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STABILIZATION AND CRYSTALLIZATION BEHAVIOUR OF THE AMORPHOUS $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ High temperature superconductor material

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Abstract

Crystallization behaviour of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ ($0<x<1$), obtained by rapidly quenching the melt, has been investigated by the differential thermal analysis (DTA) method under different atmosphere e.g. Ar, air, O_2 and vacuum. Crystallization temperatures, activation energies and heat of crystallization are found to be 708–728 K, 2.25–2.32 eV and 0.16–1.81 kJ/g-atom, respectively, depending upon the atmosphere used during DTA. This material undergoes a number of structural and thermochemical transformations on continuously heating during DTA upto the melting temperature, which depends critically upon the atmosphere used.

Keywords: amorphous materials, Bi–Sr–Ca–Cu–O compounds, crystallization behaviour, DTA, superconductors

Introduction

Pb-doped Bi–Sr–Ca–Cu–O compound close to the composition $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ possesses relative high superconducting transition temperatures [1] and is of great technological importance. Recently, the present author has reported that this material can be obtained in the amorphous state by rapidly quenching the melts and undergoes a number of structural transitions when heated continuously in vacuum from room temperature to the melting temperature [2]. In the present work, results of differential thermal analysis (DTA) of this amorphous material, carried out under different atmospheres from room temperature to the melting temperature, are presented.

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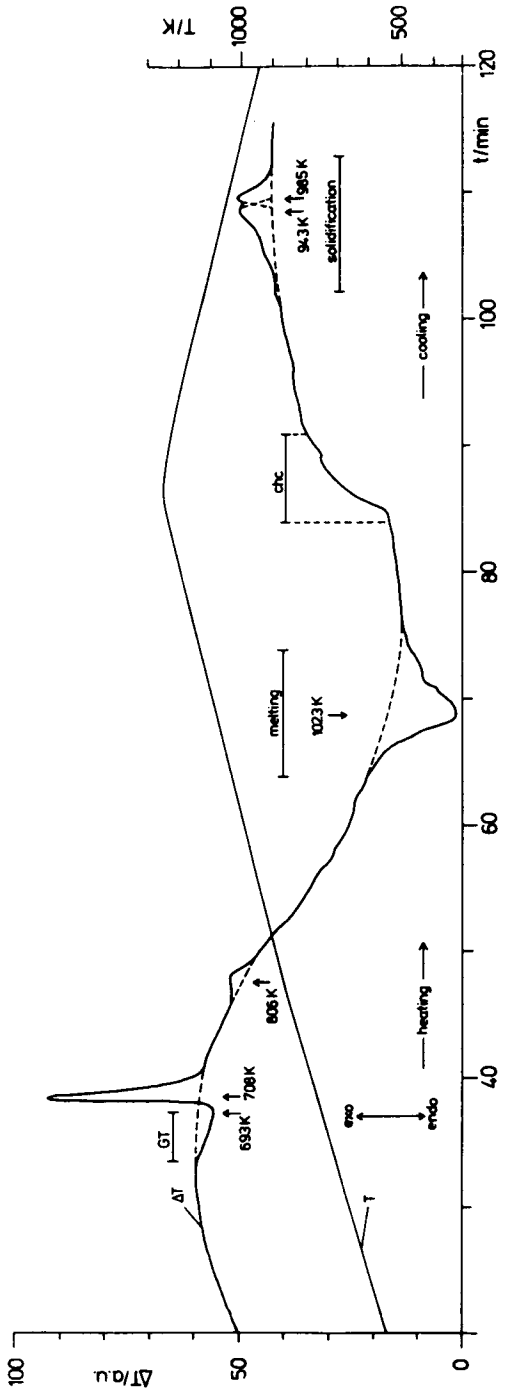

Fig. 1a DTA of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ taken at a heating rate of 10 deg/min in vacuum (0.001 mbar)
chc = change over from heating to cooling, exo = exothermic and endo = endothermic

