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Synthesis and analysis of PbO-modified Bi–Sr–Ca–Cu–O superconductors

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High T_c superconducting materials based on a PbO-modified Bi–Sr–Ca–Cu–O system with various ratios between the oxides were prepared by calcination at 800 °C and firing at 855 °C. From X-ray powder diffraction analysis data, the ratio of low- and high-temperature phases was calculated. The material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ was chosen for further experimental work. Samples fired at 800 °C contain mostly the low-temperature phase (2212). Higher firing temperatures lead to the formation of the high T_c phase (2223) with T_c ($R = 0$) over 100 K. Some samples were cold pressed and refired which increased the specific density to over 80% of the theoretical density. The composition of samples was investigated by X-ray powder diffraction analysis and by energy dispersive X-ray spectroscopy. The main phase in the material fired at 800 °C, is the low T_c phase 2212, and secondary phases are Ca_2PbO_4, unreacted CuO and traces of 2223 phase. At higher firing temperatures, the main phase is the high-temperature phase 2223. The material is still heterogeneous and contains Ca_2PbO_4.

1. Introduction

Maeda *et al.* [1] reported the synthesis of ceramic superconductors in the Bi–Sr–Ca–Cu–O system with T_c (onset) between 110 and 120 K. Two superconducting phases were reported in the system: a low T_c phase $Bi_2Sr_2CaCo_2O_x$ (2212) with $T_c = 85$ K, and a high T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$ (2223) with T_c between 110 and 120 K [2, 3]. Data in the literature indicate that it is very difficult to synthesize "pure" 2223 phase; after firing, mixtures of superconducting and non-superconducting phases are obtained [4, 5]. However, it is known that a partial exchange of Bi_2O_3 with PbO assists the formation of high T_c phase [6]. Also, long firing times and a narrow temperature "window" are needed to obtain high concentrations of the high T_c phase [7, 8]. According to the published results, a slight excess of SrO and CuO is also helpful to the formation of high T_c phase [9].

High T_c superconducting materials based on the PbO-modified Bi–Sr–Ca–Cu–O system with different compositions were prepared. The ratio between the high and low T_c phases were determined. The material with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ was chosen for further experimental work. Some samples were cold pressed to obtain a textured microstructure which, according to the literature, increases critical current densities [10]. The microstructures of samples were investigated and analysed by SEM and energy dispersive X-ray spectroscopy (EDS). For the identification of superconducting and non-superconducting phases, X-ray powder diffraction analysis (XRD) was used. The influence of the preparation conditions on the composition of the phases in the samples was determined.

2. Experimental procedure

A superconducting material of varying composition was prepared from Bi_2O_3 (99.9%, Merck), PbO (99.9%, Ventron), $SrCO_3$ (99%, BDH Chemicals), $CaCO_3$ (99%, Merck) and CuO (ASC, Ventron). Oxides and carbonates were mixed in isopropyl alcohol, pressed into pellets and calcined for 30 h (with intermediate grinding) at 800 °C. After calcination, the material was fired for 150 h at 855 °C. The heating rate was $300\ \mathrm{K\,h^{-1}}$ and the cooling rate was $60\ \mathrm{K\,h^{-1}}$. Some pellets of the material with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ were cold pressed at 280 MPa. After cold pressing, the pellets were fired again for 15 h at 855 °C. The specific density of cold-pressed samples was $5.34\ \mathrm{g\,cm^{-3}}$ (82% theoretical density), while the specific density of as fired samples was only $3.47\ \mathrm{g\,cm^{-3}}$ (53% theoretical density). The low density of as fired samples is due to the anisotropic growth of randomly oriented plate-like 2223 crystals, resulting in swelling of the material [11].

