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EFFECT OF THE SINTERING ON MICROSTRUCTURE AND SUPERCONDUCTING PROPERTIES OF $YBA_2CU_3O_{7-\delta}$ CERAMICS

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Résumé

Les céramiques supraconductrices $YBa_2Cu_3O_{7-\delta}$ (Y-123) ont été préparées par la méthode de la réaction à l'état solide. Les propriétés microstructurales et supraconductrices de nos échantillons frittés dans des conditions variées, ont été caractérisées par la diffraction des rayons X (XRD), la microscopie électronique à balayage (MEB), l'analyse thermique (TDA-TGA) et les mesures de résistivité électrique. L'étude montre que la calcination à 800°C pendant 30 heures, du mélange (Y_2O_3, $BaCO_3$ CuO), conduit à un début de formation des phases Y-123 et $BaCuO_2$. Cependant, dans l'intervalle de température 950-990°C, nous observons alors la cristallisation de Y-123 qui devient la phase prédominante. Pour des températures relativement plus élevées (aux environs de 1100°C) se forme la phase dite "verte" Y_2BaCuO_5. Enfin, l'orientation préférentielle des grains Y-123, suivant les plans (00l), a lieu après frittage à l'air libre dans l'intervalle 950-990°C pendant 30 heures. Ainsi, les échantillons texturés présentent de meilleures propriétés de transport.

Mots clés : *Supraconducteur à haute température critique $YBa_2Cu_3O_{7-\delta}$, Diffraction des rayons X (XRD), Microscopie électronique à balayage (MEB), L'analyse thermique (TDA-TGA), Mesures de résistivité électriques.*

Abstract

Superconducting $YBa_2Cu_3O_{7-\delta}$ (Y-123) ceramics were prepared by the solid-state reaction method. The microstructure and superconducting properties of the sintered samples obtained under various conditions were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TDA-TGA) and electrical resistivity measurements. The study showed that the calcination at 800°C for 30 hours of theY_2O_3, $BaCO_3$ and CuO mixture led to the starting of the Y-123 and $BaCuO_2$ phases' formation. However, in the temperature range of 950 - 990°C, Y-123 crystallized and became predominate compound. For higher temperatures (near 1100°C), green Y_2BaCuO_5 phase was formed. A (00l) preferred orientation of Y-123 grains was occured after sintering in air at temperatures 950-990°C for 30 hours. The textured samples presented the best transport properties.

Keywords: *$YBa_2Cu_3O_{7-\delta}$ high-Tc superconductors, X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TDA-TGA), Sintering.*

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ملخص

حضرت الخزفيات الفائقة الناقليـــة $YBa_2Cu_3O_{7-\delta}$ (Y-123) عن طريق التفاعل في الحالة الصلبة. إن الخـــواص المجهاريـــة والفائقة الناقلية للعينات الملبدة في ضر وف مختلفة قد شخـــصت عن طريق التحليل الطيفي للأشـــعة الـــسينية(XRD) , المـــسح ألمجهري الالكتروني(MEB) , التحليـــل الحـــر ري-(TDA TGA) و قياس المقاومية الكهربائية. فمن هذه الدراسة يتبين أن الكلسنة في 800°C لمدة 30ساعة للخلـــيط المـــسحوق (Y_2O_3, $BaCO_3$ CuO) قد تؤدي إلى بداية تكوين الطور يـــن Y-123 و $BaCuO_2$. في مجـــال درجـــة الحـــرارة (950-990°C) نلاحض تبلور Y-123 الذي يصبح يمثل الطور المهيمن. و أما في حالة الحرارات المرتفعة نسبيا (حوالي 1100°C) يتـــشكل الطور الأخضر Y_2BaCuO_5. يحدث الاتجاه التفاضلي للحبيبـــات حسب المستويات (00l) بعد عملية التلبد في الهواء فـــي مجـــال درجة الحرارة 950-990°C لمدة 30ساعة. وهكذا قد تتميز العينات ذات الاتجاه المفضل بأحسن خواص النقل.

كلمات مفتاحية : *الفائق الناقلية ذات درجـــة الحـــرارة الحرجـــة $YBa_2Cu_3O_{7-\delta}$, الأشعة الـــسيني(XRD), المـــسح ألمجهـــري الالكتروني (MEB) , التحليـــل الحـــر ري التليـــد -(TDA TGA).*

The synthesis of high-Tc superconductors by a solid-state reaction method is widely performed because of its simple technique [1, 2]. Therefore, the dependence of the structural and superconducting properties on the growth conditions is of great interest [3]. This paper presents the preparation of Y-123 superconductors from a Y_2O_3, $BaCO_3$ and CuO mixture under different heat treatment conditions and the characteristics of prepared ceramics.

