A new model for the formation of high-\( T_c \) phase in superconductive \((\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x\) glass-ceramics

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The formation mechanism of the high-\( T_c \) phase through the glass-ceramic route and the role of Pb on the formation of this phase have been investigated. It was found that a new compound with the chemical composition \( \text{Pb}_2\text{Sr}_{3-x}\text{Ca}_x\text{CuO}_y \) (\( x = 1.8 \)) precipitates at around 550 °C. This phase is stable up to 800 °C, where it begins to decompose, and at 850 °C it completely disappears. It was found that some part of the released Pb diffuses into the 2212 phase leading to the formation of Pb-containing 2212 phase, \((\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x\) On the other hand, an endothermic peak, probably arising from the melting of \((\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x\) phase or melting at grain boundaries containing \( \text{Pb}^{2+} \), was observed at 856 °C only in Pb-containing samples that were heat treated. The liquid phase attributed to the endothermic peak may enhance the formation of high-\( T_c \) phase (2223 phase). The growth kinetics for the high-\( T_c \) phase were analysed using the Johnson–Mehl–Avrami equation; the results indicate that the growth of the high-\( T_c \) phase is controlled by a diffusion process and the activation energy for its formation in the initial stage (shorter than 96 h) is 576 ± 45 kJ mol\(^{-1}\).

1. Introduction
Since the discovery of superconductivity in the system Bi–Sr–Ca–Cu–O (Bi-based system) by Maeda et al. [1], three superconducting phases with the general formula of \( \text{Bi}_n\text{Sr}_2\text{Ca}_{n+1}\text{Cu}_n\text{O}_{2n+1} \) (\( n = 0, 1, 2 \)) have been observed. Their critical temperatures, \( T_c \), are 20 K (2201 phase) for \( n = 0 \), 85 K (low-\( T_c \) phase or 2212 phase) for \( n = 1 \) and 110 K (high-\( T_c \) phase or 2223 phase) for \( n = 2 \). The high-\( T_c \) phase is the most difficult to produce by heat treatment even though its stoichiometric composition is adopted. Prolonged heat treatments in a partially melted state or in a low oxygen pressure, in which the melting temperature is lowered, were found very effective for the promotion of the high-\( T_c \) phase. Takano et al. [2] reported that the substitution of Pb for a small part of Bi enormously enhances the formation of high-\( T_c \) phase. Other substitutions such as Mo, Te and Sb [3–5] were tried but Pb remains the most effective. The difficulty in preparing the high-\( T_c \) phase revealed that an understanding of the formation of high-\( T_c \) phase is prerequisite for the fabrication of superconductors containing pure high-\( T_c \) phase with high quality. The formation mechanism of the high-\( T_c \) phase was extensively discussed by many authors [6–11]. Even though different approaches were made so far, many points concerning the formation mechanism of the high-\( T_c \) phase are still obscure.

Among various fabrication techniques of superconductors, the glass-ceramic processing is very attractive for the fabrication of dense superconductors with desired shapes such as fibres [12]. Recently, Sato et al. [13] clarified the formation mechanism of the 2212 phase in the glass-ceramic process of the Bi-based system. But the formation mechanism of the high-\( T_c \) phase in the glass-ceramic process is still unclear. Detailed understanding of the formation of the high-\( T_c \) phase will shed valuable light on the fabrication of excellent superconducting glass-ceramics and fibres. We examine the formation mechanism of the high-\( T_c \) phase in the glass-ceramics with the composition \( \text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7 \). And we propose a new vision of the role of Pb, i.e a new model of the formation mechanism.

2. Experimental procedure
Grade reagents of \( \text{Bi}_2\text{O}_3 \), \( \text{Pb}_2\text{O}_4 \), \( \text{SrCO}_3 \), \( \text{CaCO}_3 \) and \( \text{CuO} \) with high purity were weighed to the composition of \( \text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x \). They were mixed...
with methanol in a ceramic mortar and released in air until no methanol was supposed to exist. The powders were then put in an alumina plate and calcined at 1250°C for 10 min in an electric furnace. The black powders were ground again and melted in a platinum crucible at 1250°C for 10 min in an electric furnace. The melt was rapidly poured on an iron plate and pressed with another one to a thickness of about 1.5 mm. The obtained glassy samples were annealed at different temperatures for different periods. The crystalline phases present in the annealed samples were studied by X-ray diffraction (XRD) analyses using a Geigerflex model 2038 with CuKα radiation. Thermal behaviour was studied using a Seiko Instruments TG/DTA 220. Microstructure observations were performed using a JSM-5400 model scanning electron microscope. The a.c. magnetic susceptibility, $\chi = \chi' - i\chi''$, were measured by a four-probe Hart shorn-type-bridge with a frequency of 713 Hz at an a.c. field amplitude of 0.26 Oe (21 A m⁻¹).

3. Results and discussion
Fig. 1 shows the differential thermal analysis (DTA) curve for the as-quenched sample carried out on bulk in air at a heating rate of 10 K min⁻¹. The glass transition $T_g$ and crystallization peak $T_x$ temperatures are 378°C and 451°C, respectively. Similar to all Bi-based cuprates prepared by a melting method, an endothermic peak and an exothermic peak are observed at 760°C and 780°C, respectively. According to Komatsu et al. [14], it is considered that the endothermic peak is attributable to the formation of a liquid phase and the exothermic peak is related to the formation of the 2212 phase. The sample melts at around 880°C.

Before discussing the formation mechanism of the high-$T_c$ phase, we briefly describe the crystalline phases present in various annealed samples. Fig. 2 shows the XRD patterns for the samples annealed at different temperatures for 24 h in air. At 550°C the 2201 phase is well formed, and Cu$_2$O and (Sr, Ca)$_3$Cu$_2$O$_4$ are detected. Other peaks appeared at $2\theta = 17.8°$ and 31.0°. The phase causing those peaks is designated “Pb-compound” because the peaks are observed for the sample of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ containing Pb, but not for the sample of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$. At 750°C the 2212 phase is formed, and the 2201 phase is still traced. The peaks assigned to CuO are observed, indicating the oxidation of some part of Cu$^+^+$ into Cu$^{2+}$. The intensity of the CaO peak is weak, indicating that CaO participates in the formation of the 2212 phase. The intensity of peaks attributing to the Pb-compound is very strong. At 800°C the main crystalline phases are the 2212 phase and Pb-compound. The 2201 phase and Cu$_2$O are no longer detectable in the XRD pattern. This suggests that the 2201 phase is stable thermally at least below 800°C and that all Cu$_2$O is oxidized into CuO. At 850°C only 2212 phase and (Sr,Ca)$_3$Cu$_2$O$_4$ are present, and the Pb-compound disappears completely.

3.1. Composition of Pb-compound
Up to now, the Pb-compound which has been considered to form in samples of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ is Ca$_2$PbO$_4$ [15]. But the peak positions corresponding to the Pb-compound shown in Fig. 2

![Figure 1 DTA curve for the as-quenched sample of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_x$, heating rate was 10 K min⁻¹.](image)

![Figure 2 XRD powder patterns for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_x$ heat-treated at different temperatures for 24 h in air (a) 550°C, (b) 750°C, (c) 800°C, (d) 850°C, (e) 2212 phase, (f) 2201 phase, (g) CaO, (h) Pb$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$, (i) Sr$_2$Cu$_2$O$_3$, (+) Cu$_2$O, (+) CuO.](image)