The Meissner effect (the levitation of a superconducting pellet over a magnet in liquid nitrogen) was checked and the resistivity versus temperature was measured by the four-probe technique. The presence of superconducting and non-superconducting phases was determined by X-ray powder diffraction analysis. The ratio of low- and high-temperature phases was calculated from the ratio of the intensities of the 2223 (0 0 12) and 2212 (1 1 5) reflections [12]. Microstructures of fractured and polished samples with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ were investigated by SEM. The material was analysed on a Jeol JXA-840A electron probe microanalyser by EDS. The TRACOR MICROQ program using multiple least squares analysis and ZAF correction procedures was used. Samples were analysed under the following conditions: accelerating voltage 25 kV, probe current 250 pA, spectra acquisition time 100 s.

Standards of the elements analysed with their characteristic peaks and energy regions are given in Table I.

3. Results and discussion

The nominal composition of the samples is shown in Table II. In most samples the ratio between bismuth and lead oxide was fixed (20 mol % Bi_2O_3 is exchanged for PbO), while the concentrations of SrO, CaO and CuO were varied. Sample "H" is unleaded with 2223 composition. The results of X-ray diffraction analysis, i.e. main and secondary phases, and the ratio between the low- (2212) and high- (2223) temperature phases, calculated from X-ray spectra, are presented in Table III.

T_c (onset), T_c ($R = 0$) and the Meissner effect for samples with different nominal compositions are presented in Table IV. Resistivity versus temperature diagrams are shown in Figs 1 (samples A and C), 2 (samples E, F and G) and 3 (samples B, D and H).

TABLE I Standards

Standard	Element	Region of interest (keV)
Bi_2O_3	BiL_α	10.20–11.47
PbO	PbL_α	9.96–11.07
$SrTiO_3$	SrL_α	1.51– 2.00
$CaTiO_3$	CaK_α	3.38– 4.27
CuO	CuK_α	7.45– 9.45

TABLE II Nominal compositions of superconducting materials

Sample	Nominal composition				
	Bi	Pb	Sr	Ca	Cu
A	2	0.5	2	2	3
B	2	0.5	2	2	3.5
C	2	0.5	2	2.5	3.5
D	2	0.5	2	3	3.5
E	2	0.5	2	2.5	3
F	2	0.5	2	2.5	4
G	2	0.5	2.5	2.5	3.5
H	2	–	2	2	3

TABLE III Summarized results of X-ray diffraction analysis of superconductors with different nominal compositions, calcined at 800 °C and fired at 855 °C (150 h)

Sample	"Main" phases	"Secondary" phases	Ratio 2223:2212
A	2223	2212, Ca_2PbO_4	70:30
B	2223	2212, Ca_2PbO_4	75:25
C	2223	2212, Ca_2PbO_4	95:5
D	2223	2212, Ca_2PbO_4	75:25
E	2223, 2212	Ca_2PbO_4	50:50
F	2223	2212, Ca_2PbO_4	80:20
G	2212	2223, Ca_2PbO_4	30:70
H	2212	–	–

TABLE IV Superconducting characteristics of samples with different nominal compositions calcined at 800 °C and fired at 855 °C (150 h)

Sample	T_c (onset) (K)	T_c ($R = 0$) (K)	Meissner effect
A	118	96	Yes
B	118	94	Yes
C	115	107	Yes
D	118	98	Yes
E	119	110	Yes
F	119	102	Yes
G	118	105	No
H	100	70[a]	No

[a] Extrapolated.

All PbO-containing samples have T_c (onset) between 115 and 120 K. The results of X-ray diffraction analysis (Table III) show the presence of high-temperature 2223 phase in all samples with the exception of the sample H, which was not doped with PbO. The concentration of 2223 phase was highest in sample C with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ (Bi/Pb/Sr/Ca/Cu 2/0.5/2/2.5/3.5). This material, which was chosen for further study, also has a "smooth" resistivity versus temperature dependence (Fig. 1) indicating that the 2223 phase is continuous throughout the material. Resistivity versus temperature curves of the other samples indicate a significant influence of the 2212 phase, as implied by the bend in the curves (Figs 1–3).

