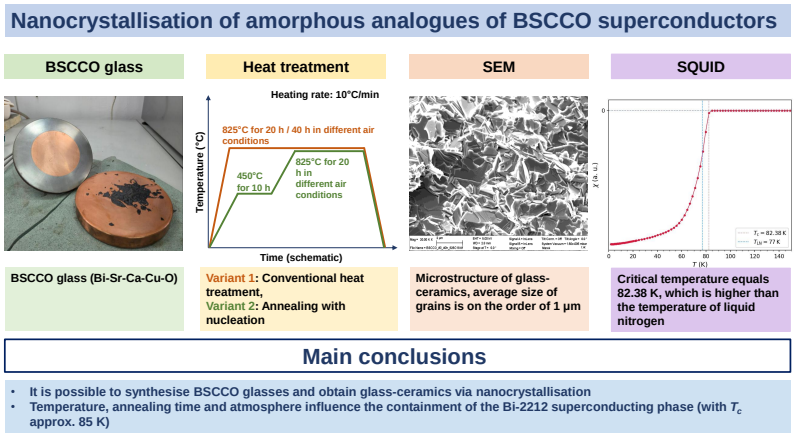
Nanocrystallisation of amorphous analogues of BSCCO superconductors

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Abstract

BSCCO ($Bi_2Sr_2Ca_{n-1}Cu_nO_x$) is a promising superconducting material that exhibits a high critical temperature (T_c). BSCCO superconductors can be mainly used in superconducting tapes in which the energy losses are very low, strong magnets, or particle accelerators at CERN. In this work, we synthesised glass samples using the melt-quenching method and subjected them to a proper thermal treatment, using nanocrystallisation approach to obtain glass-ceramic materials. The thermal, structural, and magnetic measurements were conducted using DTA, XRD, SEM, DC and RSO SQUID magnetometry methods. In samples annealed at 825°C at different times and air conditions, the Bi-2212 superconducting phase (with T_c of approx. 85 K) has been observed. The SEM investigation proves that the sample annealed at 825°C for 40 hrs in air conditions has a typical glass-ceramic microstructure, with well-distinguishable crystalline grains of the average size of 1 μm. The DC SQUID magnetometry of the sample annealed at 825°C for 20 hrs in air conditions showed that the obtained glass-ceramic has T_c = 82.38 K. Future investigations include either low-temperature and magnetic measurements of electrical conductivity, and optimising annealing conditions to gain the Bi-2223 phase (with T_c of approx. 105 K).



Keywords: superconductivity, glass-ceramics, BSCCO, high-temperature superconductors, cuprate superconductors

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1. Introduction

BSCCO ($Bi_2Sr_2Ca_{n-1}Cu_nO_x$) belongs to a family of cuprate superconductors exhibiting high critical temperature (T_c). It was first discovered by Maeda in 1988 [1] showing that BSCCO, in contrast to YBCO high–T_C superconductors (HTCS), exhibits even higher T_C. Furthermore, BSCCO does not require doping with rare earth elements. Subsequently, this group of materials was studied by many other researchers.

There are three main known types of BSCCO: 2201 ($n = 1$), 2212 ($n = 2$) and 2223 ($n = 3$), having T_c of approximately 20 K, 85 K and 110 K [2]. In Fig. 1, the tetragonal unit cells are shown.

One of the methods applied to obtain BSCCO was the synthesis of their glassy analogues and subjecting them to a proper thermal treatment, eventually obtaining glass-ceramics [3, 4]. This approach allows material to be obtained with significantly improved, among others, magnetic, mechanical, and electrical properties due to the presence of nanoscopic crystals of the size around 1-100 nm [5]. Such a method was applied, among others, by a group from Gdańsk University of Technology at the beginning of the third millennium [6, 7].

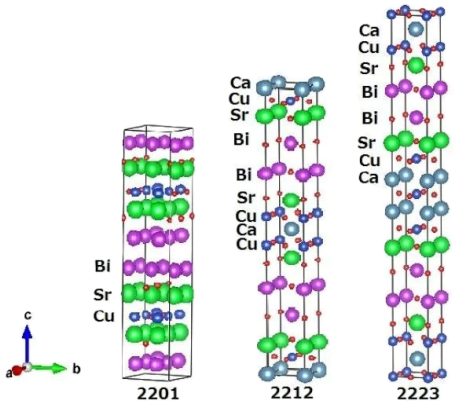


Figure 1: Crystal structure of three superconducting phases of BSCCO [8].

