

## **Bi-2223 FREEZE-DRIED CERAMIC: SPECIFIC FEATURES, RELATED PROBLEMS AND SEARCH FOR NEW SOLUTIONS**

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The paper presents a review of our data and the current status on synthesis and processing of Bi-2223 superconducting ceramic, by spray frozen, freeze drying method (SF-FD). By this method powders of 200-300 nm were obtained and processed by several different routes to the final superconducting product. Optimization process and comparative analysis with the literature data revealed intrinsic problems associated to the specific nature (i.e high degree of mixing and large surface area relative to the volume) of the SF-FD material. The paper focuses on the effects induced by the specific features of the SF-FD material, sometimes opposite to those observed in the conventional materials produced by solid-state method. It resulted that in order to take full advantage of the specific features for a nano SF-FD material, it is necessary to consider a special, non-conventional, processing approach and some examples in this regard will be presented.

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### **1. Introduction**

Cryochemical technologies for synthesis of different materials consist of two processes: fast solidification at low temperatures of salt solutions or slurries being in liquid, vapor or aerosol state and elimination of the solvent by physical or chemical processes. Usually the used salt solutions or slurries are water-based and, in this case, in the second step, the solvent to be removed is water. A convenient way that can be applied with success to many types of salt solutions, their mixtures and/or slurries is vacuum freeze-drying (FD) based on sublimation process of the water. Generally, by FD are obtained powders. In the first processing step a fine aerosol is frozen by a cooling agent, e.g. liquid gases or cooled alcohols, and then is freeze-dried. The technology received the name spray-frozen freeze-drying (SF-FD) and even if this is not universally recognized terminology, we shall use it in our paper. Freeze drying can be also applied to frozen layers produced on different substrates by methods like dip-coating, doctor-blade, spin-coating, casting/freeze-casting. The final products are tapes, coatings, thick films, bulks and porous media. Some examples are presented in ref. [1,2] and it is worth mention that application of freeze-drying to processing of such products is a relatively unexplored and new field. Freeze drying might have also a good potential for synthesis of composite materials [3,4].

Several specific features make this technique more attractive when applied to powder synthesis. Authors of ref. [5] wrote: "*freeze dried precursors often lead to the formation of solids or phases which are synthetically inaccessible through conventional solid state or flux techniques. This property of*

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*freeze dried precursors originates from the high degree of mixing of the parent materials and the extremely high crystallite surface area to volume ratio*". Freeze dried (FD) precursors are usually expected to induce during next steps of processing faster kinetics, modification of the phases stability, decrease in the reaction temperatures. Also, high purity and good stoichiometry control should be retained for the FD materials. The method allows synthesis of nano-particles (crystalline or amorphous) in the precursor powder and/or in the final product, it is simple if compared with flux methods, additions and substitutions can be easily introduced and by using industrial freeze driers is possible to synthesize large amounts of high quality precursor powders of several kg/run or more. For some materials it was also observed that SF-FD precursors are suitable to obtain high-density ceramics [6,7].

In the superconducting Bi-Pb-Sr-Ca-Cu-O system, synthesis of pure Bi-2223 phase is difficult. Phase formation kinetics is slow (hundreds of hours are necessary) and bulk density is low. Moreover residual carbon decreases critical current density that is a key parameter for application of superconductor and also enhances the formation of the non-superconducting phases [8]. By using salts without carbon (usually nitrates), and considering the above advantages of the SF-FD, this technique would be a potentially good choice for synthesis of high quality Bi-2223 phase.

In this paper we review our data and discuss specific problems and solutions identified during optimization process for synthesis of superconducting BSCCO ceramic produced from SF-FD nitrate precursor nano-powders. The paper will focus especially on Bi-2223 phase. This phase has the highest critical temperature ( $T_c=110\text{K}$ ) in the BSCCO system and is among the most promising superconductors for commercial applications. Some data for Ca:Cu=1:1 (0011) and Bi-2212 SF-FD nitrate powders will be also presented since these powders can be used as precursors for synthesis of Bi-2223 phase and for understanding the phase formation processes.

