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Preparation of superconducting Bi–Sr–Ca–Cu–O ceramics by the sol–gel method

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Superconducting Bi–(Pb)–Sr–Ca–Cu–O ceramics were prepared through the sol–gel method using an aqueous solution of metal acetates containing acetic acid and tartaric acid. The conditions of gelation and conversion of gel to $Bi_2Sr_2CaCu_2O_x$ phase were studied by thermal analysis, infrared absorption spectroscopy and X-ray diffraction technique. It was found that transparent gels were obtained from the solutions containing tartaric acid, with a molar ratio of $C_4H_6O_6/Cu$ of about 0.4. The gel matrix was assumed to be composed of carboxylate anions and metal cations. A gel of molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 was decomposed to $CaCO_3$, CaO, CuO and $Bi_{1-x}Sr_xO_y$ ($x = 0.2$ to 0.3) at low temperatures of 270 to 600° C and produced $Bi_2Sr_2CaCu_2O_x$ phase at 800° C via complex intermediate states. A rapid cooling of the heated product increased T_c (end) in the gel of molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3, while a slow cooling increased T_c (end) in the lead-containing gel of molar composition Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1. The latter showed T_c (onset) at 115 K and T_c (end) at 105 K.

1. Introduction

Since the discovery of high-T_c superconducting oxide [1], considerable attention has been paid to the sol–gel preparation of superconducting oxides. From the viewpoint of ceramic processing, the sol–gel method is promising in giving homogeneous and fine starting powders which can produce well-sintered materials. The sol–gel method can also produce ceramics in various forms such as rods or sheets, fibres and coating films [2, 3] without going through powder processing. Recently, we have applied a sol–gel processing to the synthesis of $YBa_2Cu_3O_x$ superconductor using aqueous solutions of yttrium, barium and copper acetates as starting compounds [4–8].

The superconducting oxides of the Bi–Sr–Ca–Cu–O system is known for a higher superconducting transition temperature, T_c, and better chemical durability than that of the Y–Ba–Cu–O system. This paper describes the preparation of the Bi–Sr–Ca–Cu–O superconducting oxides by the sol–gel method using aqueous solutions of bismuth, strontium, calcium and copper acetates containing acetic acid and tartaric acid. The gelation of the starting solutions, the conversion of the gels to Bi–Sr–Ca–Cu–O ceramics on heat treatment and the effect of addition of lead on T_c have been studied.

2. Experimental procedure

2.1. Preparation of samples

Superconducting oxides of the Bi–Sr–Ca–Cu–O system with or without lead were prepared from reagent grade $BiOCH_3COO$ (Mitsuwa Pure Chemicals, Osaka, Japan), $Pb(CH_3COO)_2 \cdot 3H_2O$ (Wako Pure Chemical Industries, Osaka, Japan), $Sr(CH_3COO)_2 \cdot 1/2H_2O$ (Nacalai Tesque Inc., Kyoto, Japan), $Ca(CH_3COO)_2 \cdot H_2O$ (Nacalai Tesque Inc.), $Cu(CH_3COO)_2$ (Wako Pure Chemical Industries Ltd). 0.7103 g $BiOCH_3COO$ was dissolved in 50 ml acetic acid solution of composition $H_2O : CH_3COOH$ = 4 : 1 in volume and stirred for 24 h at room temperature. After filtering, the bismuth content of the resultant solution was analysed so that the quantities of other chemicals to be added might be adjusted. $Pb(CH_3COO)_2 \cdot 3H_2O$, $Sr(CH_3COO)_2 \cdot 1/2H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$ and $Cu(CH_3COO)_2$ were dissolved at 20° C in the solution to make aqueous solutions of molar compositions, Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 or Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1. After adding a given amount of tartaric acid, the solution in an uncovered 100 ml beaker was concentrated by heating at 70°C for 70 h to gel.

In order to make sintered pellets, the gels were pulverized. The gel powders were calcined at 400° C for 1 h and pressed at 2300 $kg\,cm^{-2}$ at room temperature into a pellet. The pellets for the molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3, which contained no lead, were sintered at 845° C for 40 h, and quenched in the ambient atmosphere (Sample A) or cooled down in the furnace (Sample B). The pellets for the molar composition Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1, which contained lead, were heated at 835° C for 130 h, and quenched (Sample C) or cooled down in the furnace (Sample D).