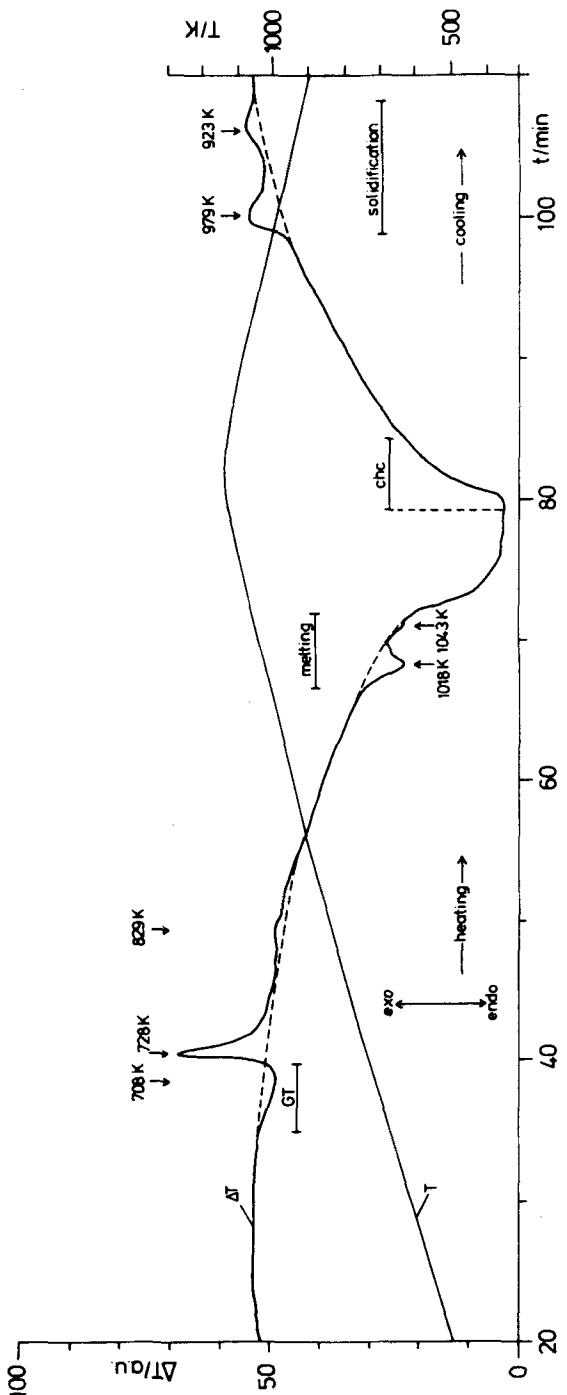

Fig. 1b *DTA of the amorphous* $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ *taken at a heating rate of 10 deg/min in a pressure of 400 mbar Ar, chc = change over from heating to cooling, exo = exothermic and endo = endothermic*

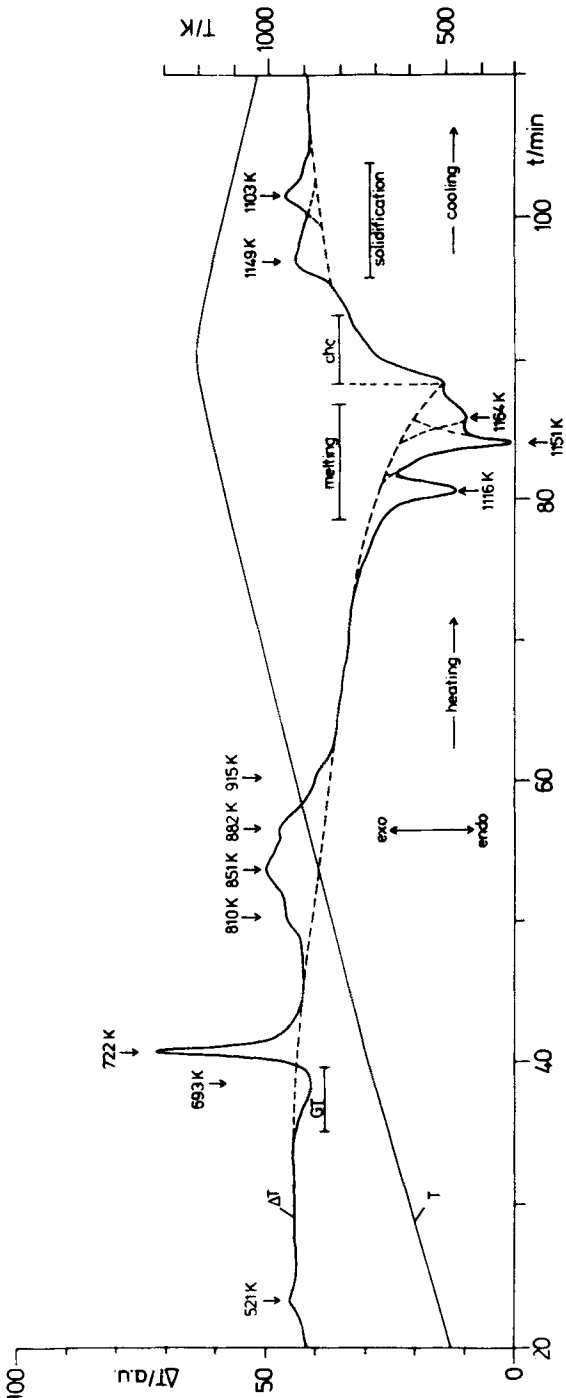

Fig. 1c DTA of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{3+x}$ taken at a heating rate of 10 deg/min in a pressure of 400 mbar of air chc = change over from heating to cooling, exo = exothermic and endo = endothermic