## **2. Experimental**

Individual water-based nitrate solutions were prepared, mixed to obtain the desired cation ratio and sprayed by pneumatic plastic nozzle into liquid nitrogen under intensive stirring. Cryo-particles were dried in an industrial freeze-drier TG 50.4 from  $-60^\circ\text{C}$  to  $+30-40^\circ\text{C}$  at 9-10Pa, for 24-48 hrs. Dried powders have green-blue color, are composed of soft aggregates and the particle size is 200-300 nm, are not stable in air absorbing moisture at room temperature, but can be stored for long time at lower temperatures ( $0-(-4)^\circ\text{C}$ , or lower). Mancic et al. [9] determined for BSCCO SF-FD nitrate powders a particle mean size of 231 nm and BET surface area of  $2.5\text{ m}^2\cdot\text{g}^{-1}$ . Nitrate powders have been decomposed in air at different temperatures and for different times followed or not by subsequent reactive-sintering or reactive field-assisted-sintering (R-FAST) in order to form superconducting phase. Samples on different stages of synthesis were investigated by thermal analysis, X-ray and neutron diffraction, SEM/EDS, electrical and magnetic properties, measurements of volumetric characteristics.

## **3. Results and discussion**

### **3.1 Conventional route**

In the early stages of our research the nitrate SF-FD powder was thermally decomposed at different temperatures, grinded and pressed into pellets, and sintered in a conventional manner (two step synthesis). Generally the required sintering time to maximize the amount of superconducting phase Bi(Pb)-2223 with enhanced morphology and properties is long, around 150-250 hrs, depending on starting cation composition. Considering ac susceptibility the best samples have been obtained for the

compositions in the following order (1,2)→5→4→3, where 1 =  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ , 2 =  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2.5}\text{Cu}_{3.5}\text{O}_x$ , 3 =  $\text{Bi}_{1.6}\text{Pb}_{0.5}\text{Sr}_{2.7}\text{Ca}_{2.7}\text{Cu}_3\text{O}_x$ , 4 =  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.5}\text{Ca}_{2.5}\text{Cu}_3\text{O}_x$  and 5 =  $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Ba}_{0.2}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_3\text{O}_x$  [10]. It is important to emphasize that high amount of Bi-2223 phase in the sample does not necessarily leads to high quality product. There is a complex interplay between phase assembly, composition, crystal structure, microstructure of the grains and grain boundaries, and properties. Therefore, it is possible that one sample is excellent from some point of view, but is extremely weak from another. The quality criterion should be mentioned each time in the discussions in order to avoid confusion and we shall follow this rule. In most situations details will not be given and they can be found in the indicated references.

Other parameters that control the kinetics and/or quality of the final superconducting product for a given composition are: decomposition temperature and time of the SF-FD powder, the crucible used during decomposition, temperature and time during reactive sintering. Our studies of the influence of different technological parameters on the synthesis and quality of Bi-2223 ceramics can be summarized as follows:

1. Decomposition temperature and time of the SF-FD nitrate powder is important for future phase evolution and its quality. For example, ac-susceptibility curves, measured on pellets sintered in the same conditions, but from batches of the same SF-FD powder, decomposed in different conditions, are given in Fig. 1 [11]. Higher decomposition temperatures (around 840 °C) are resulting in higher amount and quality (grains are larger, less porous, improved superconducting characteristics are obtained) of the Bi-2223 [5, 11].

2.  $\text{Al}_2\text{O}_3$  crucibles have shown better results than Ni crucibles for any investigated composition. Contamination from  $\text{Al}_2\text{O}_3$  crucibles can play a positive role in formation of BSCCO whiskers [12], while Ni additions are suppressing Bi-2223 phase formation and superconductivity [13].

3. Sintering time is generally increasing the phase amount and is improving the morphology of the pellets and quality of the grain boundaries [11,14]. For example, up to 170 h, the magnitude of the diamagnetic signal is increasing with sintering time (Fig. 2, [11]). For 170 h and 235 h of sintering time, the magnitude of the signal does not change significantly, i.e. the amount of the superconducting phase is constant, while the shoulder in the  $\chi'(T)$  curve due to contribution of the intergranular regions has vanished for longer times suggesting improvement of grain boundaries quality. Nevertheless, at even longer times of sintering (more than 300-320 h) decomposition of Bi-2223 phase, accompanied by morphology changes and decrease in magnetic and transport properties, have been observed [14] (Fig. 3). This effect seems to be associated with cation losses (in literature, more often such data are given for Pb and/or Bi [15]), and/or changes in the oxygen content. Unanimous opinion among researchers in this regard has not been reached and probably depends on a certain situation (processing conditions, material).

