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Structure and crystallization behaviour of amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ high-temperature superconductor material

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Pb-doped Bi–Sr–Ca–Cu–O superconductor materials are of great technological importance because of their high superconducting transition temperatures (T_c) [1]. Although most of the Pb escapes during sintering of these Pb-doped materials [2, 3], additions of Pb are necessary to produce high-T_c Bi–Sr–Ca–Cu–O superconducting compounds. The solid-state reaction method is usually used for the preparation of superconducting materials on the basis of this quinary system [1–3]. However, in recent years the method of crystallization from the amorphous materials (obtained by rapidly quenching the melts) with subsequent heat-treatment of the crystallized product has led to homogeneous good-quality Bi–Sr–Ca–Cu–O superconducting materials ([4, 5] and references cited therein). In order to understand the crystallization kinetics, the crystallization behaviour of these amorphous materials was investigated by a continuous heating–cooling process, as is the case for the dynamic temperature X-ray diffraction (DTXD) [6] and differential thermal analysis (DTA) methods. Results are reported for the $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ compound ($0 < x < 1$).

About 20 g of a mixture of $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$, containing appropriate amounts of the starting materials Bi_2O_3, PbO_2, $SrCO_3$, $CaCO_3$ and CuO, was thoroughly mixed in a planetary agate mortar using ethanol as lubricant. The dried mixture was fired at 1025 ± 5 K in air for 2 h in alumina crucibles in a muffle furnace. The product was ground in a hand agate mortar and heated at 1075 ± 5 K for 16 h in the same way as above. The last treatment was repeated two or three times in order to ensure homogeneity. The final product was ground and melted in Pt crucibles in air in a muffle furnace at 1350–1375 K. The viscous melt was quenched in air by squeezing it between two rapidly rotating Cu rollers (each about 5 cm in diameter and 10 cm in length) in contact with each other. In this way thin flakes (about 10–30 mm long, 5–15 mm wide and 40–100 μm thick) were obtained, which were found to be X-ray amorphous. Microanalysis and X-ray fluorescence analysis showed that more than half of the total weighed amount of Pb was lost during the whole preparation process.

For room-temperature X-ray diffraction analysis, an Enraf–Nonius Guinier camera was used. High-temperature X-ray diffraction analysis was carried out in a dynamic vacuum of 10^{-1}–10^{-4} Pa at a heating rate of 50 K h^{-1} by DTXD [6], using CuK_α radiation. It should be mentioned that due to continuity of the diffraction lines along the ordinate in a DTXD pattern, even minute details become visible. X-ray diffraction intensities were measured by a modified microcomputer-controlled Zeiss–Jena MD100 microdensitometer. Thermal anomalies corresponding to structural changes detected in the DTXD pattern were recorded by a modified DTA instrument using Pt crucibles and under conditions similar to those in the DTXD method.

The rapidly quenched $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ ($0 < x < 1$) material was found to be amorphous by X-ray diffraction methods, characterized by the presence of three diffraction haloes in its X-ray diffraction pattern, however with intensity sequence weak, strong and weak (Figs 1 and 2) in contrast with the Fraunhofer diffraction haloes (having intensity sequence very strong, very weak and very very weak) expected for the conventional Bernal-type amorphous solids [7, 8]. Similar X-ray diffraction results have been reported for amorphous Mg–Zn alloys [9]. The weighted averages of these three diffraction haloes could be indexed by means of conventional crystallography on the basis of a perovskite-type cubic unit cell with lattice parameter $a = 0.426(3)$ nm (Fig. 2 and Table I), implying that this amorphous material was not of the Bernal-type, but must have consisted of microcrystals 10–15 unit cells (of the perovskite-type) in size as calculated from the breadth of the diffraction haloes using the Scherrer formula [10]. The X-ray diffraction pattern reported by Chaudhuri *et al.* [5] for the amorphous Bi–Sr–Ca–Cu-oxides has also been found to contain three diffraction haloes with the same intensity sequence as found for the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ compound in this work.

The weak, sharp X-ray diffraction lines (marked with q in Fig. 1) were due to some unreacted CaO in the sample. These X-ray diffraction lines were always detected for these amorphous materials at high cooling rates without, however, having any influence on the shape or size of the intensity sequence of the diffraction haloes due to the amorphous state of these materials.