2.2. Measurements

The chemical analysis of the acetic acid solution of $BiOCH_3COO$ on bismuth was made by volumetric analysis. The solution was diluted with distilled water. The pH of the solution was adjusted to 1 to 3 with

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HNO_3 by using xylenol orange as indicator. The solution was then titrated using ethylene diamine tetra acetic acid.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) for the gel powders were performed at a heating rate of 5° C min^{-1}.

Powder X-ray diffraction patterns and infrared absorption spectra were taken for the gel-derived materials heated to various temperatures at a rate of 5° C min^{-1}. The KBr method was used for the infrared spectra measurement.

D.c. electrical resistance was measured for the sintered pellets as a function of temperature by the four-probe method. Silver paste served as electrode.

3. Results

3.1. Formation of transparent gels

Table I summarizes the appearance of the solutions and gels which change with the tartaric acid content. It is seen that the pH of the solutions is similar (3.2 to 3.3) for all the solutions. Transparent gel pieces, as shown in Fig. 1, are formed at 70° C in 70 h from the solutions containing tartaric acid in an amount of 0.39 to 0.43 in $C_4H_4O_6$/Cu molar ratio, regardless of the presence or absence of lead. In solutions containing tartaric acid less than 0.26 in $C_4H_4O_6$/Cu ratio, dark blue crystals are formed during concentration. White precipitates are formed on the addition of tartaric acid when the molar ratio $C_4H_4O_6$/Cu is larger than 0.52.

Fig. 2 shows the X-ray diffraction patterns of the dark blue crystals, transparent gels and white precipitates. The X-ray patterns indicate that the dark blue crystal is copper acetate hydrate, $Cu(CH_3COO)_2 \cdot H_2O$, and the transparent gel and white precipitate are amorphous, as shown by the absence of sharp X-ray diffraction peaks.

3.2. The nature of the gels and the change with heating

The transparent gels were hygroscopic and soluble in acetic acid solution. When heated, gel pieces became vigorously bloated in the temperature range 150 to 270° C, where they turned into porous pieces and the porous nature remained even after heating to 800° C. The sintered pellets, prepared from the calcined powders, did not bloat. The colour of the gel changed from blue to green, brown and black with increasing heating temperature as shown in Table II.

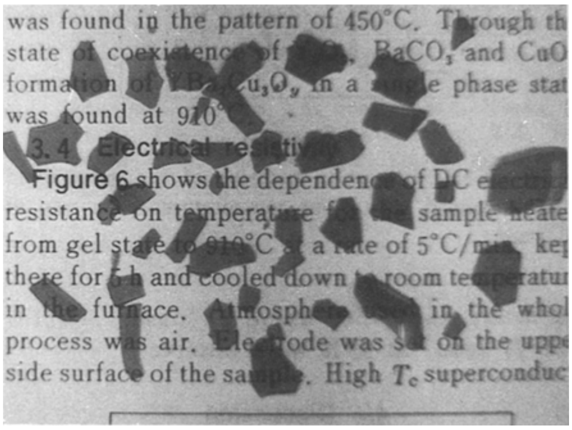

Figure 1 Appearance of the transparent gel pieces derived from the acetate solution.

Fig. 3 shows DTA and TG curves for the gel powders. A small and a large exothermic peak at 230 and 370° C, respectively, are found on the DTA curve, accompanied by weight losses at 180 to 270° C and 330 to 400° C on the TG curve. A weight loss is also found below 150° C.

