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Influence of High Pressures and Temperatures on the Behaviour of Bismuth-Based Superconductors

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Abstract

The present study demonstrates the possibility of preparing Bi-based SC-ceramics with almost theoretical density and high level of superconductive and mechanical properties in a short time by temperature treatment under high pressure conditions. It is shown that there is a P-T-τ-region where the 2223 phase content may be increased. The variation of unit cell volume of 2223 phase is also observed. The critical current density of the samples can be increased after the P–T–τ treatment by a factor of 25 times.

Die vorliegende Untersuchung zeigt, daß es möglich ist, in kurzer Zeit mittels Wärmebehandlung und hohem Druck auf Bi basierende SC-Keramiken mit nahezu der theoretischen Dichte und einem hohen Maß an supraleitenden und mechanischen Eigenschaften herzustellen. Die Existenz eines P–T–τ-Bereichs mit möglichem, erhöhtem 2223-Phasenanteil wird diskutiert. Weiterhin konnte die Veränderung des Volumens der Einheitszelle der 2223-Phase beobachtet werden. Der kritische Strom der Proben ließ sich nach der P–T–τ-Behandlung um einen Faktor 25 steigern.

Nous démontrons qu'il est possible de préparer des céramiques supraconductrices à base de Bi, approchant la densité théorique, possédant d'excellentes propriétes supraconductrices et mécaniques, ceci par un court traitement thermique à haute pression. Nous montrons qu'il y a un domaine de la courbe P–T–τ dans lequel la proportion de phase 2223 peut être augmentée. Nous avons aussi observé les variations du volume de la maille élémentaire de la phase 2223. Par un traitement P–T–τ on peut multiplier le courant critique par un facteur de 25.

Introduction

The present work deals with the study of effects of high pressures (0·5–5 GPa) and high temperatures (700–1000°C) on the structure, superconducting and mechanical properties of the high-temperature Bi–Pb–Sr–Ca–Cu–O superconductors.

In the previous investigations of high pressure and temperature effects on $YBa_2Cu_3O_{7-\delta}$ it was demonstrated that the structure of $YBa_2Cu_3O_7$ remains unchanged at treatment temperatures of ≈900°C (P = 2 GPa; τ = 2 h); the samples possessed nearly theoretical density and high values of microhardness, Young modulus; the superconductor critical temperature remained at a high level, i.e. T_c = 93 K, ΔT_c = 1·5 K.[1] By increasing treatment temperature it was possible to attain the $YBa_2Cu_3O_{7+\delta}$ phases which are superstoichiometric by oxygen.[2]

These interesting results obtained on Y-based superconducting (SC) ceramics have stimulated us to study the influence of the such treatment on Bi-based SC-ceramic materials.

It is now well established that the samples of Bi-based SC-ceramic materials sintered under normal pressure are characterized by low values of density and mechanical properties and, in addition, they fail to keep their initial form after the sintering.

The hot pressing technique[3] and the technique of intermediate high pressure treatment at room temperature[4] lead to densification of Bi SC-ceramics (up to 79% and 85% of theoretical as reported in Refs 4 and 3, respectively) with practically no decrease in the superconductor critical temperature (T_c) (85 K and 113–105 K in Refs 4 and 3, respectively) if compared to the starting samples. But the described processes are rather time-consuming (above 5 h[4] and above 102 h[3]).

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The present investigation shows that high pressure and temperature treatment results in higher content of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223 phase) in the samples which were prepared by the solid-phase synthesis and included two SC-phases $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223 phase) and $(Bi,Pb)_2Sr_2Ca_1Cu_2O_y$ (2212 phase).

It should be also noted that the starting samples containing both 2223 and 2212 phases and some amount of impurities (for the sample preparation the nominal composition of a starting mixture was chosen such that the only 2223 phase be produced) can transform into the single 2223 phase samples in a short time (several minutes) under the high pressure and temperature conditions. It may be recalled that an increase of the 2223 phase content in the samples in the case of solid phase synthesis will take dozens of hours. After temperature treatment under the high pressure conditions the samples also acquire density close to theoretical and high level of the mechanical properties (microhardness and Young's modulus). The critical current of the samples (at 77 K in zero magnetic field) can be increased after the P–T–τ treatment by a factor of 25 times.

2 Experimental

The high pressure, high temperature conditions were generated using the recessed-anvil-type apparatus (see detailed description in Ref. 2). The accuracy of the pressure measurements was ±0·15 GPa and that of the temperature measurements was ±20°C. The samples were heated at a rate of ≈1000°C/min and were cooled at a rate of ≈400°C/min.