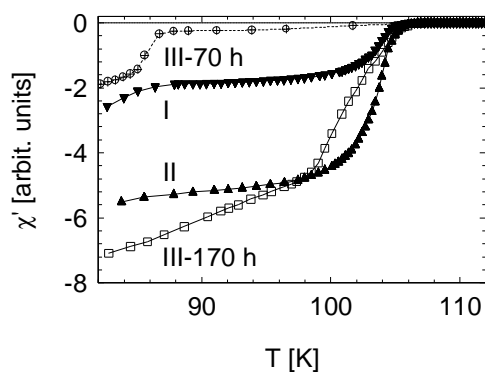


Fig. 1. AC susceptibility curves for pellets sintered in air for 70 and 170 h, produced from SF-FD nitrate powders decomposed at I) 570 °C/180 min, II) 570 °C/180 min + 815 °C/30 min and III) 815 °C/30 min.

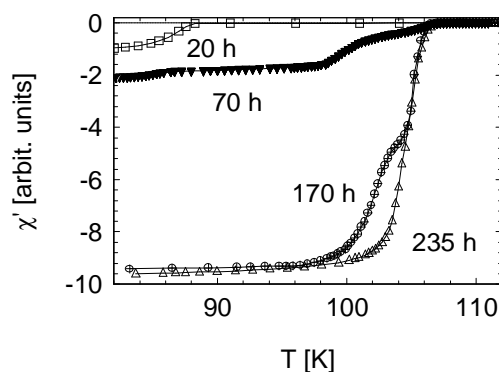


Fig. 2. AC susceptibility curves for pellets sintered in air and produced from SF-FD nitrate powder decomposed at IV) 840 °C/30 min.

Although, more than 90% high quality Bi(Pb)-2223 phase was obtained, the major questions were: how to decrease the synthesis time and how to use powder's high reactivity at its maximum potential. The fact that SF-FD powders are more reactive than the others has been proven by Yavuz et al [16], by comparing with powders produced by spray-drying, co-decomposition and solid-state two-powder oxide method.

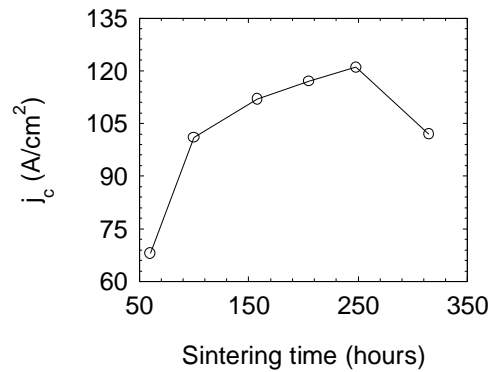


Fig. 3. Critical current density  $J_c$  as a function of sintering time.

Based on the above results, as well as on the observation that on the first stages of sintering big grains of Ca-Cu-O phases form (hundreds of  $\mu\text{m}$ ), and this effect results in long synthesis times [11, 14], studies on intermediate grinding at short sintering times (1, 3, 5, 7 hours) and on sintering in different environments (in air, “on powder” and immersed “in powder” of the same composition as for the samples and sintered for 100h) are of interest [17-19]. Samples have been compared with the samples without intermediate grinding, prepared “in powder” and with previous results when sintering was in air. Some results are gathered in Figs. 4, 5 and 6.

For the samples with intermediate grinding the most unfavorable situation is for pellets sintered “on” the powder and the best one is for the pellets sintered “in” powder when intermediate grinding is performed after 7 hours (compare Fig. 4 a and b [19]).