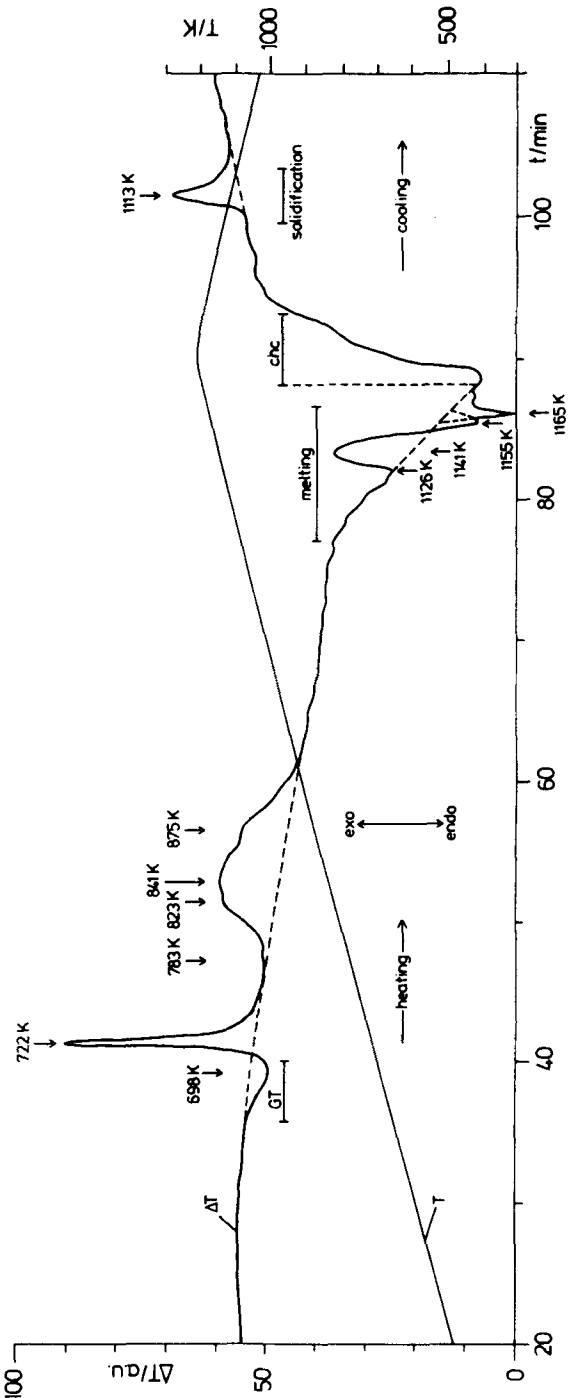

Fig. 1d DTA of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ taken at a heating rate of 10 deg/min in a pressure of 400 mbar of O_2. chc = change over from heating to cooling, exo = exothermic and endo = endothermic

Table 1 Differential thermal analysis data for amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ taken at a heating rate of 10 deg·min^{-1} in different atmosphere

Atmo-	Glass transition			Crystallization			Recrystallization			Phase change		
sphere	T_g	ΔE_g	ΔH_g	T_{cr}	ΔE_{cr}	ΔH_{cr}	T_R	ΔE_R	ΔH_R	T_c	ΔE_c	ΔH_c
Dynamic vacuum (10^{-3} mbar)	693	2.20	0.44	708	2.25	0.61	806	2.58	0.39	–	–	–
Ar (400 mbar)	708	2.25	0.50	728	2.32	1.61	829	2.66	0.97	–	–	–
Air (1000 mbar)	693	2.20	0.46	722	2.30	1.61	851	2.73	4.99	–	–	–
O_2 (400 mbar)	698	2.22	0.63	722	2.30	1.80	841	2.70	5.26	1113	3.68	1.59

Table 1 Continued

Atmo-	Melting 1			Melting 2			Solidification 1			Solidification 2		
sphere	T_m	ΔE_m	ΔH_m	T_m	ΔE_m	ΔH_m	T_s	ΔE_s	ΔH_s	T_s	ΔE_s	ΔH_s
Dynamic vacuum (10^{-3} mbar)	1023	3.31	$\overline{1.68}$	–	–	–	993	3.21	1.31	986	3.18	0.91
Ar (400 mbar)	1018	3.29	$\overline{1.11}$	–	–	–	979	3.16	1.33	923	2.97	0.89
Air (1000 mbar)	1116	3.62	$\overline{0.93}$	1151	3.74	$\overline{2.72}$	1149	3.73	2.20	1103	3.58	1.65
O_2 (400 mbar)	1155	3.75	$\overline{0.42}$	1163	3.78	$\overline{0.62}$	1113	3.61	1.27	–	–	–

