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Thermal Properties of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Superconductor and Determination of the Optimal Processing

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Abstract

This research investigates the thermal properties of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ high-temperature superconductor using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The study aims to understand the thermal behavior and optimize processing conditions for enhanced superconducting performance. A 40 mg sample was synthesized using a one-step solid-state reaction method and analyzed in air atmosphere from room temperature to 1200°C at a heating rate of 10°C/min. DSC analysis revealed four distinct exothermic peaks at 824°C, 839°C, 907°C, and 935°C, corresponding to superconducting phase formation, crystallographic transformations, phase decomposition, and structural breakdown, respectively. The optimal thermal processing window was identified as 820-840°C for controlled structural formation. TGA analysis demonstrated excellent thermal stability with total weight loss not exceeding 5% up to 1200°C. Specific heat capacity measurements identified two major thermal transitions: the first at 824°C (Cp = 10 J/g·°C) related to secondary phase melting, and the second at 933°C (Cp = 12 J/g·°C) corresponding to primary superconducting phase melting. These findings provide valuable insights into the optimal processing conditions for $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$, emphasizing the importance of precise temperature control to maximize phase purity, thermal stability, and superconducting performance.

Keywords: Thermal properties; Differential Scanning Calorimetry; Thermogravimetric Analysis; Thermal stability.

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1. Introduction

Thallium-based superconductors, particularly the $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ (Tl-2234) compound, are of significant interest due to their high superconducting transition temperatures, reaching up to 120 K. This exceptional performance is largely attributed to their complex crystal structure, which features four CuO_2 planes that enhance current-carrying capacity and elevate critical temperatures [1, 2]. The Tl-2234 system exhibits notable flexibility in its chemical composition, allowing for partial substitution of thallium with calcium. This substitution has been shown to improve the physical and electrical properties by modifying the charge carrier concentration in the CuO_2 layers [3]. Compared to other thallium-based superconductors such as Tl-2201 and Tl-2223, Tl-2234 demonstrates superior performance owing to its additional CuO_2 layers and enhanced structural coherence [4]. Studies have reported that Tl-2234 samples can achieve a superconducting transition temperature onset (T_c onset) of up to 120 K and zero resistance at 113 K in optimally prepared samples. These properties are significantly influenced by synthesis methods, thallium content, and external magnetic fields [5, 6]. Therefore, understanding the influence of processing conditions is critical for practical application. Thermal conductivity is a key physical property for evaluating the practical usability of superconductors. While direct measurements on Tl-2234 are scarce, analogous studies on Tl-2223 provide important insights. These materials typically exhibit a decrease in thermal conductivity below the superconducting transition due to interactions between electrons and lattice vibrations (phonons). Additionally, factors such as porosity, grain size, and crystallographic defects strongly affect thermal transport [7, 8]. The specific heat capacity analysis offers further understanding of the electronic and structural behavior of superconductors during phase transitions. For example, Tl-2201 exhibits only minor changes (~1%) in specific heat at Tc, indicating a small shift in free energy during the transition. This trend is comparable to that seen in Bi-2212 and YBCO superconductors [9, 10]. Processing conditions also have a crucial impact on the superconducting properties of Tl-2234. Sintering in an argon atmosphere typically results in a Tc around 90 K, while post-annealing in oxygen-rich environments can raise Tc to 115 K [11]. Reducing the oxygen partial pressure not only improves the crystal quality but also lowers the synthesis temperature, as observed in Tl-2223 and other related phases [12, 13]. Variations in thallium content, including calcium substitution, are critical for optimizing superconducting and magnetic properties. Compositional adjustments such as $Tl_{1.7}Ba_2Ca_{3.3}Cu_4O_{12}$ have demonstrated improvements in phase purity and electronic performance [14, 15]. Oxygen content is another essential parameter, as increased oxygenation or prolonged vacuum treatment has been linked to enhanced superconducting behavior and even magnetic transitions above 116 K [3]. In this study, we investigate the thermal behavior of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ using Differential

Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The sample, weighing 40 mg, was analyzed in ambient air from room temperature up to 1200 °C at a heating rate of 10 °C/min. These techniques aim to elucidate melting behavior, phase stability, and thermal decomposition-crucial for optimizing synthesis protocols and performance.