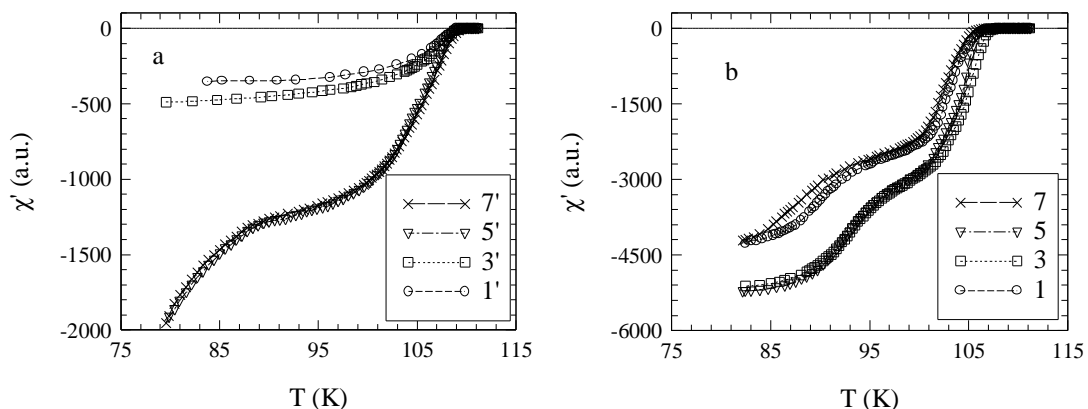


Fig. 4. AC susceptibility curves for pellets with intermediate grinding after 1, 3, 5, 7 h and sintered for 235 h - a) “on powder” and - b) “in powder”.

The influence of sintering environment is strong and for “on” powder pellets phase formation processes are sluggish (Fig. 5, [17]).

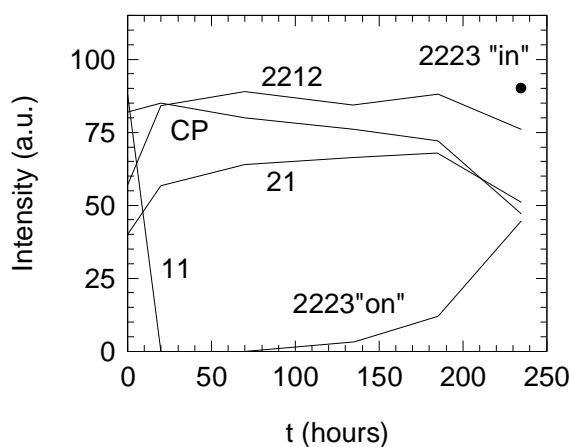


Fig. 5. Phase evolution (XRD data) for the pellets sintered “on powder” up to 235h of sintering. Concentration of Bi-2223 at 235h of sintering “in the powder” is also indicated.

The reason seems to be consumption of the 1:1-phase ( $(\text{Sr,Ca})\text{CuO}_2$ ) before the Bi-2223 phase formation. Phases 1:1, 2:1 ( $(\text{Ca,Sr})_2\text{CuO}_3$ ) and 14:24 ( $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-8}$ ), together with Bi-2212, are recognized to participate in the formation of the Bi-2223 phase. D. Shin et al [20] suggested that there is a preferential nucleation of Bi-2223 in close vicinity of Ca(Sr)-Cu-O phases. They explained this by low lattice parameter mismatch of 4.4% and based on structural similarities of the Ca(Sr)-Cu-O and Bi-2223 phases. If we extend this analysis, the best similarities with Bi-2223 are for 1:1 phase. For the other two phases some rearrangement of Sr and Ca should be considered.

Other authors [21, 22] reported that the activation energy for the Ca(Sr)-Cu-O phases is 5 times lower than that for Bi-2223, but again data are not enough to give an answer to the question which phase is the most favorable to formation of the superconducting phases. In this discussion one has also to take into account the fact that the domain of stability for the Ca(Sr)-Cu-O phases might be slightly different for different sintering environments. Baurceanu et al [23] found that in the powder-in-tube (PIT) tapes Ag/Bi-2223, in air, at 835°C, the most stable phase is 14:24, while in 4%O<sub>2</sub>, at 815°C is 2:1. In our case, for a constant sintering temperature, volume and mass data [18] led us to the conclusion that “in” powder pellets are placed in an atmosphere with lower partial oxygen pressure that is closer to optimum oxygen partial pressure effective for Bi-2223 phase synthesis, as reported in the literature [24]. At present, the data are not enough to decide which Ca(Sr)-Cu-O phase is more important for certain synthesis conditions and a detailed and systematic research on stability of Ca(Sr)-Cu-O phases in connection with kinetics of Bi-2223 phase formation, in T-p<sub>O<sub>2</sub></sub> space, is required.