EXPERIMENTAL DETAILS

Ceramics samples were prepared by the solid state reaction method. Fine powders of Y_2O_3, $BaCO_3$ and CuO in appropriate proportions were thoroughly mixed and calcined in alumina crucibles in the atmosphere at 800-1100°C for a period of 16-100 hours with a heating rate of 2°C/min and a slow cooling. The samples were pressed into pellets form and then sintered at 930-1100°C for a period of 30-50 hours. The oxygenation annealing was realized at 500°C for 24 hours. The samples have been characterized by XRD, SEM and DTA-TGA techniques and through their electrical resistivities.

RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra for the samples calcined for a period of 30 hours at different temperatures. At 800°C (Figure 1a), XRD measurements reveal the formation of superconducting $YBa_2Cu_3O_{7-\delta}$ phase of which the proportion of its peaks is in the minority, the presence of the intermediate BaCuO2 phase as well as the starting products.

At 920°C (Figure 1b), the Y-123 phase appears clearly but with peaks of weak intensity, indicating that the superconducting phase is not well crystallized. At 990°C (Figure 1c), the intensities increase considerably, i.e. the crystallization and the stabilization of the Y-123 phase are well improved. The splitting of the peaks in 2θ = (32.65°, 32.90°) is explained by the increase of the oxygen content [4]. At 1100°C (Figure 1d), XRD spectrum shows that the amount of the Y-123 phase decreases enormously and the green Y_2BaCuO_5 phase appears with a majority proportion.

This phase results from the peritectic decomposition of the Y-123 phase in presence of CuO [5]. After sintering of products, in form of pellets, at 930°C, the texture is not observed (Figure 2a). On the contrary, at 960 - 990°C one notes an important texture according to the (00l) direction (Figure 2b, c). Besides, an oxygenation annealing carried out at 500°C for 24 hours improves the texture. However, the texture disappears at 1100°C (Figurec 2d).

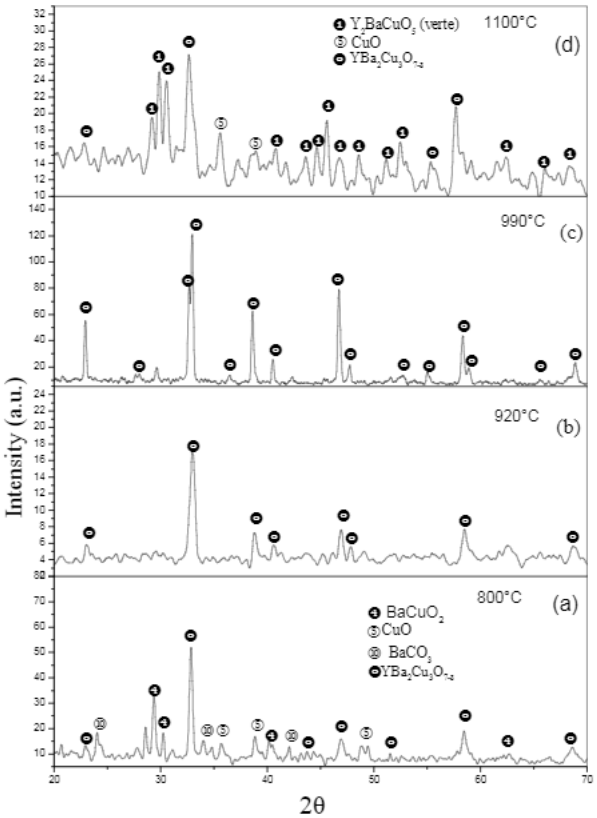

Figure 1: XRD patterns of the powders of the mixture ($BaCO_3$, Y_2O_3, CuO) calcined for 30 hours at 800 (a), 920 (b), 990 (c), 1100°C (d).

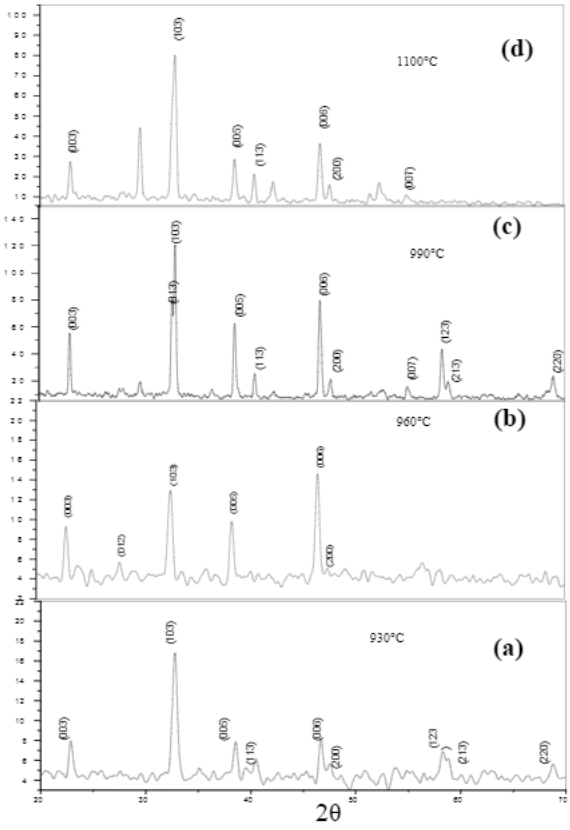

Figure 2: XRD patterns of Y-123 pellets sintered for 30 hours at 930 (a), 960 (b), 990 (c), 1100°C (d).