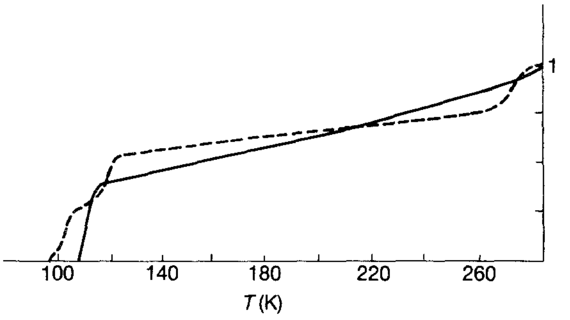


Figure 1 Resistivity versus temperature for superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3O_x$ (– – –, sample A) and $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ (——, sample C), fired at 855 °C.

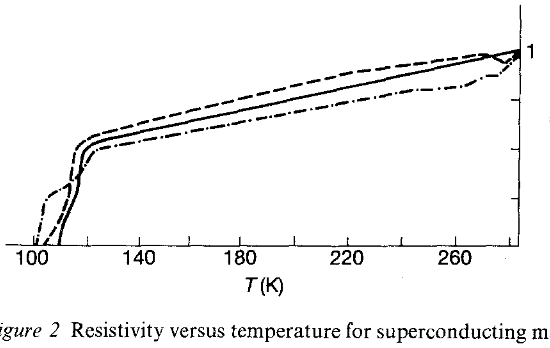


Figure 2 Resistivity versus temperature for superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_3O_x$ (——, sample E), $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_4O_x$ (—·—, sample F) and $Bi_2Pb_{0.5}Sr_{2.5}Ca_{2.5}Cu_{3.5}O_x$ (– – –, sample G), fired at 855 °C.

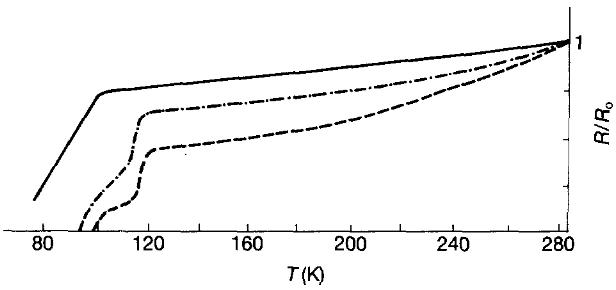


Figure 3 Resistivity versus temperature for superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_2Cu_{3.5}O_x$ (—·—, sample B), $Bi_2Pb_{0.5}Sr_2Ca_3Cu_{3.5}O_x$ (– – –, sample D) and $Bi_2Sr_2Ca_2Cu_3O_x$ (——, sample H), fired at 855 °C.

T_c (onset) and T_c ($R = 0$) of the superconducting material with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$ are presented in Table V. Samples fired at 855 °C were first calcined for 30 h at 800 °C.

Samples fired at 800 °C contain mostly the low-temperature phase, as can be seen from the T_c (onset) at 80 K. No Meissner effect was observed and the zero resistivity temperature was around 65 K. Higher firing temperatures lead to the formation of the high T_c phase, as shown by the increasing values of T_c (onset) to 115 K and T_c ($R = 0$) above 105 K for samples fired at 855 °C and for cold-pressed samples.

X-ray diffractograms of superconducting material, prepared under different conditions, are shown in Figs 4 (800 °C) and 5 (855 °C). The results of X-ray diffraction analysis are summarized in Table VI.

TABLE V T_c (onset) and T_c ($R = 0$) of superconductors with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$

Firing conditions		Meissner effect	T_c (onset) (K)	T_c ($R = 0$) (K)
(°C)	(h)			
800	30	No	80	65[a]
855	150	Yes	115	107
855	150	Yes	117	107
Cold pressed				

[a] Extrapolated.