Dynamic temperature crystallization, i.e. crystallization upon continuously varying temperature as is the case during continuously heating–cooling in DTXD or DTA, revealed that this amorphous material crystallizes at 685 ± 2 K (Figs 1 and 3). The crystal structure of the first product of crystallization was highly distorted, as is seen from the broadness of

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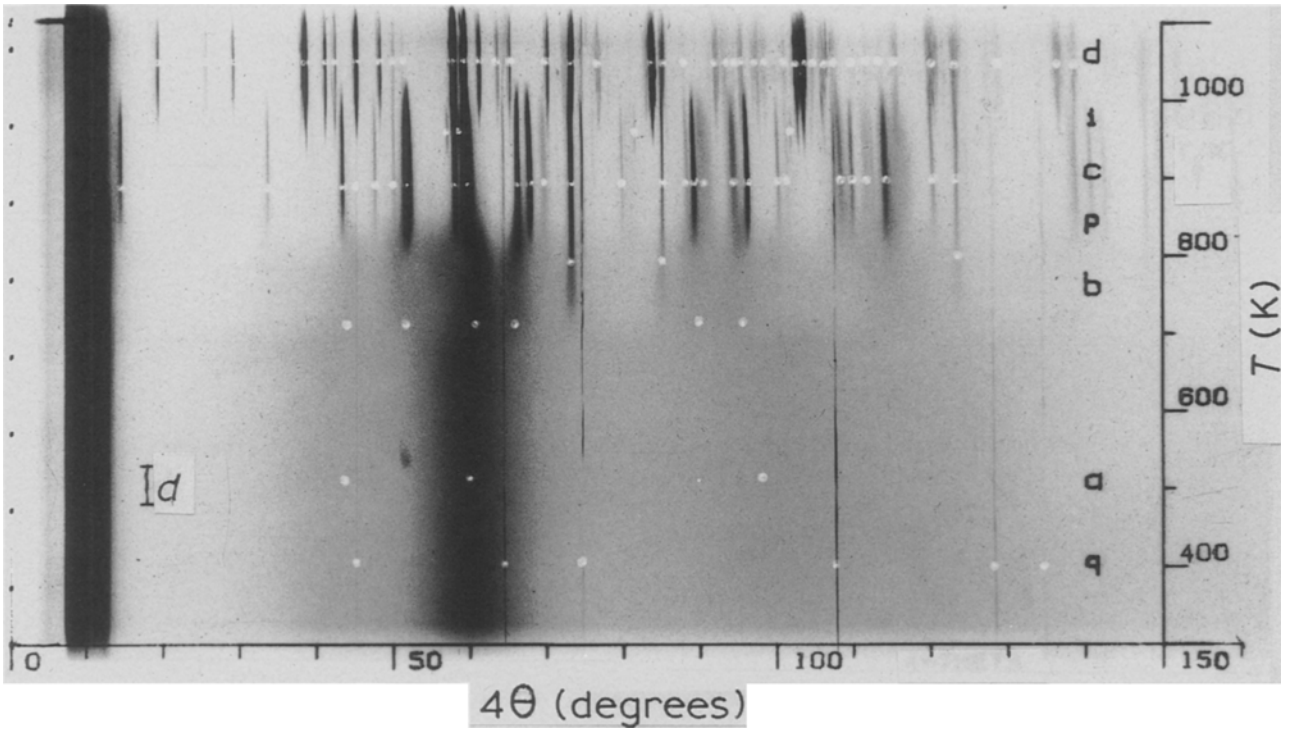

Figure 1 DTXD pattern of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ flakes (CuK_α radiation, 30 kV and 40 mA) taken at a heating rate of 50 K h^{-1} in a dynamic vacuum of 10^{-4} Pa. X-ray diffraction lines marked with white dots on a horizontal line belong to the phase designated by lower case letters on the right (explained in the text). Black dots along the ordinate on the left are the primary beam marks 100 °C apart. The slit width is given by *d* on the left.

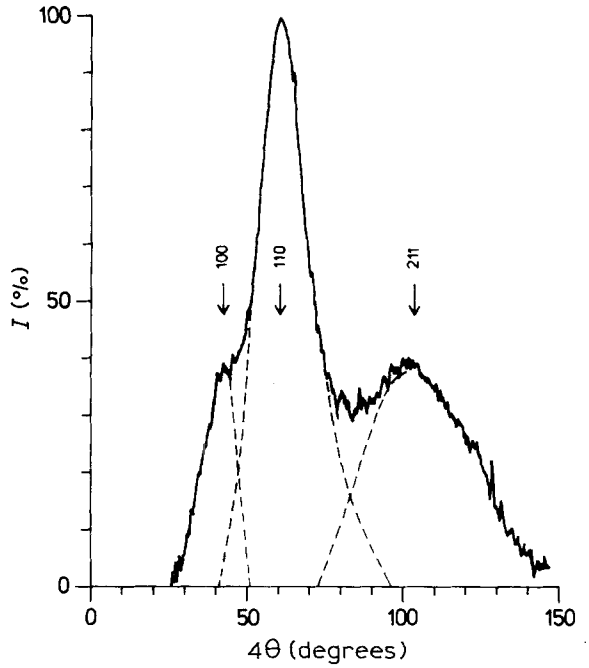

Figure 2 Microdensitometer scan at 400 K of the DTXD pattern shown in Fig. 1. The Miller indices (*h k l*) are based on a perovskite-type cubic unit cell.