Transformation temperatures, T_g, T_{cr}, T_R, T_c, T_m and T_s, are peak maximum temperatures and are given in K
Activation energies, ΔE_g, ΔE_{cr}, ΔE_R, ΔE_c, ΔE_m and ΔE_s, are given in eV
Latent heats, ΔH_g, ΔH_{cr}, ΔH_R, ΔH_c, ΔH_m and ΔH_s are given in kJ/g-atom
A bar on the value of latent heats means that the corresponding process is endothermic
A dash in place of a value means that the corresponding anomaly was not detected

Experimental

The samples close to the composition $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ were prepared by appropriate mixtures of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO first by the solid state reaction and then melted in Pt-crucibles. Amorphous samples in the form of thin flakes (10–30 mm×5–15 mm×40–100 μm) were obtained by squeezing the melts between two rapidly rotating copper rollers at speeds 100–200 revolutions/min as described elsewhere [2]. Differential thermal analysis (DTA) was carried out using a modified Linseis DTA apparatus in vacuum (10^{-3} mbar) or in air, Ar and O_2 gases at pressures of 400 mbar from room temperature to the melting temperature. Activation energies of crystallization and other structural and thermochemical transitions/transformations were determined by using the following equation [3]:

$$\Delta E = k_B T_p[\ln\{(T_p - T_o)/\varphi\} + 29.1]$$

where k_B = Boltzmann constant (= $8.625 \cdot 10^{-5}$ eV/K), T_o = 300 K, T_p = peak maximum temperature of the reaction, φ = heating/cooling rate in deg·s^{-1}. Latent heats were obtained by the DTA peak areas using $K_2Cr_2O_7$ as calibration standard.

Results and discussion

Differential thermal analysis (DTA) diagrams for the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ taken at a heating rate of 10 deg·min^{-1} in the temperature range 300–1200 K using different atmospheres are given in Figs 1a–d. Thermal data, i.e. transition temperatures, activation energies and latent heats of different thermochemical transformations observed for this amorphous material are compiled together in Table 1. Although this amorphous material is extremely brittle, a glass transition is found to occur at 693–708 K absorbing a heat of 0.44–0.63 kJ/g-atom before this amorphous material crystallizes at 708–728 K with a release of heat of 0.61–1.80 kJ/g-atom depending upon the atmosphere used. The product of crystallization was found to be a distorted tetragonal phase of the 24 Å-type [2] with a ≈4.96 Å, c = 24.56 Å by X-ray diffraction analysis. It can be seen that apart from small differences in glass transition and crystallization temperatures, crystallization behaviour of the amorphous $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ compound is qualitatively independent of the atmosphere used during DTA. However, the recrystallization and melting processes critically depend upon the atmosphere in which DTA is carried, in

particular, the melting and solidification temperatures, T_m and T_s, respectively, are about 100 K lower in vacuum or inert gas than those in air or oxygen. The highest melting temperature of about 1155 K is observed in oxygen, whereas the maximum of the latent heat of melting is found in air (Table 1 and Fig. 1). Similarly, the recrystallization behaviour depends upon the atmosphere used during DTA. Whereas in vacuum or inert gas, only one recrystallization anomaly at about 806–829 K with a release of heat of 0.39–0.97 kJ/g-atom is detected, there occurs a number of recrystallization anomalies with maximum temperature of anomaly at 851 K with a release of heat of about 4.99–5.26 kJ/g-atom (Table 1 and Fig. 1). On cooling, two anomalies are found in vacuum, Ar and air except oxygen, where only one anomaly is detected. This difference in the cooling behaviour may be due to different degree of undercooling of melts in different atmospheres.

References

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Zusammenfassung — Mittels DTA wurde in verschiedener Atmosphäre (z.B. Ar, Luft, Sauerstoff und Vakuum) das Kristallisierungsverhalten von amorphem $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_{5+x}$ (mit 0) untersucht, welches durch schnelles Abkühlen der Schmelze erhalten wurde. Für Kristallisierungstemperaturen, Aktivierungsenergien und die Kristallisationswärme wurden – je nach Atmosphäre bei der DTA-Analyse - Werte zwischen 708 und 728 K, 2.25–2.32 eV sowie 0.16 und 1.81 kJ/Grammatom gefunden. Bei kontinuierlichem Erhitzen während des DTA-Durchganges bis zum Schmelzpunkt, der im übrigen stark von der Atmosphäre abhängt, unterliegt diese Substanz einer Zahl von strukturellen und thermochemischen Umwandlungen.