Coming back to the influence of intermediate grinding many authors (e.g. ref. [25]) noted that intermediate grinding and pressing enhances the concentration of the Bi-2223 phase in conventional powders. For SF-FD material good homogeneity of the constituents makes unnecessary this step; optimum sintering-time is not decreasing (even for the “in” powder samples) and the properties are not improving, but have shown higher scattering (Fig. 6 a, b) [19]. Intermediate grinding induces ceramics defects that are not eliminated during further processing. It should be pointed out that two parallel opposite processes are taking place. First, due to high reactivity of the SF-FD powder large non-superconducting grains form. Under these circumstances an intermediate grinding would be a forthcoming operation. Secondly, intermediate grinding destroys the already formed microstructure and long time sintering cannot totally recover induced defects.

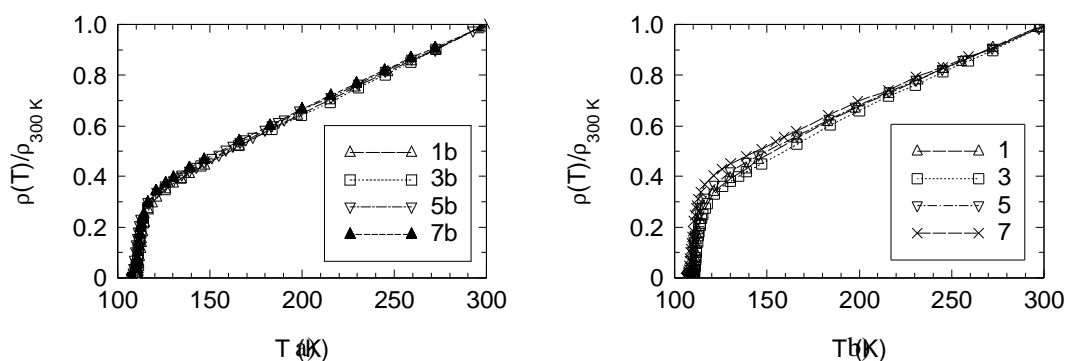


Fig. 6. Electric resistivity curves vs temperature for the pellets “in powder” sintered for 235h a) without intermediate grinding and b) with intermediate grinding.

We conclude that:

1) It is important to know when intermediate grinding must be done and be strictly correlated to other technological and/or processing conditions. Our data suggest that at different stages of synthesis it is necessary to use environments with different levels of oxygen partial pressures. Recent experiments [23] confirmed that by such methodology high quality Bi-2223 superconductor with improved  $J_c$  is obtained in Ag-PIT tapes.

2) A new, non-conventional approach is necessary for the processing of the SF-FD precursor. One idea, although not practical, is to decrease the reactivity of the nitrate precursor powder [26] through the decrease in mixing level. Several mixtures of 2212+0011 powders, where the first or second powder is the nitrate (raw powder) or the oxide (decomposed at high temperature), as well as 2223 SF-FD powder, were compared from the reactivity point of view and the quality of the final Bi-2223 ceramic (resistivity versus temperature). 2212 and 0011 nitrate raw powders were prepared by SF-FD technique. As expected the optimum precursor powder was found to be the mechanical mixture of (2212-nitrate+0011-nitrate). The most unfavorable mixture for Bi-2212 and Bi-2223 phase formation is when using a precursor (2212-nitrate+0011-oxide). After the decomposition of this mixture the lack of 1:1 phase has been noticed. Once again the data indicates that this phase is important for evolution of the superconducting phases, as discussed in the above paragraph. Second idea is to use different salts. Primo et al [27] succeeded in fast synthesis of Bi-2223 (22h of sintering) from acetic SF-FD powders. Third is to use Bi-2223 germs mixed into the un-reacted material. The method gave relatively good results for some compositions (closer to the stoichiometric one). Sintering time has been decreased to 25-50h [9].