Three types of starting samples produced by solid-phase synthesis were used: (1) samples containing mainly (85%) 2223 phase (the balance, 2212 phase and some amount of the complex calcium and copper oxides), sample density was 2·9 g/cm^3; (2) with the prevailing content (70%) of 2212 phase (the balance, 2223 phase and some amount of the complex calcium and copper oxides), sample density was 4·8 g/cm^3; (3) with the content ratio of 2223 to 2212 phase being ≈1:1; sample density was 4·8 g/cm.^{3}

Lattice parameters and phase composition were determined with the automated X-ray diffractometer and scanning electron microscope Superprobe 733 (JEOL, Japan).

Density of the samples was measured by using the hydrostatic weighing.

The Vickers microhardness under a load of 4·91 N was measured by the microhardness tester Matsuzawa Mod. MXT 70 (indentation size exceeds greatly that of grain). The Young's modulus and microhardness under a load of 0·05 N were determined by mechanical microanalyser Nano-indenter 11—Nano Instrument Inc. (USA) (rate of loading was 3 mN/s; the depth of the Berkovich indentation was recorded as a function of load; the depth resolution was 0·04 nm; the load resolution was 10^{-5} g; the device measured the hardness under loading and the Young modulus (from the unloading curve); the dimensions of the indentation is below grain size.

The critical temperature T_c was measured by a four-probe technique at a current through the sample of 100 mA and the critical current J_c was measured by a pulse method.[5]

3 Results and discussion

Tables 1 and 2 give the experimental results showing the influence of the P–T–τ treatment on the unit cell parameters and behaviour of the ceramic samples of the Bi–Pb–Sr–Ca–Cu–O system.

The X-ray diffraction study shows that there is a P–T–τ-region where the content of 2223 phase increases (both for the type 1 and 2 starting samples). The starting samples of type 1 (with the prevailing content of 2223 phase) can be transformed into the single 2223 phase samples under high pressure and temperature conditions in a comparatively short time (Fig. 1). The 2223 phase content increases most intensively at temperatures ≈750°C. With a temperature rise above 750°C the opposite tendency takes place; i.e. the 2223 phase content decreases and the 2212 phase content increases. At temperatures of ≈800°C there is no 2223 phase in the samples. At ≈1000°C the decomposition of the 2212 phase is observed. In the case of lower pressures, e.g. 0·5 GPa, the decomposition with the formation of $Bi_2Sr_2CuO_x$ (2201 phase) takes place. When the starting samples of type 3 were used (the content ratio of 2223 to 2212 phase was ≈1:1) the homogenization effect was not pronounced.

The results summarized in Table 1 show the unit cell parameters in the samples prior to and after the P–T–τ treatment. In addition, the more portion of 2212 phase transforms into 2223 phase, the greater is the variation in the unit lattice volume (ΔV). The pressure and loading time also contribute to ΔV. For example, ΔV = 1·6 Å^3 at P = 2 GPa and τ = 20 min, but ΔV = 1 Å^3 at P = 1 GPa and τ = 30 min. Thus, the unit cell volume increases with pressure and holding time. This V variation may be attributed to the filling of possible cation vacancies or to the substitution of Sr atoms for Ca atoms.