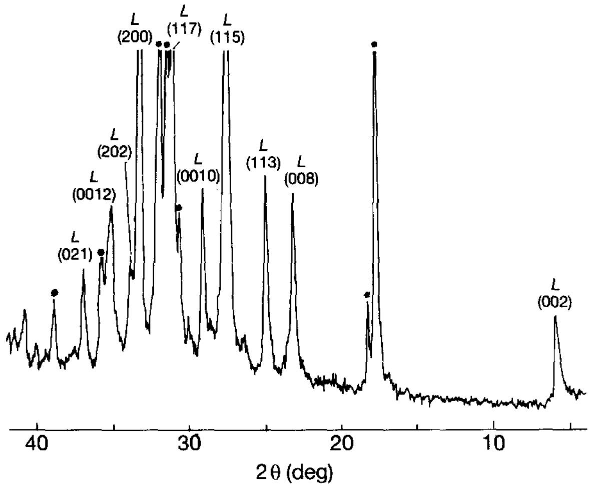


Figure 4 X-ray powder diffraction spectrum of a sample with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, fired for 30 h at 800 °C. (∗) Ca_2PbO_4, (●) CuO, *L* (*h k l*) is 2212 phase.

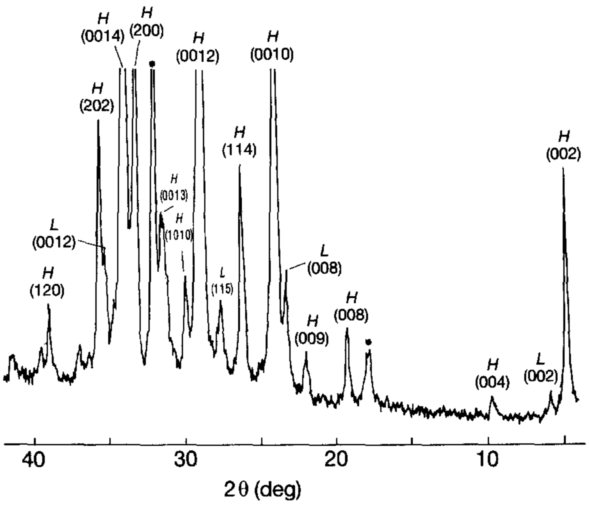


Figure 5 X-ray powder diffraction spectrum of a sample with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, fired for 150 h at 855 °C. (∗) Ca_2PbO_4. *H* (*h k l*) is 2223 and *L* (*h k l*) is 2212 phase.

TABLE VI Summarized results of X-ray diffraction analysis of superconductors with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$

Firing conditions		"Main" phase	Secondary phases
(°C)	(h)		
800	30	2212	Ca_2PbO_4, CuO
855	150	2223	2212, Ca_2PbO_4
855	150	2223	2212, Ca_2PbO_4
Cold pressed			

The main phase in the material fired at 800 °C is the low-temperature phase 2212. Ca_2PbO_4 and unreacted CuO are also present. At higher firing temperatures, the main phase is the high-temperature 2223 phase, while the concentration of 2212 radically decreases. The material is still heterogeneous and contains Ca_2PbO_4. This is in accordance with the increased critical temperatures of samples fired at 855 °C.

The microstructures of broken and polished samples are shown in Figs 6 (800 °C), 7 (855 °C) and 8 (855 °C, cold pressed). The microstructure of the cold-pressed sample is ordered, with plate-like grains (2223 phase) oriented perpendicular to the direction of the applied pressure.

The phases in the superconducting material were analysed by EDS. Results of quantitative EDS analysis are shown in Table VII. The results were normalized to Cu = 2 for the 2212 phase and to Cu = 3 for the 2223 phase.

The material fired at 855 °C is mostly 2223 phase. 2212 phase is located on the boundaries between 2223 grains. Traces of non-superconducting phases Ca_2PbO_4, Ca_2CuO_3 and $(Sr, Ca)_3Cu_5O_8$ are also present.