### 3.2 Non-isothermal decomposition of the Bi-2223 SF-FD powder (one step synthesis)

We have seen that 2223 SF-FD nitrate powder is giving better results if it is decomposed at high temperatures, intermediate grinding is not efficient and powders reactivity is too high. On the other side, homogeneity of the powder is high so that we assume that each particle has the same cation composition. All these observations are good arguments for fast decomposition of the nitrate SF-FD powder, at elevated temperatures, if possible at the reaction temperature for Bi-2223. Moreover, for  $YBa_2Cu_3O_x$  SF-FD nitrates powders fast decomposition rates are recommended in ref. [28] in order to avoid segregation as a consequence of the formation of transitional liquid phases. Decomposition of particles in an individual manner would be an advantage.

Experiments have been done by employing a technique closely related to spray-pyrolysis [29].

Namely, nitrate SF-FD powder has been introduced into a long vertical crucible positioned in a pre-heated furnace at 847 °C by casting a certain amount through a funnel. In Fig. 7 [29] for a powder with composition 5 containing Ba, Bi-2223 phase can be clearly detected after 5 min of decomposition at 847 °C.

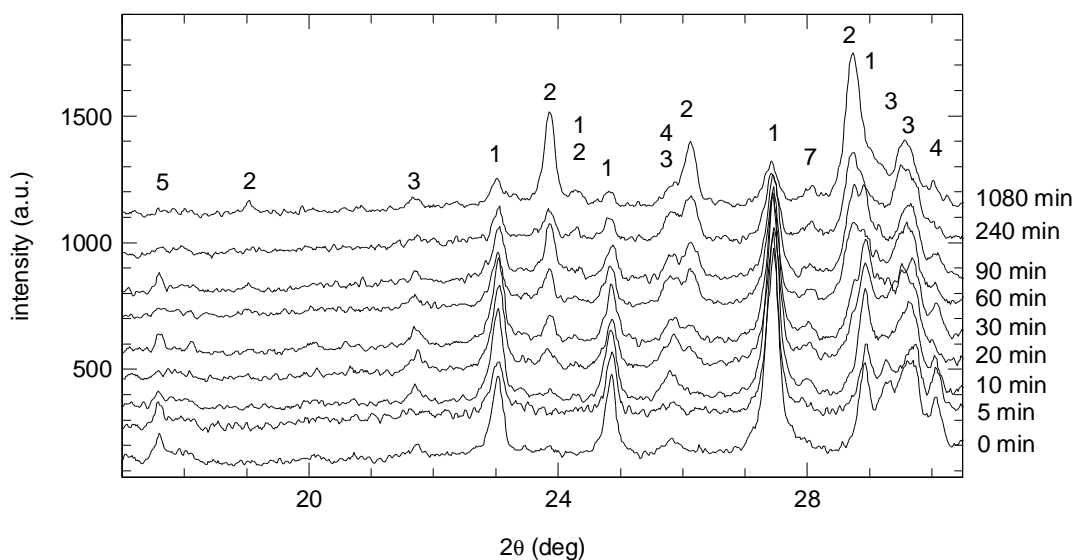


Fig. 7. XRD patterns for the decomposed powders at different heat treatment times.

It is interesting that for a Bi-2212 composition with Ba ( $6= \text{Bi}_{1.8}\text{Pb}_{0.4}\text{Ba}_{0.2}\text{Sr}_{1.8}\text{Ca}_{1.2}\text{Cu}_2\text{O}_x$ ), phase Bi-2223 has been also observed and up to 20-30% of this phase can form after 20hrs of decomposition. For Bi-2223 compositions usually more than 80-90% Bi-2223 phase is determined by XRD. Powder with composition 5 requires a special discussion. Despite the fact that on initial stages Bi-2223 phase formation is extremely fast we could not obtain more than 80% Bi-2223. A detailed analysis is presented in ref. [30]. Briefly, secondary synthesis processes, induced by the Ba presence, are producing a special morphology with glassy grains mainly crystallized as 2201-phase, that incorporates Ca(Sr)-Cu-O phases (Fig. 8, [30]). Isolation of these phases makes difficult supply of Ca(Sr) and Cu species to the reaction site and the phase formation reaction of Bi-2223 phase stops.



Fig. 8. SEM image of the glassy grains with inclusions of Ca-Sr-Cu-O phases.