Table 1. Unit cell parameters of the samples before and after treatment

Sample No.	*Treatment conditions*			*Unit cell parameters*[a] *(Å)*				*Sample type*
	P(GPa)	*T(°C)*	*τ (min)*	*2223 phase*		*2212 phase*		
				$\frac{a_s}{a_t}$	$\frac{c_s}{c_t}$	$\frac{a_s}{a_t}$	$\frac{c_s}{c_t}$	
1[b]	0·5	750	15·0	5·412 5·416	37·06 37·12	— —	— —	1
2	1·0	750	15·0	5·40 5·42	37·04 37·15	5·40 5·42	30·69 30·70	1
3	1·0	750	30·0	5·412 5·429	37·12 37·20	5·412 —	30·76 —	1
4	1·0	800	15·0	5·41 5·42	37·07 37·16	— —	30·74 —	1
5	2·0	700	5·0	5·42 5·417	37·09 37·15	5·42 —	— —	1
6	2·0	700	15·0	5·409 5·413	37·07 37·14	5·409 —	30·72 —	1
7	2·0	750	5·0	5·405 5·432	37·09 37·15	— —	30·76 —	1
8	2·0	750	12·5	5·40 5·42	37·09 37·12	5·40 5·42	30·76 30·67	1
9	2·0	750	15·0	5·409 5·400	37·07 37·09	— —	30·73 —	1
10	2·0	750	20·0	5·399 5·422	37·04 37·15	— —	30·69 —	1
11	2·0	750	30·0	5·415 5·417	37·13 37·18	— —	30·78 —	1
12	2·0	750	120·0	5·412 5·436	37·07 37·07	— —	— —	1
13	5·0	750	15·0	— 5·404	— 37·07	— —	— —	1
14	1·0	750	30·0	— —	— —	5·404 5·404	30·72 30·69	2
15	1·0	800	15·0	— —	— —	5·412 5·404	30·74 30·73	2
16	2·0	700	5·0	— —	— —	5·411 5·414	30·75 30·67	2
17	2·0	750	15·0	— —	— —	5·42 5·40	30·76 30·62	2
18	2·0	900	5·0	— —	— —	5·412 5·509	30·72 30·76	2
19	2·0	750	15·0	— —	— 37·18	— 5·405	— 30·68	3

[a] a_s, c_s and a_t, c_t: unit cell parameters of the starting and treated samples, respectively.
[b] The 2201 phase appeared in the sample.

Under high pressures and temperatures the transformation of 2212 phase into 2223 phase occurs through the formation of an amorphous phase. The presence of the amorphous phase is defined from the increase of the X-ray diffraction pattern phone in the 20–40° 2θ region (Fig. 1b). At the first stage some amount of 2212-phase passes into amorphous state and then (a) this amorphous phase may recrystallize into 2223 phase and complex (Bi, Sr, Cu) oxides or (b) the amorphous phase and the complex oxides (which were formed in the starting samples) may recrystallize into 2223 phase.

The T_c values of the samples (Table 2) varied with treatment parameters. In the case of samples of type 2 one can observe the narrowing of superconductive transition interval ΔT_c (T_{c2} increases by ≈ 14 K, but some decrease of T_{c1} also takes place). The T_c variation may be attributed to (a) the phase transitions, (b) the variations in the cation composition, or (c) the presence of an amorphous phase (probably at the grain bound-

Table 2. Superconductor critical temperatures (T_c), microhardness (H) and Young's modulus (E) of the samples obtained under different treatment conditions

Sample no.	*Treatment conditions*			*T_{c1} (K)*	*T_{c2} (K)*	*H (GPa)*		*E (GPa) at 0·05 N*	*Sample type*
	P (GPa)	*T (°C)*	*τ (min)*			*Vickers at 4·91 N*	*Berkovich at 0·05 N*		
1		Starting		115	102	0·02	—	—	1
2	1·0	750	5	96	73	—	—	—	1
3	1·0	750	15	107	98	1·52	3·0	84	1
4	1·0	750	30	110	93	—	—	—	1
5	2·0	750	5	108	88	—	—	—	1
6	2·0	750	15	114	101	—	—	—	1
7	2·0	750	20	—	—	1·52	3·8	111	1
8	2·0	750	120	105	88	1·66	3·5	89	1
9	2·0	800	5	86	46	—	—	—	1
10	5·0	750	15	115	90	—	—	—	1
11		Starting		115	65	—	—	—	2
12	1·0	750	30	92	79	—	—	—	2
13	2·0	750	15	105	79	—	—	—	2