3.3. Infrared spectra and X-ray diffraction

The infrared spectra of the gel and gel-derived materials heated to various temperatures are shown in Fig. 4. The band assignments are summarized in Table III. The presence of carboxylate anions, undissociated carboxylic acids and water is confirmed in the spectra of the gel. The amount of dimeric carboxylic acids, i.e. hydrogen bonded, unassociated carboxyl groups, decreases when the gel is heated to 180° C which is revealed in the reduction of the 2500 to 2700 and

TABLE I Appearance of the solution and gels derived from metal acetate solutions containing different amounts of tartaric acid

Number	Molar ratio of metals in the solution					Molar ratio of Cu and tartaric acid		pH	Appearance		
	Bi	Sr	Ca	Cu	Pb	Cu	$C_4H_6O_6$		Solution preparation at 20° C	After concentrating and drying at 70° C for 48 h	After concentrating and drying at 70° C for 70 h
(1)	2	2	2	3	0	1	0	3.3	Solution	Blue crystals precipitated	Transparent gel with crystals
(2)	2	2	2	3	0	1	0.13	3.3	Solution	Blue crystals precipitated	Transparent gel with crystals
(3)	2	2	2	3	0	1	0.26	3.3	Solution	Homogeneous solution	Transparent gel with crystals
(4)	2	2	2	3	0	1	0.39	3.2	Solution	Homogeneous solution	Transparent gel
(5)	2	2	2	3	0	1	0.43	3.2	Solution	Homogeneous solution	Transparent gel
(6)	2	2	2	3	0	1	0.52	3.2	Solution	White precipitates	Precipitate
(7)	2	2	2	3	0	1	0.65	3.2	Precipitate and solution	White precipitates	Precipitate
(8)	2	2	2	3	0.6	1	0.43	3.2	Solution	Homogeneous solution	Transparent gel

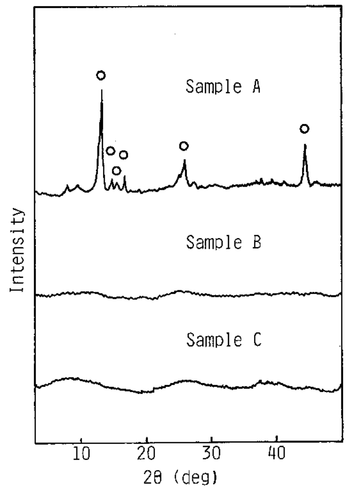

Figure 2 X-ray diffraction patterns of blue crystals (A), transparent gel (B) and white precipitate (C). (○) Copper acetate hydrate $Cu(CH_3COO)_2 \cdot H_2O$.

$1704\,cm^{-1}$ bands and $1300\,cm^{-1}$ shoulder characteristic of dimeric carboxylic acids, and the 3200 to $3500\,cm^{-1}$ band attributed to hydrogen-bonded OH groups. Reduction of the 3200 to $3500\,cm^{-1}$ band may also reflect a decrease in the water content.

In the spectra of the sample heated to 270° C, the bands attributed to acetate and tartrate anions are lost, and the peaks at 1473, 857 and $710\,cm^{-1}$ attributed to carbonate and a broad band below $700\,cm^{-1}$ assigned to metalloxane bonds, appear. It is noticed that the metalloxane bands are absent in the gel and gel-derived material heated up to 180° C. When the samples are heated up from 270 to 800° C, the absorption peaks of the carbonate become smaller, indicating the loss of the carbonate in the heating process.

Fig. 5 shows the X-ray diffraction patterns of the samples heated to various temperatures. The gels before and after heating to 180° C are amorphous in X-ray diffraction patterns. At 270 and 400° C, $Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3) [9], $CaCO_3$, CuO and CaO are found. $Bi_2Sr_2CuO_x$ appears at 600° C at the expense of $Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3) and $CaCO_3$, and $Bi_2Sr_2CaCu_2O_x$ appears at 700° C. When the sample is heated to 800° C, $Bi_2Sr_2CuO_x$ disappears and $Bi_2Sr_2CaCu_2O_x$ become a main phase. CuO is not found in the sample heated to 820° C but CaO still remains. Table IV summarizes the identified phases in the heated samples.

3.4. Electrical resistivity of the sintered pellets

Fig. 6 shows the temperature dependence of d.c. electrical resistance for sintered pellets with and without lead. T_c (onset) and T_c (end) are summarized in Table V. It is seen that the samples without lead (A and B) show similar T_c (onset) at 110 K, while a higher T_c (end) is given by the quenched sample (A) than the slowly cooled sample (B). Fig. 7 shows the X-ray diffraction patterns of these sintered materials. It is seen that the quenched sample (A) is composed of $Bi_2Sr_2CaCu_2O_x$ and CaO, whereas the slowly cooled sample (B) contains an extra phase, $Bi_2Sr_2CuO_x$. The samples with lead (C and D) showed higher T_c (end) than those without lead. Higher T_c (onset) at 115 K and T_c (end) at 105 K were found for the slowly cooled sample (D) than those at 107 and 100 K for the quenched sample (C). Fig. 7 shows that the slowly cooled sample (D) contains a larger amount of high-T_c phase ($Bi_2Sr_2Ca_2Cu_3O_x$) than the quenched sample (C).