Typical EDS spectra of superconducting and non-superconducting phases which are commonly present in Bi–Sr–Ca–Cu–O-based superconducting materials, are shown in Fig. 9. EDS spectra of the low- and high-temperature phases are obviously different, and

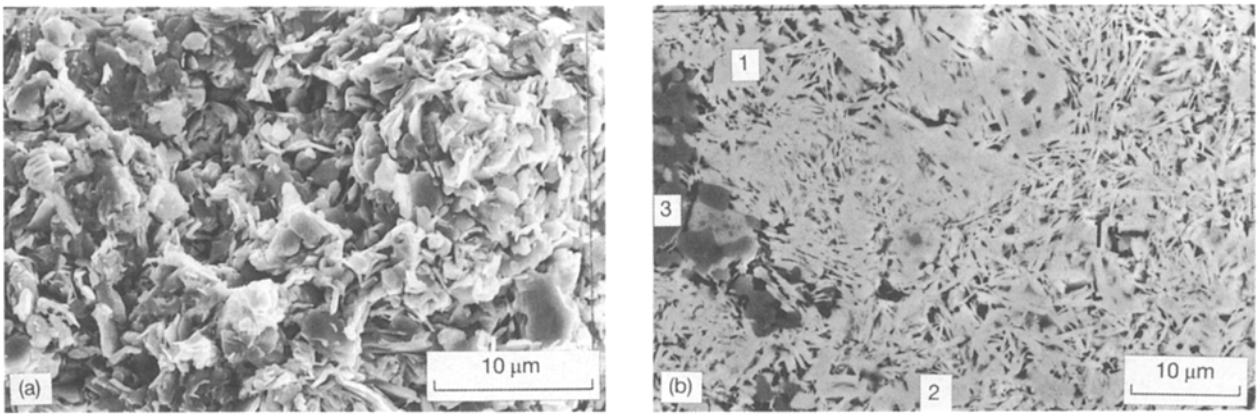


Figure 6 The microstructure of superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, fired for 30 h at 800 °C. (a) Fracture, (b) polished. Phases analysed by EDS are: (1) 2212 superconducting phase, (2) Ca_2PbO_4, (3) CuO.

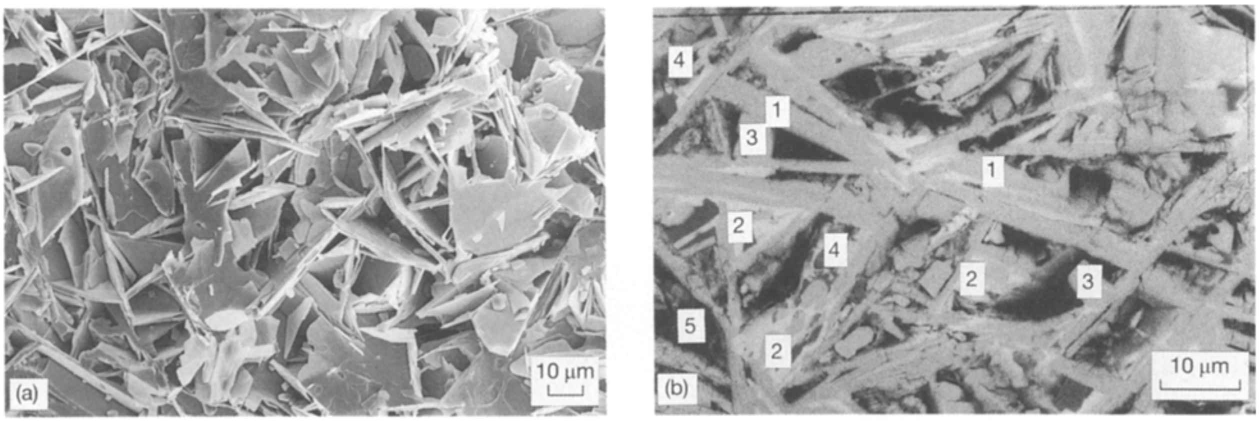


Figure 7 The microstructure of superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, fired for 150 h at 855 °C. (a) Fracture, (b) polished. Phases analysed by EDS are: (1) superconducting phase 2223, (2) superconducting phase 2212, (3) Ca_2PbO_4, (4) $(Sr, Ca)_3Cu_5O_8$, (5) Ca_2CuO_3.