The Y-123 phase has been also made by use of $BaCuO_2$ and $Y_2Cu_2O_5$ as precursors, initially obtained by calcination of ($BaCO_3$, CuO) and (Y_2O_3, CuO) mixtures at 990°C for 16 hours respectively (Figure 3 a, b). The pellets of the $BaCuO_2$ and $Y_2Cu_2O_5$ mixture have been sintered at 990°C for of 100 hours (Figure 4). However, the Y-123 phase grains are not textured in this case. The dependence of the electrical resistivity on the temperature of the samples calcined at 940°C for 16 hours, sintered at 950°C for 50 hours (wa) and then oxygenated (sa) is shown in Figure 5. According to the Table, the critical Tc temperature of of (sa) sample is higher than that of (wa).The relatively high value of the transition ΔTc width in (sa) is attributed to the weak-links [6] and the non homogeneity of oxygen vacancies in this sample [7].

Table 1: Critical values obtained from electrical resistivity measurements.

Samples	Tc^{on}(K)	Tc^{off}(K)	Tc (K)	Δ Tc (K)
(sa)	97.2	87.3	92.3	9.9
(wa)	92.4	88.1	90.3	4.3

Fig. 6 shows a typical microstructure of samples sintered at 950°C for 50 hours after calcinations (951°C, 30hours). As can be seen, the grains growth, the size of which is ranging from 4 to 45 µm, is not uniform with

prevalence of flattened form and a notable reduction in porosity. The DTA curve of starting powders mixture (Figure 7a) shows the presence of two endothermic peaks at 810 and 895°C attributed to the $BaCO_3$ decomposition and the beginning of the superconducting Y-123 phase formation respectively.

The TGA analysis of the same mixture (Figure 7b) confirms the $BaCO_3$ decomposition by a loss o f mass at temperatures higher than 810°C. The results of thermal analysis are in good agreement with those of XRD.

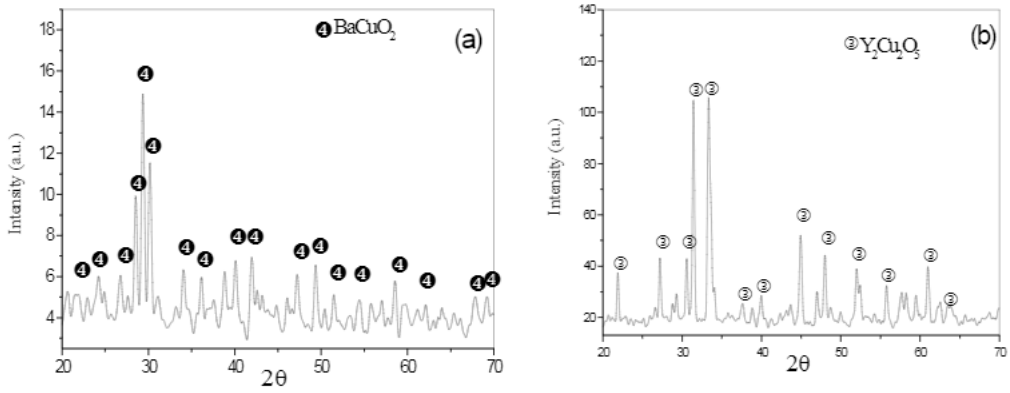

Figure 3: XRD patterns of the powders of mixtures ($BaCO_3$, CuO) (a) and (Y_2O_3, CuO) (b) calcined at 950°C for 16 hours.

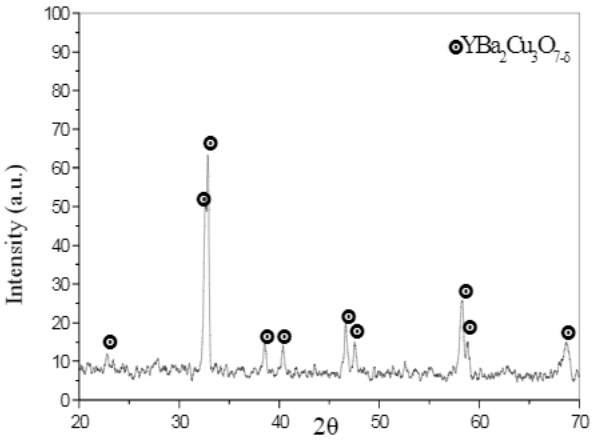

Figure 4: XRD patterns of pellets of the mixture $BaCuO_2$ and $Y_2Cu_2O_5$ sintered at 990°C for 100 hours.