TABLE II Appearance of the samples obtained by heating gels to various temperatures at a heating rate of $5°C\,min^{-1}$

Temperature (° C)	Appearance
20	Transparent
180	Porous, green
270	Porous, brown
400	Porous, brown
600	Porous, black
800	Porous, black

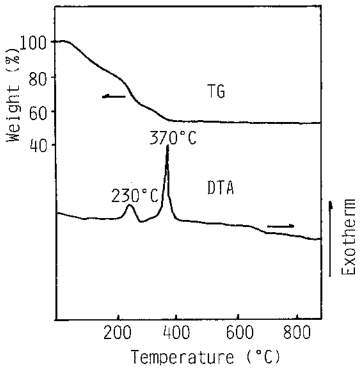

Figure 3 TG and DTA curves of the gel powder of molar composition, Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3. Heating rate $5°C\,min^{-1}$.

4. Discussion

4.1. Gel formation

Formation of transparent, amorphous gels in the Bi–(Pb)–Sr–Ca–Cu–O system could be achieved by concentrating the aqueous solutions of metal acetates containing acetic acid and tartaric acid. Tartaric acid was found to be effective in gel formation, especially in preventing the crystallization of copper acetate hydrate during concentration.

The presence of the bands attributed to carboxylate anions and the absence of metal–oxygen bands in the infrared spectra of the amorphous samples suggest that the acetate and tartrate anions play a role in

TABLE III Band assignment of the infrared spectra

Wavenumber (cm^{-1})	Species	
468	CH, COO	
617	CH, COO	
667	COO	
940	CC	
1021	CH_3	
1051	CH_3	
1092	COH	
1300		Acid dimers
1341	CH_3, CH_3CO	
1419	COO, CH_3	
1559	COO	
1704	C=O	Acid dimers
2500–2700		Acid dimers
2860	CH, CH_3	
2950	CH, CH_3	
3200–3500	OH, Bonded OH···O	

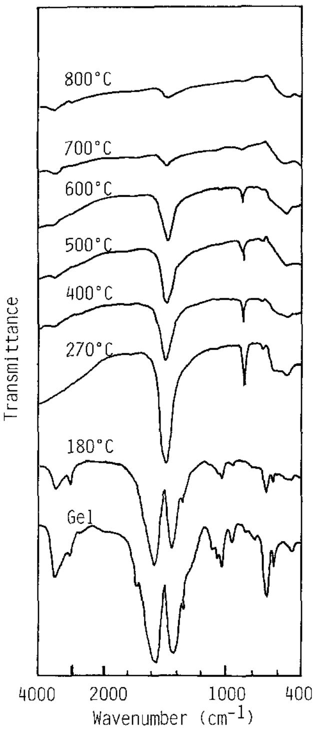

Figure 4 Infrared spectra of the gel and gel-derived materials heated to various temperatures at a rate of 5° C min^{-1}.