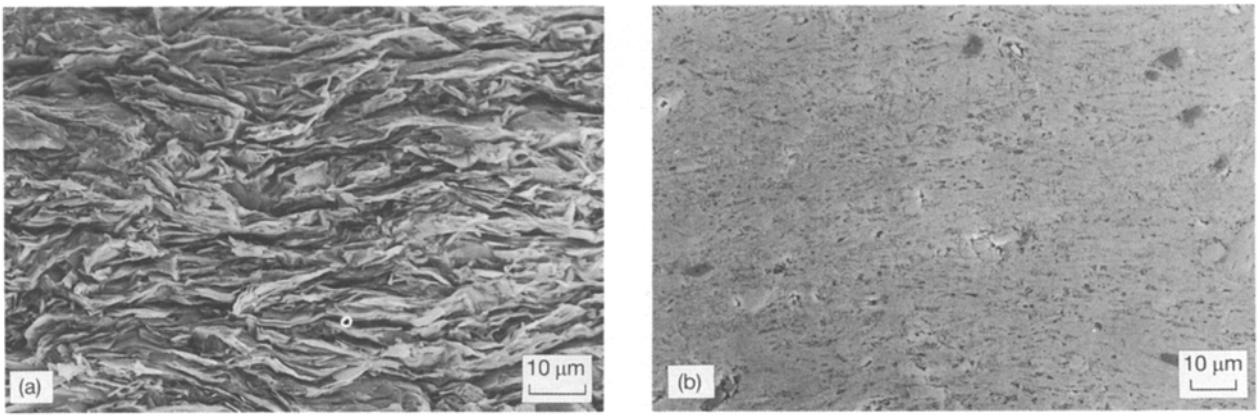


Figure 8 The microstructure of superconducting material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, fired for 150 h at 855 °C and cold pressed. The microstructure of the cold-pressed sample is ordered, with the plate-like grains (2223 phase) oriented perpendicular to the direction of applied pressure. (a) Fracture, (b) polished.

can be used for rapid and convenient identification of the phases.

4. Conclusion

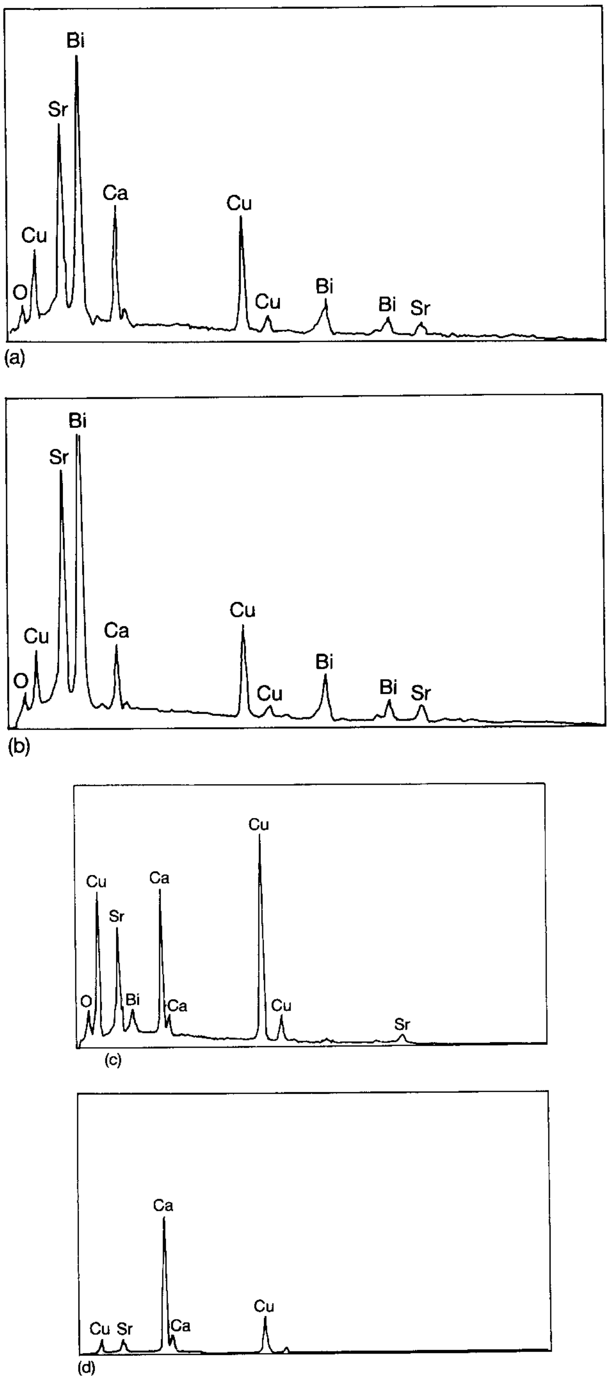
High T_c superconducting materials based on the PbO-modified Bi–Sr–Ca–Cu–O system with various ratios between the oxides were prepared by calcination at 800 °C and firing at 855 °C. From X-ray powder diffraction analysis data, the ratio of the low- and high-temperature phases was calculated. The concentration of high T_c phase was highest for the material with the nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$, which was chosen for further experimental work.

