
r. t.		r. t.		$Cu(NO_3)_2 \cdot 6.87\ H_2O$	311.40	$Cu(NO_3)_2 \cdot (6+n)H_2O$	-	
48	Endo-peak max	-						**A)** Room to 108°C incongruent melting and water loss
108		***108***		$Cu(NO_3)_2 \cdot 6.51\ H_2O$	304.87	-	-	
-		138	Change in slope					**B)** 108–235°C H₂O loss in 2 main steps:
-		143	max.					
-		165		$Cu(NO_3)_2 \cdot 4.08\ H_2O$	261.12	-	-	108–165°C
178	Endo-peak max	-						165–235°C
-		195	Max.					
235		***235***		-	122.59	$0.25[Cu(NO_3)_2 \cdot 3\ Cu(OH)_2]$	120.05	
-		251	Max.					**C)** 235–290°C
267	Endo-peak max	***267***	Change in slope	-	92.12	$0.25\ CuO + 0.75\ Cu(OH)_2$	93.05	Thermal decomposition of $[Cu(NO_3)_2 \cdot 3Cu(OH)_2]$
>***290***		>***290***		-	79.53	CuO	79.53	**D)** No transformations

The significance of temperature values in bold italics and in italics is the same as in Table II.

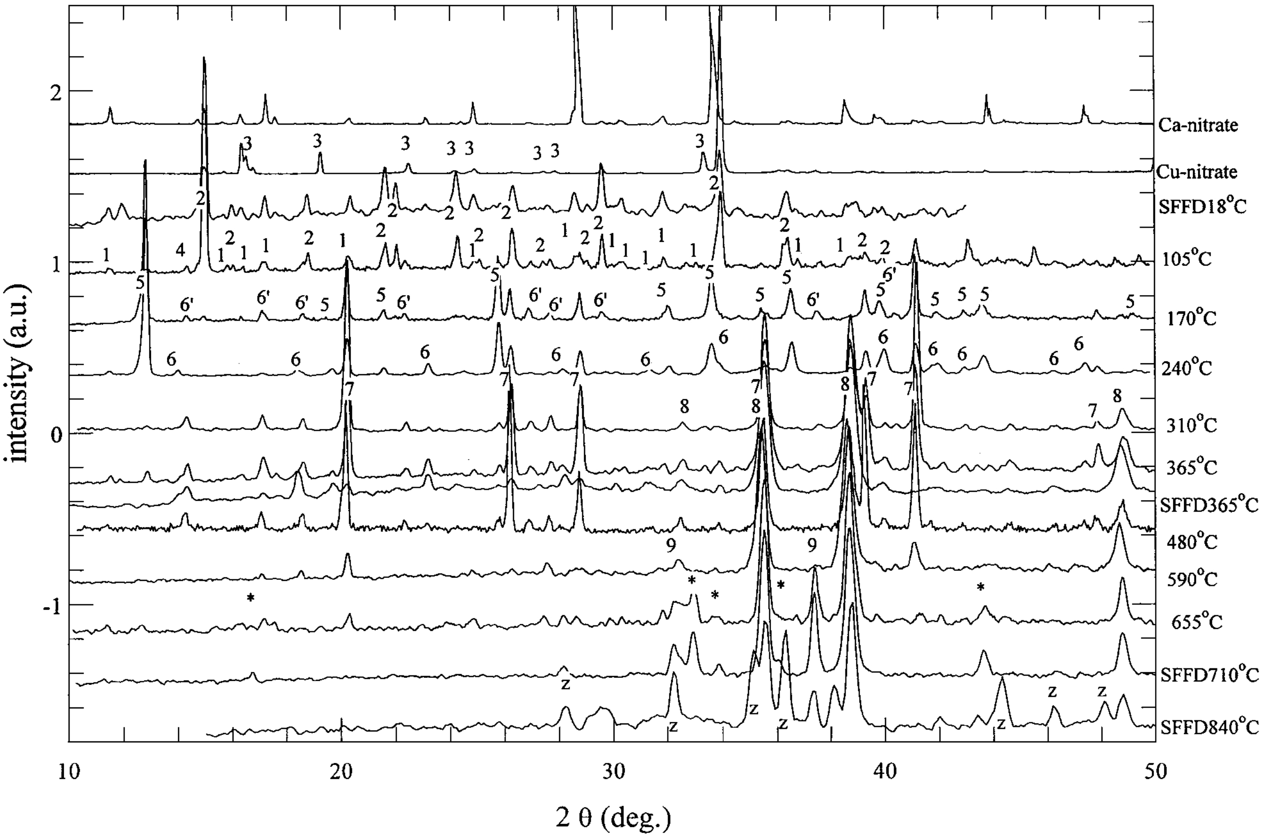

Figure 2 XRD patterns for 1 : 1 nitrate mixtures decomposed at various temperatures.

the second step of decomposition of $Ca(NO_3)_2$ in 1 : 1-powders, and the intensity of the peaks is increasing with the mixing level.