2. Experimental Methods

The compound $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ was synthesized through a one-step solid-state reaction, starting with carefully selected high-purity precursors: thallium oxide (Tl_2O_3), barium peroxide (BaO_2), calcium oxide (CaO), and copper oxide (CuO). These materials were thoroughly mixed using an agate mortar, sieved through a 64-micron mesh to ensure homogeneity, and then pressed into a pellet measuring 1.5 cm in diameter and 0.2 cm in thickness. To minimize thallium evaporation during the thermal process, the pellet was wrapped in silver foil and sealed in a quartz tube, which was placed inside a protective stainless steel tube. The sample then underwent a controlled thermal treatment-comprising gradual heating, an isothermal hold, and slow cooling-detailed in the temperature-time

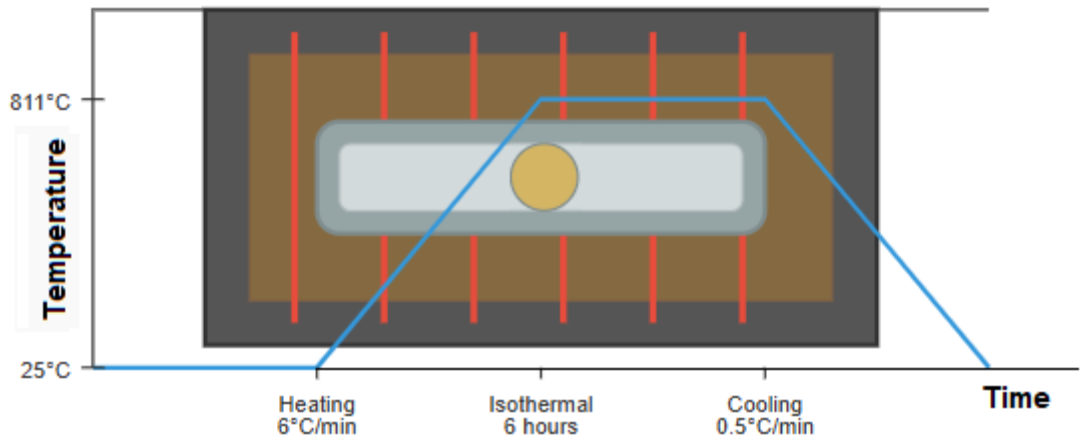

Figure 1. The thermal-time diagram for the preparation of the $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ compound.

diagram, figure1. Finally, to enhance its superconducting properties, the sample was subjected to an additional annealing step in air at 500°C. The figure shows how the temperature changes over time. The process begins at room temperature (25°C) and progresses through three main stages. In the first stage, the sample is gradually heated at a rate of 6°C per minute until it reaches 811°C. This is followed by an isothermal stage, where the temperature is held constant for six hours-an essential period to ensure proper reaction or crystallization of the materials. In the final stage, the sample is slowly cooled at a rate of 0.5°C per minute until it returns to room temperature. This controlled cooling minimizes thermal stresses and prevents the formation of cracks in the material. The figure also illustrates the furnace structure, where the sample is placed at the center of the thermal processing chamber, surrounded by insulating layers to ensure uniform heat distribution. For thermal characterization,

simultaneous differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were carried out on a 40 mg sample of the synthesized material. Measurements were performed in air atmosphere, with a constant heating rate of 10 °C/min, covering a temperature range from room temperature to 1200 °C. This experimental setup facilitated detailed evaluation of the compound's melting behavior, thermal stability, and phase transformation characteristics.