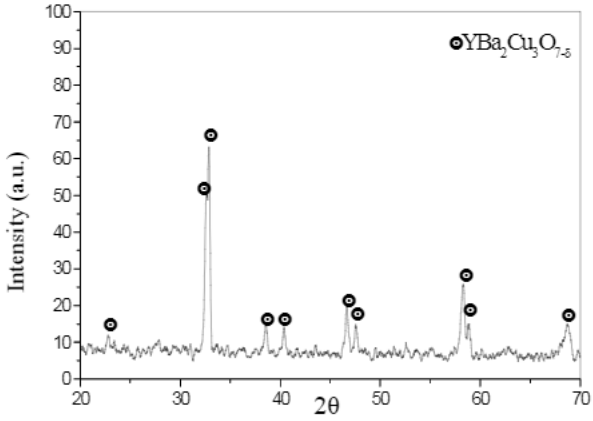

Figure 5: Temperature dependence of the electrical resistivity of samples calcined at 940°C for 16 hours, sintered at 950°C for 50 hours (wa) and then oxygenated at 500°C for 24 hours (sa).

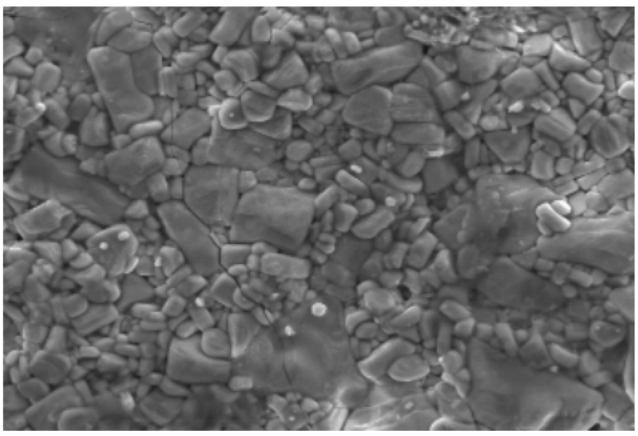

Figure 6 Typical SEM micrograph of pellets sintered at 950°C for 50 hours.

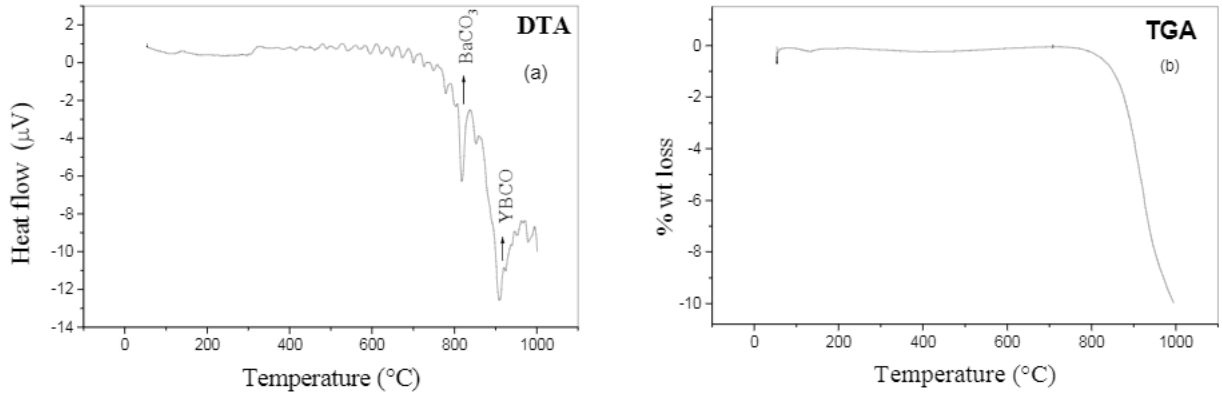

Figure 7: DTA (a) and TGA (b) curves of the powder of the mixture ($BaCO_3$, Y_2O_3, CuO).

CONCLUSION

The sintering in the atmosphere of calcined mixtures ($BaCO_3$, Y_2O_3 and CuO) at 950 - 990°C for 30 hours or ($BaCuO_2$ and $Y_2Cu_2O_5$) at 990°C for 100 hours leads to the formation of pure and well crystallized superconducting $YBa_2Cu_3O_{7-\delta}$ phase.

The sintering at 950 -990°C provides the texture of Y-123 grains according to the (00l) direction. The oxygenation annealing improves the texture.

The electrical resistivity measurements confirm the superconducting character of prepared samples with Tc=92.3K.

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