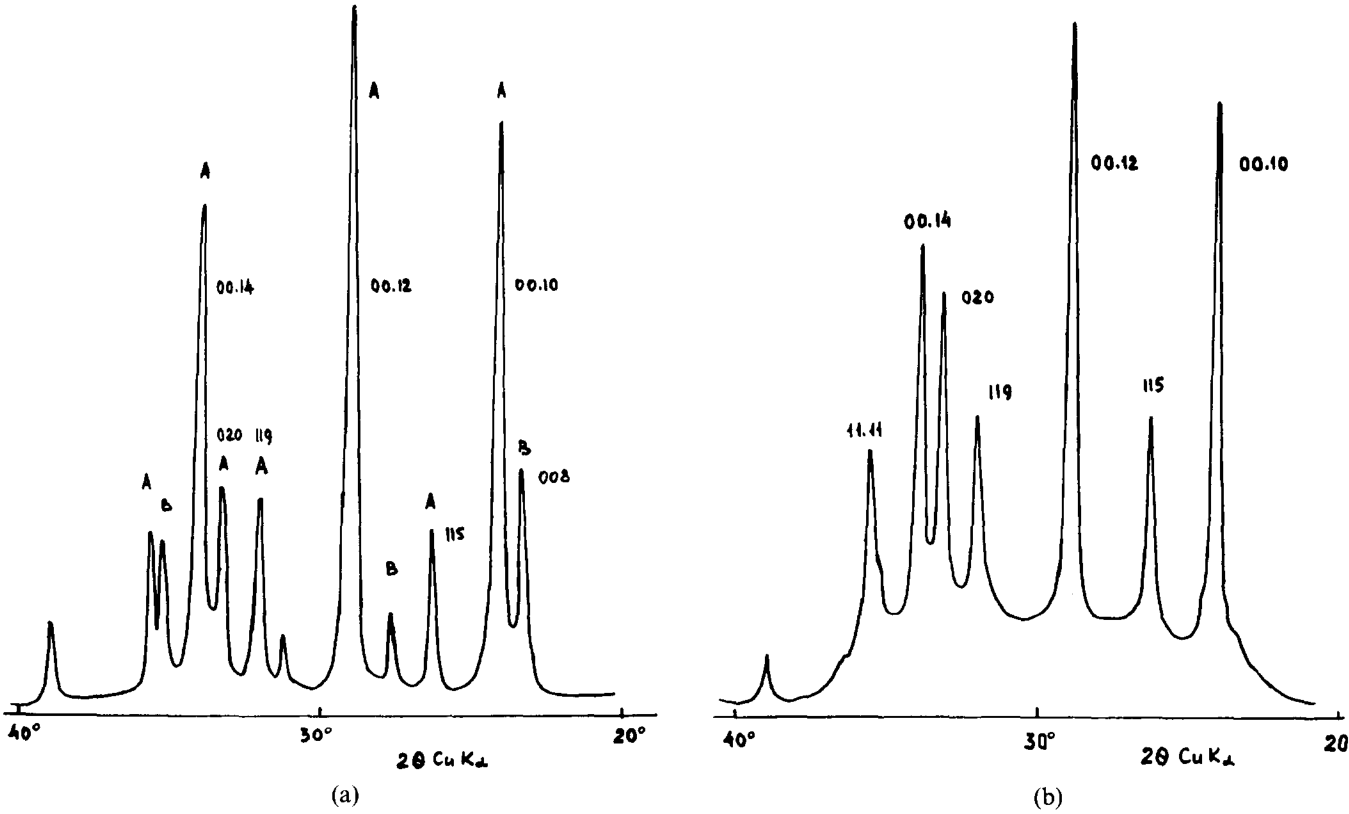
aries) which did not manage to recrystallize into 2223 or 2212 phase for a given time period.

The J_c value of starting sample of type 1 at 77 K in zero magnetic field was 40 A/cm^2 and of the treated one (No. 6, see Table 2) was 1000 A/cm^2.

After temperature treatment under the high pressure conditions the samples attain almost theoretical density (≈99%) and high level of mechanical properties, such as microhardness and Young's modulus (Table 2). We could not obtain values of Berkovich microhardness and Young's modulus of the starting samples because of their high porosity. The different values of Vickers and Berkovich microhardness of the same treated sample may be explained as follows: (a) as a rule, the microhardness increases with decreasing load; (b) the microhardness measured with the Berkovich indenter is usually higher than that measured with the Vickers indenter; (c) the microhardness at 4·91 N is the integral characteristic of the sample because the indenter size exceeds greatly that of a grain and the impurity grains can also lie in the region of the indentation.

4 Conclusions

(1) As a result of pressure and temperature treatment, Bi-based SC ceramics can combine almost



(a) (b)

Fig. 1. The diffraction pattern of type 1 initial sample (a) before and (b) after treatment. A, the 2223 phase; B, the 2212 phase.

theoretical density, high superconducting and mechanical properties. The critical current of the samples after the high pressure–high temperature treatment can be increased.

(2) The variation of 2223 and 2212 phase content with treatment parameters and, particularly, the possibility of increasing 2223 phase content in a short time are of undoubted interest. The recrystallization proceeds through the amorphous phase formation.

(3) High pressure and temperature treatment results in the increase of the unit cell volume of 2223 phase. The more portion of 2212 phase transforms into 2223 phase the greater is the variation in unit cell volume. Unit cell volume increases with pressure and holding time.

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