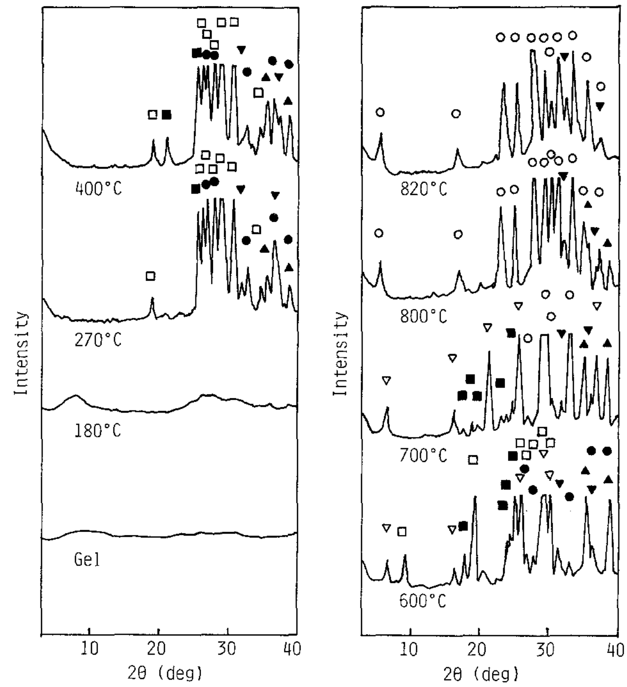

Figure 5 X-ray diffraction patterns of the gel and gel-derived materials heated to various temperatures at a rate of 5° C min^{-1}. (○) $Bi_2Sr_2CaCu_2O_x$, (▼) CaO, (▲) CuO, (▽) $Bi_2Sr_2CuO_x$, (□) $Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3), (●) $CaCO_3$, (■) unknown.

forming networks in the gel matrix. The water-soluble nature of the gel may reveal the weakly bonded structure of the gel. It is assumed that tartrate anions may be considered to contribute to the formation of the matrix because of the larger number of the sites which can be bonded to metal cations or other carboxylate groups through ionic or hydrogen bonding.

4.2. Crystallization of gel

In the temperature range 150 to 270° C, the gel softens and bloats. The bloating may be attributed to decomposition of organic acids and further loss of water.

TABLE IV Phases identified by the X-ray diffraction for the heated materials. The gel was heated at a rate of 5° C min^{-1} to various temperatures

Temperature (° C)	Phases
180	Amorphous
270	$Bi_{1-x}Sr_xO_y$ (X = 0.2 to 0.3), $CaCO_3$, CuO, CaO, unknown phase
400	$Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3), CuO, CaO, unknown phase
600	$Bi_2Sr_2CuO_x$, $Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3), CuO, CaO, $CaCO_3$, unknown phase
700	$Bi_2Sr_2CuO_x$, CuO, CaO, $Bi_2Sr_2CaCu_2O_x$, unknown phase
800	$Bi_2Sr_2CaCu_2O_x$, CaO, CuO
820	$Bi_2Sr_2CaCu_2O_x$, CaO

Single-phase formation of high-T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$ crystal is not attained from the gel of the molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3. Thermal decomposition of the gel resulted in the precipitation of various oxides or carbonates and finally in a mixture of $Bi_2Sr_2CaCu_2O_x$ and CaO. $CaCO_3$, CaO, CuO and $Bi_{1-x}Sr_xO_y$ (x = 0.2 – 0.3) are formed at 270° C, $Bi_2Sr_2CuO_x$ is formed at 600° C through the reaction between $Bi_{1-x}Sr_xO_y$ (x = 0.2 to 0.3) and CuO, $CaCO_3$ is decomposed to CaO and the low-T_c phase $Bi_2Sr_2CaCu_2O_x$ is formed at 700° C. In order to make the high-T_c phase from gel, decomposition of the gel should be controlled to suppress the formation of oxides or carbonates of the constituent species.

4.3 Superconductivity of the sintered pellets and effects of cooling condition

Fig. 6 and Table V showed that sintered sample of molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 slowly cooled to room temperature in the furnace has lower T_c (end) than the quenched one. Fig. 7 shows that quenched sample (A) is composed of $Bi_2Sr_2CaCu_2O_x$ and CaO, whereas the slowly cooled sample (B) contains an extra phase, $Bi_2Sr_2CuO_x$. This may be caused by decomposition of $Bi_2Sr_2CaCu_2O_x$ phase to CuO and the $Bi_2Sr_2CuO_x$ whose T_c (end) is 7 K during cooling. For the sintered sample containing lead of molar composition Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 :