TABLE I Structure data (at room temperature) of the amorphous phase marked a in Fig. 1. System, cubic of the perovskite-type; lattice parameter, $a = 0.426(4)$ nm; remark, since the corresponding X-ray diffraction lines were extraordinarily broad (Fig. 2), weighted averages of these lines are given here

h k l	$\sin^2\theta_0$	$\sin^2\theta_c$	I_0 (%)
1 0 0	0.0332	0.0326	20
1 1 0	0.0659	0.0652	100
2 1 1	0.1956	0.1956	30

the corresponding X-ray diffraction lines (marked b in Fig. 1) and was found to be of the 2.4 nm Bi-based superconducting compound type (Table II). At slightly higher temperature (i.e. at 693–695 K) a perovskite-type compound having lattice parameter $a = 0.427(7)$ nm formed (p in Fig. 1, Table III). At about 825 K the material recrystallized and the regular 2.4 nm Bi-based superconducting compound formed (c in Fig. 1), which decomposed at about 1020 K. However, shortly before the 2.4 nm Bi-based phase decomposed a new unstable phase (marked i in Fig. 1) was found to form at about 925 K. Finally, a new tetragonal phase with lattice parameters $a = 0.7255(9)$ nm and $c = 7.363(5)$ nm (marked d in Fig. 1, Table IV) formed at about 978 K. The corresponding thermal reaction was found to be endothermic by DTA and existed over a wide temperature range of 978–1020 K (Fig. 3). This reaction could be attributed to loss of oxygen because DTA and DTXD were carried out in dynamic vacuum (i.e. evacuating the sample chamber continuously) at a low heating rate (50 K h^{-1}).

Although this material has been found to melt at about 1063 K (as is seen from the DTA curve in Fig. 3 and diffuseness of some corresponding X-ray diffraction lines in Fig. 1), the X-ray diffraction lines remained extremely sharp up to 1115 K, i.e. about 50 K above the melting temperature (Fig. 1), implying that a well-defined long-range crystalline order corresponding to the phase (marked d in Fig. 1) must exist in the melt of this material. The melt solidified at about 1043 K upon cooling, giving rise to a broad exothermic peak (Fig. 3).

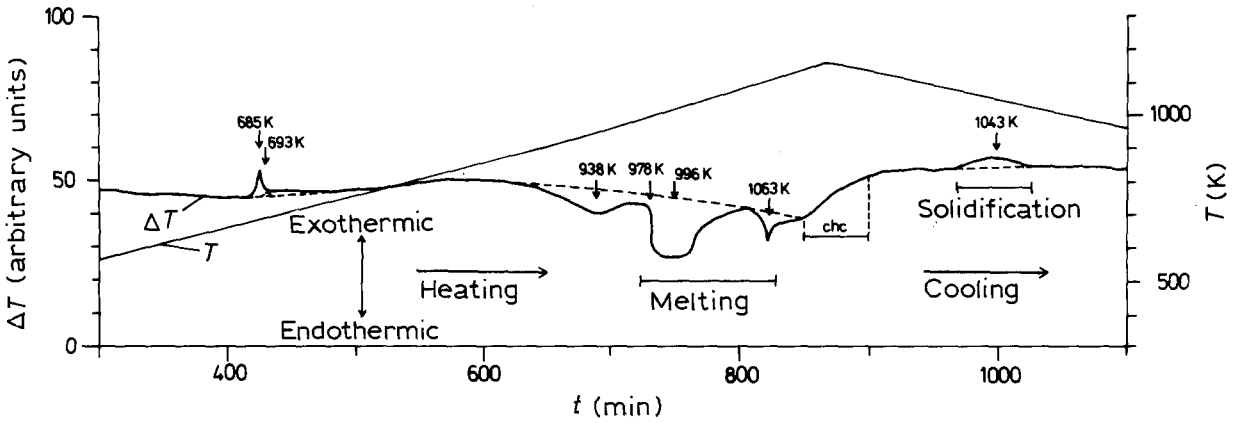

Figure 3 DTA analysis of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ compound. chc, Change-over from heating to cooling.