The material with this nominal composition, fired at 800 °C, contains mostly the low-temperature phase.

TABLE VII Quantitative EDS analysis of superconducting material with a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_x$

Firing temperature (°C)	Phase	Composition
800	2212	$Bi_{1.85}Pb_{0.15}Sr_{1.86}Ca_{1.14}Cu_2O_x$
	Ca_2PbO_4	$Ca_{1.64}Sr_{0.36}Pb_{0.75}Bi_{0.21}Cu_{0.23}O_x$
	CuO	
855	2223	$Bi_{1.85}Pb_{0.38}Sr_{1.97}Ca_{2.03}Cu_3O_x$
	2212	$Bi_{1.87}Pb_{0.36}Sr_{1.79}Ca_{1.18}Cu_2O_x$
	Ca_2PbO_4	$Ca_{1.74}Sr_{0.26}Pb_{0.88}Bi_{0.10}Cu_{0.15}O_x$
	Ca_2CuO_3	$Ca_{1.97}Sr_{0.10}CuO_x$
	$(Sr, Ca)_3Cu_5O_8$	$Sr_{1.23}Ca_{1.77}Cu_{4.76}Bi_{0.17}Pb_{0.03}O_x$

No Meissner effect was observed and the zero resistivity temperature was around 65 K. Firing at 855 °C leads to the formation of the high T_c phase, as shown by increasing values of T_c (onset) to 115 K and T_c ($R = 0$) over 105 K for as-fired and cold-pressed samples.



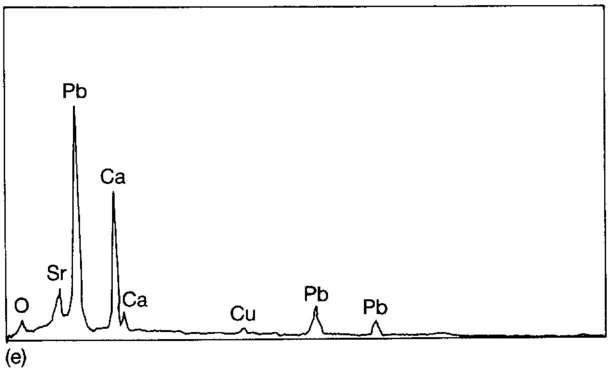


Figure 9 Typical EDS spectra of the superconducting and non-superconducting phases which are commonly present in Bi–Sr–Ca–Cu–O-based superconducting materials. (a) 2223 phase, (b) 2212 phase, (c) $(Sr, Ca)_3Cu_5O_8$, (d) Ca_2CuO_3, (e) Ca_2PbO_4.

The composition of samples was investigated by X-ray powder diffraction analysis and by EDS. The main phase in the material fired at 800 °C is the low-temperature phase 2212. Ca_2PbO_4, unreacted CuO and traces of 2223 phase are also present. At higher firing temperatures the main phase is the high-temperature phase 2223, while the concentration of 2212 radically decreases. The material is still heterogeneous with the presence of Ca_2PbO_4.

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