In the case of Cu-based compounds, there are also differences in their behavior during decomposition. We have pointed out in paragraph 3.2 that the transformation of $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ into CuO for the individual Cu-nitrate investigated by us (see Table III and Fig. 1, temperatures of ~230 to 300°C), is likely to occur in two steps. The DTGA peak is quite asymmetric and the corresponding DTA peak is broad. For the 1 : 1-powders, splitting of the DTGA peak can be noticed and the DTA peak is composed of a shoulder at lower

TABLE IV Ca : Cu = 1 : 1 nitrate mixture decomposition, including the temperatures of transformations determined from DTA and TGA/DTGA curves, the calculated molar weight considering TGA/DTGA data, the ascriebed chemical composition, and the decomposition processes

				The calculated from TGA/DTGA		The proposed		
T_{DTA} [°C]	Obs. DTA	$T_{TGA/DTGA}$ [°C]	Obs. DTGA	Chem. comp.	Molar weight (g/mol)	Chem. comp.	Molar weight (g/mol)	Process
r. t.		r. t.		$CaCu(NO_3)_4 \cdot 14.11\ H_2O$	605.98	$Ca(NO_3)_2 \cdot (4+m)H_2O +$ $Cu(NO_3)_2 \cdot (6+n)H_2O$	-	
30		-						**A)** 30–106°C
50	Max	-						incongruent melting
106		-		$CaCu(NO_3)_4 \cdot 13.36\ H_2O$	592.39	-	-	and water loss
140	Change in slope	140	Change in slope					**B)** 106–234°C two major steps:
-		146	Max.					**1.** 106–173°C
-		157		$CaCu(NO_3)_4 \cdot 9.39\ H_2O$	520.92	-	-	H_2O loss within ~3-4 substeps:
-		160						106–140/140–157/
-		163		$CaCu(NO_3)_4 \cdot 8.86\ H_2O$	511.26	-	-	157–163/163–173°C **2.** 173-234°C
-		166	Max.					weight loss within
173		173		$CaCu(NO_3)_4 \cdot 7.57\ H_2O$	488.03	-	-	~1-2 substeps: 173–180 /180–234°C
-		180	Change in slope					decomposition for Cu-nitrate, water
189	Max.	193	Max.					loss for Ca-nitrate
234		***234***		-	316.83	$Ca(NO_3)_2 \cdot 2H_2O +$ $0.25[Cu(NO_3)_2 \cdot 3Cu(OH)_2]$	320.17	
-		249	Max.					**C)** 234–285°C dec.steps **1.** 234–252°C thermal
252		***252***		-	294.31	$Ca(NO_3)_2 \cdot 2H_2O + 0.25CuO$ $+ 0.75Cu(OH)_2$	293.02	decomp. of Cu-nitrate from Cu-hidroxo-nitrate
266	Max.	266	Max.					**2.** 252–285°C, H_2O loss, Cu-hidroxide decomp.
285		***285***		$Ca(NO_3)_2 \cdot 1.4\ H_2O+CuO$	268.93	-	-	**D)** 285-435°C
435		***435***		$Ca(NO_3)_2 \cdot 1.4H_2O+CuO$	268.93	-	-	No transformation
505	Max.	480	Max.					**E)** 435–632°C steps of weight loss:
525		***525***		-	244.27	$Ca(NO_3)_2 + CuO$	243.63	**1.** 435–525°C
582	Change in slope	582	Change in slope					loss of the $2H_2O$ from $Ca(NO_3)_2 \cdot 2H_2O$
610	Max.	610						**2.** 525–632°C
-		623	Step					$Ca(NO_3)_2$ decomp.
>640		***>632***		$CaO + CuO$	135.62	$CaO + CuO$	-	**F)** End of the weight loss no DTA peaks

The significance of temperature values in bold italics and in italics is the same as in Table II.

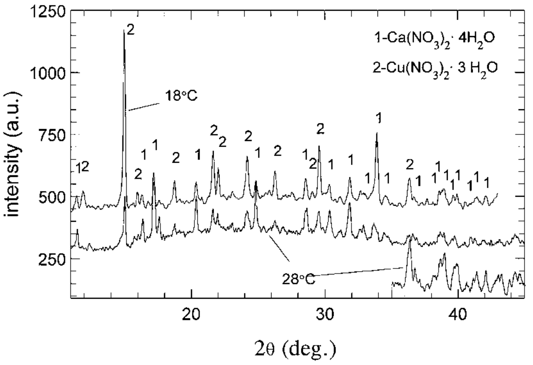

Figure 3 XRD patterns for 1 : 1 SFFD nitrate powder measured in air at 18°C (winter) and 28°C (summer).

temperatures and a narrow peak at higher temperatures. When the mixing level increase, the splitting of the DTGA-peak is more pronounced, the width of the DTA-peak is smaller and the DTA-shoulder increase. The temperature range for this process is almost the same for individual Cu-nitrate and 1 : 1-powders. CuO-phase formation temperature is not influenced by the mixing of the Cu-nitrate with Ca-nitrate.