3. Results and Discussion

3.1 DSC Analysis of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Compound

Differential Scanning Calorimetry (DSC) analysis was conducted on the $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ sample to identify the thermal changes associated with the formation of the superconducting phase. Figure 2 curve shows the heat flow (in μV) as a function of temperature, ranging from room temperature up to approximately 1200°C. Four distinct exothermic peaks were observed, indicating significant thermal events within the sample. The first peak, at around 824°C, is attributed to the initial formation of the Tl-2234 superconducting phase, where essential solid-state reactions occur among the starting materials. The second peak, at approximately 839°C, suggests a further crystallographic transformation or structural rearrangement, reflecting continued phase development. The third peak, near 907°C, may indicate the decomposition of unstable phases or internal structural reorganization. The fourth and final peak, around 935°C, is likely associated with structural breakdown or the loss of volatile components such as thallium, indicating that heating beyond this point is undesirable to avoid material degradation. In comparison with the scientific literature, Tl-Ba-Ca-Cu-O compounds typically exhibit phase transitions within the temperature range of 800–1000°C, associated with the formation of superconducting phases such as Tl-1223 or Tl-2223 [16]. The thermal peak observed at 907°C may correspond to the formation of the $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) superconducting phase, while the higher peak at 935°C is likely related to phase decomposition or the formation of impurities. This comparison underscores the importance of the 820–840°C range as an ideal thermal window for controlling structural formation, emphasizing the need for precise temperature regulation to prevent decomposition and the loss of critical elements at elevated temperatures [17].

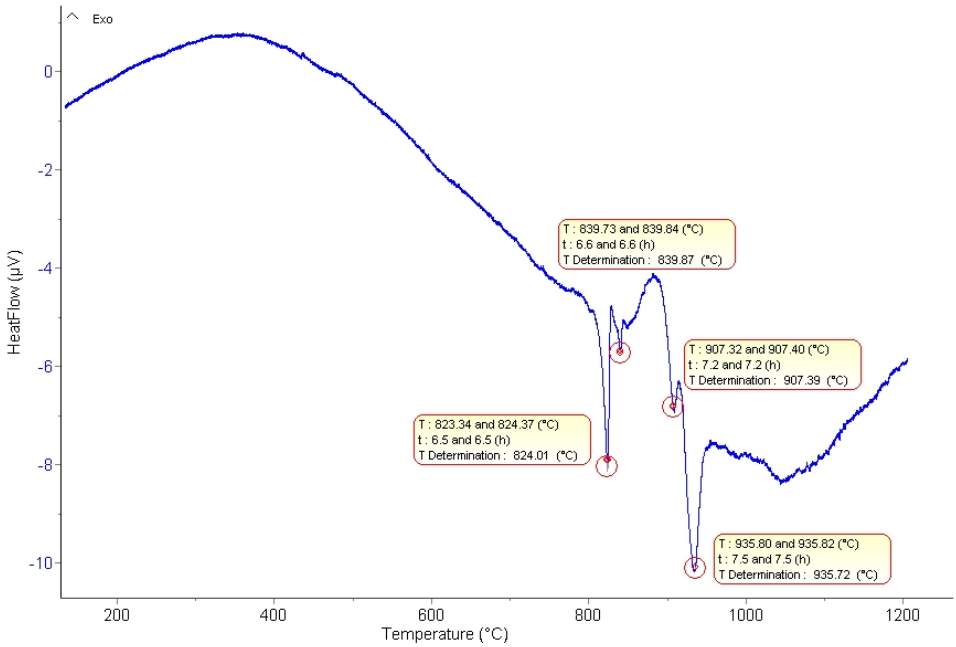

Figure 2 The heat flow as a function of temperature of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Compound

3.2 Thermogravimetric Analysis (TGA) of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Superconductor

The (TGA) graph of the Tl-2234 high-temperature superconductor provides practical evidence of the material's high thermal stability. It shows that the total weight loss during heating from the initial temperature up to 1200°C does not exceed $\Delta m=5\%$, which is consistent with findings in the scientific literature on thallium-based superconductors. Figure 3 depicts the change in the sample's weight (in percentage) as the temperature increases from room temperature to approximately T_f=1200°C. The weight starts close to 100% and gradually decreases as the temperature rises, indicating the release of volatile components from the sample, such as adsorbed water or the decomposition of thermally unstable compounds, and possibly the loss of some thallium oxide (Tl_2O_3) or copper oxide (CuO) at higher temperatures. The rapid initial weight loss at lower temperatures (up to 200°C) is attributed to the loss of crystallization water and surface moisture [18]. In the range between approximately 100°C and 800°C, the weight loss is gradual, suggesting a slow or continuous loss of volatile substances or gradual decomposition of certain compounds. Beyond 800°C, the changes in the slope become more pronounced, indicating additional reactions or decompositions occurring in the sample. The decline at higher temperatures (around 900-1100°C) may be associated with the breakdown of the primary compound or further loss of metal oxides. The continued weight loss at elevated temperatures reflects degradation of the crystal structure, emphasizing the importance of controlling the thermal treatment conditions to avoid exceeding 900°C. The thermal analysis results are in agreement with the scientific