A special remark should be made here. It is possible that for nano- SF-FD powders additions

or substitutions might behave different than for other types of powders. For example, we have found that the influence of Sc is not favorable to Bi(Pb)-2223 phase formation in Bi-2223 SF-FD powders, opposite to the literature data for Bi(Pb)-2223 ceramic with Sc-addition, obtained by solid state reaction [31]. An interesting question for one-step synthesis is: is it possible to obtain phase Bi-2223 directly from the nitrate precursor, i.e. to skip formation of stable non-superconducting and superconducting (phase 2212) oxide phases?

Although we have put much effort in investigating decomposition of the SF-FD nitrate powders the possibility of direct synthesis of Bi-2223 phase is still open for discussions and further investigations. Some arguments supporting or being against the idea of direct formation of Bi-2223 phase will be addressed in the next paragraphs.

Powders of Bi-2212, Bi-2223 and Ca:Cu=1:1 decomposed in different conditions have been investigated by XRD, in-situ neutron diffraction (pulsed reactor, IBR-2, IUCN, Dubna, Russia) and thermal analysis. For Bi-2212 and Bi-2223 compositions decomposition of the nitrates is taking place in the same way and same phases have been observed. In the room temperature – 120 °C range, some peaks remained un-identified. Krishnaraj et al [32] indicated on new phases with unusual non-integer number of H<sub>2</sub>O molecules in SF-FD nitrate Bi-2223 powder. We have proposed the following two new reactions [33-35]:  $\text{Pb}_{0.33}(\text{Ca,Sr,Ba})_{0.67}(\text{NO}_3)_2 \rightarrow (\text{Ca}_{0.9}\text{Sr}_{0.1})\text{PbO}_4$  at 640-750°C, and (Bi-rich phase)+ $\text{Pb}_{0.33}(\text{Ca,Sr,Ba})_{0.67}(\text{NO}_3)_2 \rightarrow 2201 + (\text{Sr,Ca})\text{CuO}_2$  at 650-810°C. Coppa et al. [5] also observed highly disordered bismuthates different from 2201 phase and suggested that these phases are favorable to fast formation of the Bi-2212 or Bi-2223 phases. The complex nitrate  $\text{Pb}_{0.33}(\text{Ca,Sr,Ba})_{0.67}(\text{NO}_3)_2$  is stable from room temperature up to 450°C. We have detected phase 2212 between 700 and 860°C and phase Bi-2223 between 810-870°C. The fact that in 2212 and 2223 compositions similar reactions were observed is suggesting that starting composition cannot determine the superconducting phase to be formed. Regardless composition the stability domain of phase 2212 is at lower temperature and it forms easier. On the other side during cooling, reformation of Bi-2201 and Bi-2212 was observed. It seems that reformation of the 2212 phase does not depend on phase composition just before cooling, while 2201 does. Reformation of Bi-2201 and Bi-2212 is giving a chance to think that the phases observed after the decomposition of the nitrate powders are the re-formed phases. The technical problem is that in-situ neutron diffraction does not allow investigation of the fast processing and processes (high heating and/or cooling rates). Long time processes are as well difficult to be observed.

By using KCl flux [36] single crystals of Bi-2223 can be obtained. Decomposition of nitrates is a complex process involving liquid-vapor-solid phases. The idea of some phase or liquid acting as a flux is again difficult to be checked for non-isothermal conditions. We have mentioned that bismuthates, different from 2201 phase [5], might be the media accelerating phase formation of high-T<sub>c</sub> superconducting phases. This idea seems to be also supported by the following results: our experiments on one-step decomposition of co-precipitated oxalate powder with cation composition 5, the same as for SF-FD nitrate powder, does not allow formation of Bi-2223 phase. The reason seems to be strong melting below 700 °C, different phase assembly and powder's characteristics inducing different stability domain (in this case Bi-2212 is shifted to lower temperatures). Obviously the data are not perfectly comparable and a final conclusion is not possible.