TABLE V Critical temperature for pellet samples

Sample	Composition	Sintering conditions	T_c (onset) (K)	T_c (end) (K)
A	$Bi_2Sr_2Ca_2Cu_3O_x$	845° C/40 h (quenched)	110	80
B	$Bi_2Sr_2Ca_2Cu_3O_x$	845° C/40 h (slowly cooled)	110	78
C	$Bi_{1.85}Pb_{0.35}Sr_{1.9}Ca_{2.0}Cu_{3.1}O_x$	835° C/130 h (quenched)	107	100
D	$Bi_{1.85}Pb_{0.35}Sr_{1.9}Ca_{2.0}Cu_{3.1}O_x$	835° C/130 h (slowly cooled)	115	105

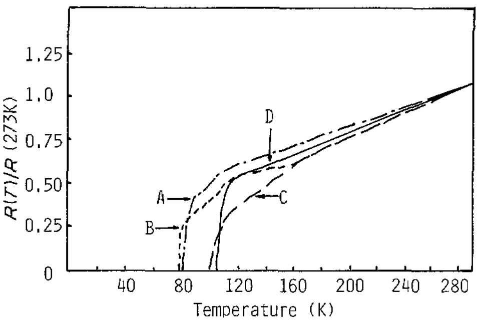

Figure 6 D.c. electrical resistance of heated materials as a function of temperature for Samples A, B, C and D. Without lead, 845° C, 40 h, (A) quenched, (B) slowly cooled. With lead, 835° C, 130 h, (C) quenched, (D) slowly cooled.

1.9 : 2.0 : 3.1, however, the situation is the opposite; the sample cooled to room temperature in the furnace has higher T_c (end) than the quenched one and a higher content of the high-T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$ was found for the sample slowly cooled. It shows part of the $Bi_2Sr_2CuO_x$ phase was converted to high-T_c phase in the slow cooling because of the addition of lead.

5. Conclusion

Superconducting Bi–(Pb)–Sr–Ca–Cu–O ceramics were prepared through the sol–gel method using an aqueous solution of metal acetates containing acetic acid and tartaric acid. The conversion of gel to $Bi_2Sr_2CaCu_2O_x$ phase was studied by thermal analysis, infrared absorption spectroscopy and X-ray diffraction technique. The following conclusions were drawn.

1. Transparent gels are obtained from the solution containing tartaric acid of molar ratios around $C_4H_6O_6/Cu = 0.4$.

2. The gel matrix is considered to be composed of carboxylate anions and metal cations.

3. During heat treatment, the gel softens and bloats vigorously at 150 to 270° C which is caused by decomposition of organics and evaporation of water.

4. The gel of molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 decomposes to $CaCO_3$ CaO, CuO and $Bi_{1-x}Sr_xO_y$ ($x = 0.2$ to 0.3) at 270° C and $Bi_2Sr_2CaCu_2O_x$ phase is formed at 800° C through complex intermediate states.

5. For the sintered pellet of the molar composition Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 a rapid cooling of the heated material increases T_c (end). On the other hand, for the sintered pellet with lead of molar composition Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1, a slow cooling of the heated material increases T_c (end).

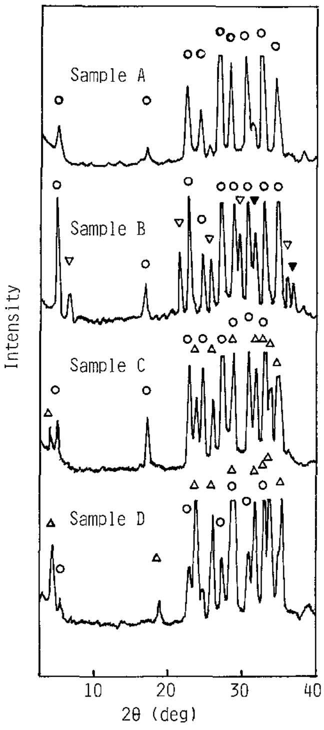

Figure 7 X-ray diffraction patterns of Samples A, B, C and D. Without lead, 845° C, 40 h, (A) quenched, (B) slowly cooled. With lead, 835° C, 130 h, (C) quenched, (D) slowly cooled. (○) $Bi_2Sr_2CaCu_2O_x$, (▽) $Bi_2Sr_2CuO_x$, (△) $Bi_2Sr_2Ca_2Cu_3O_x$, (▼) CaO.

6. For the sintered pellet of molar composition Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1, T_c (onset) at 115 K and T_c (end) at 105 K are observed.

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