TABLE II Structure data (at about 730 K) of the phase marked b in Fig. 1. System, tetragonal; lattice parameters, a = 0.4967(8) nm, c = 2.456(6) nm, c/a = 4.492(6)

$h\,k\,l$	$\sin^2\theta_0$	$\sin^2\theta_C$	I_0 (%)
0 0 6	0.0364	0.0355	10
1 0 4		0.0356	
1 1 3	0.0478	0.0486	10
1 0 7	0.0681	0.0681	100
2 0 0	0.0795	0.0795	20
0 0 10	0.0981	0.0985	30
0 0 12	0.1418	0.1418	10
1 1 11	0.1590	0.1589	10
2 0 0		0.1590	

TABLE III Structure data (at about 750 K) of the phase marked p in Fig. 1. System, cubic of the perovskite-type; lattice parameter, a = 0.4271 (7) nm; remark, note that only fcc-type reflexes have so far been detected

$h\,k\,l$	$\sin^2\theta_0$	$\sin^2\theta_c$	I_0 (%)
1 1 1	0.0986	0.0986	100
2 0 0	0.1314	0.1315	50
2 2 0	0.2630	0.2630	20
3 1 1	0.3618	0.3616	10

TABLE IV Structure data (at about 1075 K) of the phase marked d in Fig. 1. System, tetragonal; lattice parameters, a = 0.7255(9) nm, c = 7.363(5) nm, c/a = 10.14(8)

$h\,k\,l$	$\sin^2\theta_0$	$\sin^2\theta_c$	I_0 (%)
0 0 8	0.0069	0.0070	50
0 1 3	0.0123	0.0123	30
0 0 12	0.0159	0.0158	40
1 1 7	0.0278	0.0279	80
0 0 16		0.0281	
1 1 9	0.0317	0.0315	50
1 1 10	0.0338	0.0335	40
1 1 12	0.0381	0.0384	75
0 1 17	0.0432	0.0430	40
0 0 20		0.0438	
1 0 18	0.0465	0.0468	10
2 0 4		0.0469	
2 0 6	0.0487	0.0491	5
2 1 7	0.0621	0.0618	100
1 1 9		0.0621	
1 0 22	0.0648	0.0643	80
2 1 9		0.0653	
0 1 23	0.0692	0.0693	50
2 1 11		0.0697	

TABLE IV Cont.

0 0 26	0.0745	0.0741	30
1 0 24		0.0744	
2 1 13	0.0761	0.0750	5
1 1 22		0.0756	
1 2 14	0.0782	0.0779	30
2 2 0	0.0903	0.0903	50
2 1 19	0.0955	0.0960	5
2 0 27	0.0981	0.0982	60
0 0 30		0.0986	
2 2 10	0.1013	0.1013	50
0 3 3	0.1028	0.1026	5
0 3 7	0.1071	0.1070	20
0 3 15	0.1267	0.1262	60
0 0 34		0.1267	
1 2 26	0.1306	0.1305	50
0 1 33		0.1306	
3 2 6	0.1514	0.1507	20
2 3 7		0.1521	
2 3 9	0.1558	0.1556	5
2 1 31	0.1622	0.1618	10
3 2 12		0.1625	
3 2 14	0.1680	0.1682	<5
1 2 32	0.1690	0.1687	5
2 0 34	0.1720	0.1719	<5
4 0 0	0.1806	0.1806	<5
2 3 19	0.1860	0.1863	60
2 2 30	0.1894	0.1889	60
1 4 4	0.1939	0.1936	<5
0 3 29		0.1938	
4 1 7	0.1977	0.1973	20
1 1 40		0.1979	
2 2 32	0.2026	0.2025	20
1 4 10		0.2028	
1 0 44	0.2244	0.2235	5
4 0 20		0.2244	
4 1 19	0.2314	0.2315	20
2 2 38	0.2489	0.2486	30
4 1 25	0.2605	0.2604	20
3 0 40	0.2769	0.2770	5
2 0 46		0.2771	
5 0 2	0.2828	0.2826	5
3 3 27		0.2831	
5 1 9	0.3026	0.3024	<5
2 2 44		0.3025	
5 1 13	0.3127	0.3120	50
2 3 39		0.3134	
0 5 19	0.3216	0.3218	30
3 2 40		0.3221	
4 1 39	0.3588	0.3586	5
2 5 17		0.3590	

From the above discussion it follows that the dynamic temperature crystallization behaviour of amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ is quite complex. A number of metastable or unstable phases form up to the melting temperature. There is strong evidence for the existence of a long-range crystalline order in the liquid state of this type of materials. No Bernal-type structure was found for amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ solid.

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