Stability domain of the phases is depending also on the mixing and mixing degree. We have analyzed in detail decomposition of a SF-FD 0011 nitrate, of a mechanical mixture 0011 and of individual Ca and Cu nitrates used to prepare both mixtures. Formation of the peritectic phase  $\text{Ca}_{0.45}\text{Cu}_{0.55}\text{O}$  was faster for the SF-FD nitrate powder [37]. Temperatures [38] at which decomposition-processes occur change by  $\pm 30$  °C, usually being lower for mixtures and are decreasing with mixing level. An exemption is the temperature for the CuO phase formation, being constant to 266°C for individual Cu-nitrate and both 0011- mixtures. In the individual Ca-nitrate only  $\alpha$ -type



$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  phase was observed, while in SF-FD 0011 powders  $\alpha$ - and  $\beta$ -type phases coexist. Based on these results we extrapolate the following idea to Bi-2223 compositions: by understanding the relationship between the mixtures, their degree of mixing and stability and/or occurrence of phases and their role it might be possible to better control synthesis processes of Bi-2223 phase in a more efficient manner. Identification of a phase playing the role of a flux, or by a different mechanism, allowing direct synthesis of Bi-2223 phase, could not be revealed, up to now.

### 3.3 Field-Assisted-Sintering of SF-FD powders

Reactive-Field-Assisted-Sintering (R-FAST) is a relatively new technique for rapid sintering of dense ceramics [39]. The FAST technique involves the use of an external electrical field (combination of on/off pulses and dc current), pressure application and a high heating rate. The latter is favorable to the synthesis of 2223-phase in SF-FD nitrate powder, as presented above. RFAST has been applied on decomposed SF-FD powders (compositions 2, 5 and 6 and the same compositions with addition of  $\text{Ag}_2\text{O}$ ) between 700 and 850°C. Decomposed powders were loaded into the punch and die carbon unit (20mm) of the FAST machine. RFAST processing was performed in vacuum (4Pa) using 'Dr Sinter Spark Plasma Sintering System', Sumitomo Coal Mining Co, Japan (at Univ. of California, Davis USA). A uniaxial pressure of 17.5Pa was applied throughout the whole sintering cycle of approximately 15min total time. Depending on the starting powders (decomposition conditions and starting composition) phase conversion to superconducting phases was more advanced or not and high values for bulk density between 5.3-6.3g/cm<sup>3</sup> have been attained. But, we could not detect Bi-2223 phase and a post-annealing step was necessary. In the post-annealed samples density is decreasing, but the conversion to Bi-2223 phase is faster than in the conventional two-step processing for SF-FD powder presented in section 3.1. At the same time, final transport properties (resistivity measurements) are better than for the pellets also processed under a combination of pressure and electrical field - Plasma-Activated-Sintering - and applied to almost fully reacted Bi-2223 powders produced from sol-gel, glass-ceramic and solid-state powders [40]. After 70hrs of post-annealing FAST-samples contain up to 75% Bi2223-phase and have  $T_c = 109\text{-}112\text{K}$  and  $\Delta T_c = 14\text{-}17\text{K}$ . In these pellets some unknown phases were observed by SEM/EDS and XRD. We suppose that electrical field used in the FAST approach is inducing some disorder effects and/or phases that can result in faster conversion to Bi-2223 phase. It would be also interesting to investigate disordered regions as possible pinning centers enhancing critical current density.

Conventional hot-pressing of the FD powders [41] showed high degree of grain alignment, increased density up to 99% of theoretical and maximum  $J_c$  of 2100 A/cm<sup>2</sup> at 77K and zero field that is 10 times higher than in the pellets sintered under normal pressure. Although RFAST is investigated as an alternative and potentially superior technique than conventional hot-pressing, at present, research on application of RFAST to BSCCO powders is incipient and the advantages of this method for synthesis of Bi-2223 are still under evaluation. Systematic optimization studies have to be done in the case of Bi-2223. For Bi-2212, RFAST processing is already resulting in high-density ceramics after short sintering times (15min).

## 4. Conclusions

FD has proven to be a promising method for synthesis of high quality Bi-2223 superconductor. Specific features of SF-FD powders are inducing several limitations and, at the same time, are opening new perspectives for better control of synthesis processes, finally leading to higher quality of the superconducting material. New methodologies and processing techniques have to be designed and

applied considering not only phase assembly and chemical composition of the powders, but also their granular specific features (particle size, mixing degree, homogeneity, ratio between surface area to volume). The effects of specific features of the SF-FD nitrate nano-powders on some phase formation and phase stability aspects, sometimes opposite to the effects observed in the conventional solid-state powders, are evidenced reviewed and discussed.

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