literature, confirming that processing Tl-2234 within the 850-900°C range achieves the best balance between structural preservation, thermal stability, and good electrical performance [19].

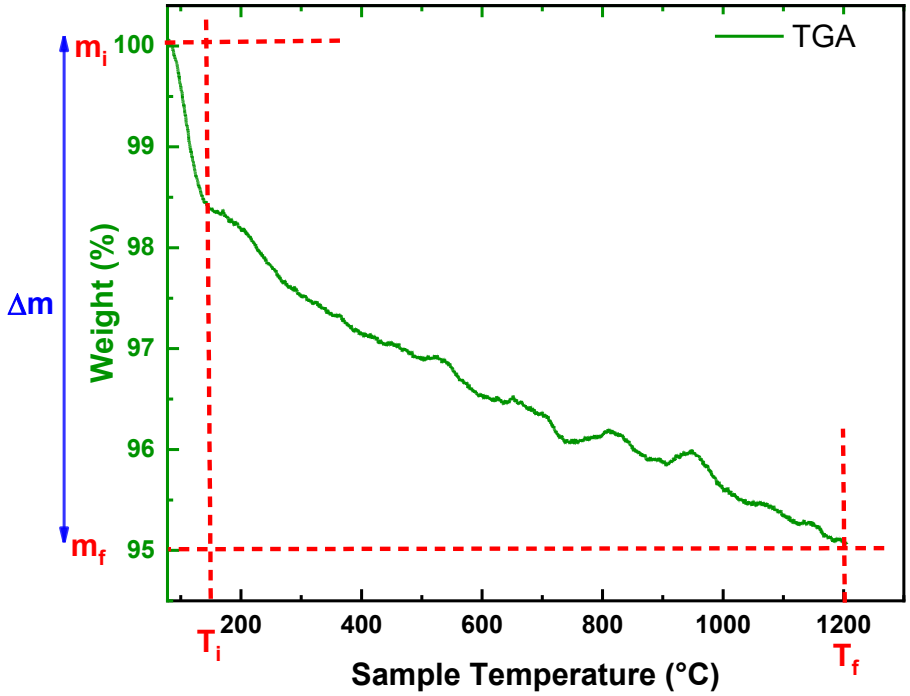

Figure 3 T_{GA} Curves of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Compound

3.3 Specific Heat Capacity Analysis of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Superconductor

The specific heat capacity (C_p) of the $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ superconductor was evaluated using Differential Scanning Calorimetry (DSC), a sensitive method for detecting thermal transitions and heat flow changes. In this method, a precisely weighed sample (typically ~40 mg) was subjected to a controlled heating rate of 10 °C/min in air. The heat flow data was recorded across a temperature range extending beyond the superconducting transition (Tc), typically from room temperature up to 1200 °C. To determine Cp, the area under the heat flow curve was integrated over a selected temperature interval (ΔT), and the specific heat was calculated using the equation [20]:

$$C_p = \frac{Heat\ flow\ (W)}{\beta \times m} \qquad (1)$$

Where:

β = Heating rate

m = sample mass

Figure 4 presents the Differential Scanning Calorimetry (DSC) analysis of the Tl-2234 high-temperature superconductor, illustrating how its specific heat capacity (C_p) varies with temperature at a heating rate of 10°C/min (0.1667°C/s). The inset focuses on the temperature range between 800°C and 980°C, where the DSC data reveals two distinct thermal transitions, reflecting a complex melting behavior associated with the multiphase nature of the material [21].The first thermal transition occurs between 799.94°C and 827.67°C, with a peak in Cp around 824.05°C. This increase in specific heat capacity indicates a significant thermal event, likely related to the melting or decomposition of a secondary phase or crystallographically distinct regions within the Tl-2234 structure. At 824°C, the specific heat capacity (Cp) is approximately 10 J/g·°C, representing a moderate increase that reflects a minor phase transformation or secondary melting. The second, larger and more prominent transition takes place between 918.59°C and 954.20°C, with a central C_p peak at 933°C. This substantial rise in specific heat capacity corresponds to the primary melting event of the main superconducting phase, where the Tl-2234 superconductor undergoes its main phase transition [22]. At 933°C, C_p reaches about 12 J/g·°C, indicating a larger increase associated with the main phase melting of Tl-2234.

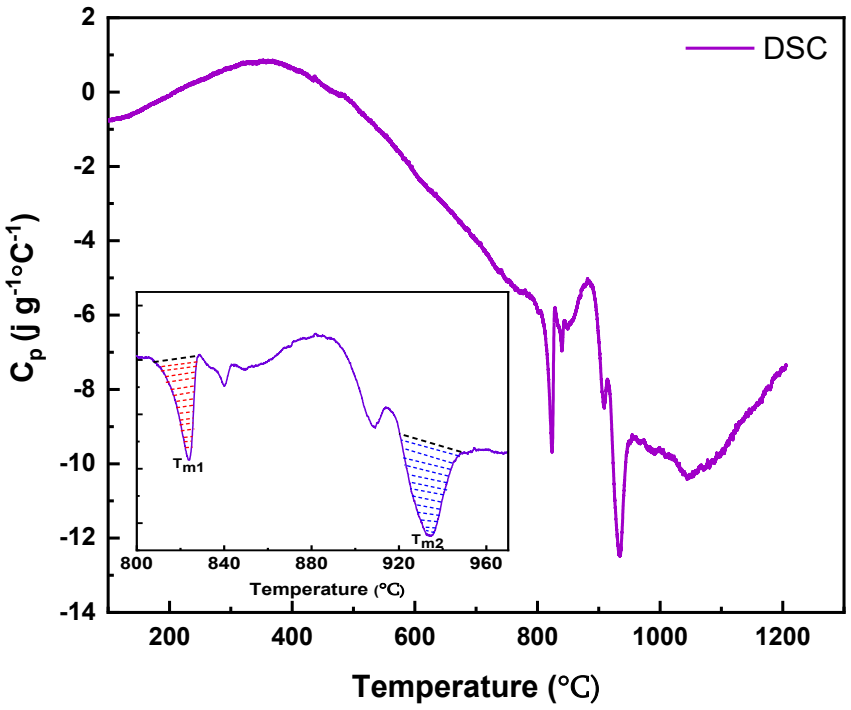

Figure 4. The specific heat capacity vs Temperature for $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ Superconductor

These increases in specific heat capacity (C_p) across the temperature range reflect the additional heat absorbed by the material during phase transitions and serve as precise indicators for understanding the complex thermal transformations occurring in these multiphase superconducting materials [23,24].

4. Conclusion

This comprehensive thermal analysis of $Tl_2Ba_2Ca_3Cu_4O_{11+\delta}$ superconductor using DSC and TGA has successfully established optimal processing parameters for high-performance synthesis. The DSC analysis identified four critical thermal events: superconducting phase formation at 824°C, crystallographic development at 839°C, phase instability onset at 907°C, and structural decomposition at 935°C. TGA results demonstrate exceptional thermal stability with less than 5% weight loss up to 1200°C, confirming the material's suitability for high-temperature applications. Specific heat capacity analysis revealed two major thermal transitions at 824°C (Cp = 10 J/g·°C) and 933°C (Cp = 12 J/g·°C), providing precise benchmarks for process control. The optimal processing temperature range is established at 850-900°C, ensuring maximum phase purity and superconducting performance (Tc up to 120 K) while preventing thermal degradation. The thermal processing procedures contribute significantly to the fundamental understanding of thallium-based superconductors and provide practical guidance for achieving optimal superconducting properties. This research establishes DSC and TGA as essential tools for understanding phase relationships in superconducting systems.

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