At temperatures higher than 640–660°C there are no weight-loss processes. The DTA curve for 1 : 1-mixture is very close to a horizontal line suggesting that, in our experimental conditions, the processes can not be evidenced because they are developing too slowly. For the SFFD-powder, the DTA curve (measured in the same conditions) shows a very broad exothermic peak with a maximum around 710–720°C (Fig. 1) that can be ascribed to crystallization of $Ca_{0.45}Cu_{0.55}O$ phase. A detailed discussion of the kinetics and synthesis of the above mentioned phase from nitrate 1 : 1-powders is presented elsewhere [16]. Another process at high temperatures developing without a visible DTA-effect is the formation of the Ca_2CuO_3 phase (Fig. 4) at about 750°C [17].

TABLE V Ca : Cu = 1 : 1 SFFD nitrate powder decomposition, including the temperatures of transformations determined from DTA and TGA/DTGA curves, the calculated molar weight considering TGA/DTGA data, the ascriebed chemical composition, and the decomposition processes

				The calculated from TGA/DTGA		The proposed		
T_{DTA} [°C]	Obs. DTA	$T_{\mathrm{TGA/DTGA}}$ [°C]	Obs. DTGA	Chem. comp.	Molar weight (g/mol)	Chem. comp.	Molar weight (g/mol)	Process
r. t.		r. t.		$CaCu(NO_3)_4 \cdot 9.4\ H_2O$	521	$Ca(NO_3)_2 \cdot (4+m)H_2O + Cu(NO_3)_2 \cdot (3+n)H_2O$	-	
41		-						**A)** 41–147°C
53	Max.	-						incongruent melting and
89		-		$CaCu(NO_3)_4 \cdot 8.9\ H_2O$	512.01		-	loss of water in 2 steps:
106	Max.	140						41–89°C
147		***147***	Change in slope	$CaCu(NO_3)_4 \cdot 7.38\ H_2O$	484.58		-	89–147°C
-		171	Max.					**B)** 147–234°C
176	Max.	*176*		$CaCu(NO_3)_4 \cdot 4.97\ H_2O$	441.18		-	2 major steps of weight loss: **1.** 147–191°C
-		181	Max.					H_2O loss within 2 substeps:
-		*191*		$CaCu(NO_3)_4 \cdot 2.83\ H_2O$	402.63	-	-	147–176°C and 176–191°C **2.** 191–234°C
-		199	Max.					Cu-nitrate decomposition
234		***234***		-	341.52	$[Ca(NO_3)_2 \cdot 2H_2O] + 0.25[Cu(NO_3)_2 \cdot 3Cu(OH)_2]$	320.17	
-		249						**C)** 234-280°C **1.** 234–253°C thermal decomp. of Cu-nitrate from Cu-hidroxonitrate
253		*253*		-	316.52	$[Ca(NO_3)_2 \cdot 2H_2O] + 0.25CuO + 0.75Cu(OH)_2$	293.02	**2.** 253–280°C H_2O loss and Cu-hidroxide decomposition
265	Max.	265	Max.					from Cu-hidroxo-nitrate
280		***280***		-	285.8	$Ca(NO_3)_2 \cdot 2H_2O + CuO$	279.6	**D)** 280–400°C,
400		***400***		-	285.8	$Ca(NO_3)_2 \cdot 2H_2O + CuO$	279.6	no transformations
450		-						**E)** 400–625°C
459	Max.	-						two weight loss steps accompanied by
466		-						other processes (DTA) as melting-vaporization
485		-						**1.** 400–553°C with the following steps in DTA:
494	Max.	494	Max.					400–450°C
518		-						450–466°C 466–485°C 485–518°C
553		*553*		-	236	$Ca(NO_3)_2 + CuO$	243.63	518–553°C
603		603	Max.					**2.** 553-625°C decomposition of $Ca(NO_3)_2$
625		***625***		$CaO + CuO$	135.62	-	-	**F)** End of the weight loss at 700–740°C,
710-720	Max.	-		-	-	$Ca_{0.45}Cu_{0.55}O + 0.55Ca + 0.45CuO$		formation of the $Ca_{0.45}Cu_{0.55}O$-phase
>***750***		>***800***		$CaO + CuO$	135.62	$0.25[Ca_2CuO_3 + CuO] + 0.5[CaO + CuO]$	135.62	**G)** No detectable DTA peaks

The significance of temperature values in bold italics and in italics is the same as in Table II.

5. Conclusion

A comparative thermal analysis and XRD studies for the decomposition of calcium and copper nitrates and their mixtures having Ca : Cu = 1 : 1 ratio was performed. 1 : 1-powders were obtained by both conventional and SFFD techniques. Some differences in materials' behavior when mixed or not are presented. However, processes are overlapping and it is very difficult to separate them completely. Apart from the phases discussed in the paper, XRD patterns have shown also the presence of unidentified peaks that could not be ascribed to the known phases. In these circumstances, there is the possibility for the formation of unknown oxides or compounds that might be suitable for synthesis of high-T_c superconductors. Even if new compounds were not discovered, nitrates mixing changed the domain of stability of some phases, e.g., $\beta Ca(NO_3)_2 \cdot 2H_2O$. The results presented in this work may also be useful for synthesis of new precursor powders and/or superconductors, pending on further investigations.

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