A similar method has been used in the Solid State Ionics Division at the Faculty of Physics (WUT) for decades to synthesise nanocrystalline analogues of selected cathode materials for lithium and sodium-ion batteries. Such nanocomposites exhibited significantly improved electrical properties due to the presence of nanocrystallites with highly disordered shells embedded in a glassy matrix [5].

In this work, we used the aforementioned experience to synthesise BSCCO glass-ceramics. Initially, five batches of glasses (labelled #1, #2, etc.) were synthesised by the melt-quenching technique. Then, the samples were examined in an air atmosphere using Differential Thermal Analysis (DTA) – to determine the glass transition and crystallisation temperature, and X-Ray Diffraction (XRD) – to verify amorphousness. Based on the results, an annealing process at different times, temperatures, and atmospheric conditions was conducted to obtain glass-ceramic samples. Then, all samples were characterised by XRD to identify their phase composition, while selected samples were further examined by Scanning Electron Microscopy (SEM) to investigate their microstructure. Eventually, the magnetic properties of one glass-ceramic sample were measured using a Superconducting Quantum Interference Device (SQUID) magnetometer in a DC, and RSO modes.

2. Results and discussion

DTA shows that the glass transition occurs between 400°C and 450°C, so the glass transition temperature (T_g) can be estimated as ca. 420°C. Also, the crystallisation temperatures are approximated as ca. 466°C, ca. 513°C, and ca. 828°C. Finally, the melting temperature equals ca. 850°C, which is shown in Fig. 2.

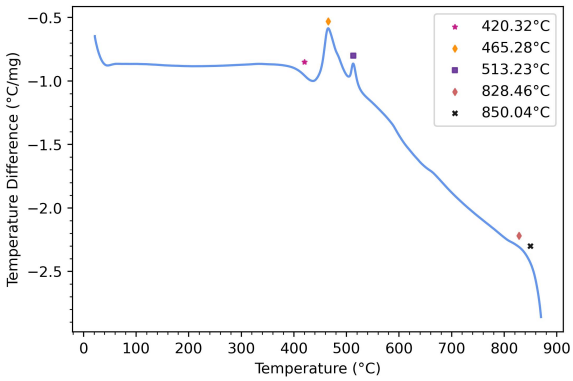


Figure 2: DTA trace for glass sample BSCCO #1 acquired upon heating from 21.5°C to 900°C with heating rate 10°C min^{-1}.

XRD of BSCCO #1, #3, and #4 confirms that the samples are amorphous, as shown in Fig. 3. However, some crystalline peaks are visible, especially those of cubic CaO ($a = 4.82$ Å). The remaining batches (i.e., #2 and #5) appeared to be crystalline from the very beginning, and they were not studied further.

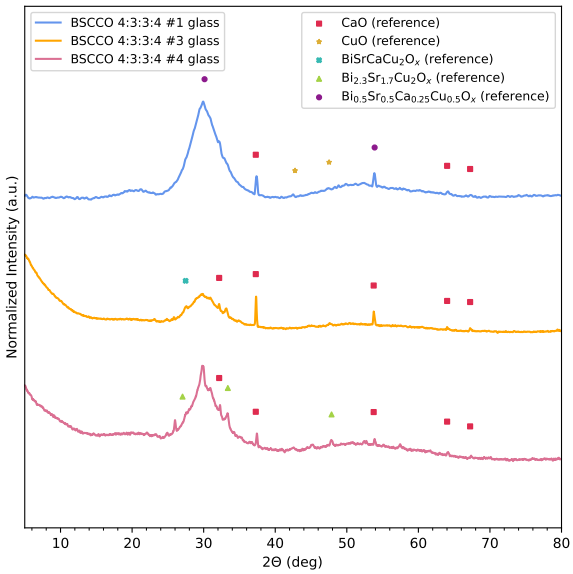


Figure 3: XRD patterns of the amorphous samples. Some crystalline phases can be noticed.

XRD of glass-ceramics annealed at 825°C for: i) 20 hrs, ii) 40 hrs, and subjected to nucleation at 450°C for 10 hrs, followed by annealing at 825°C for 20 hrs, at different atmospheres, confirms that all samples include the Bi-2212 tetragonal crystalline phase ($a = b =$ 5.3979 Å, $c =$ 30.6850 Å), as shown in Fig. 4.

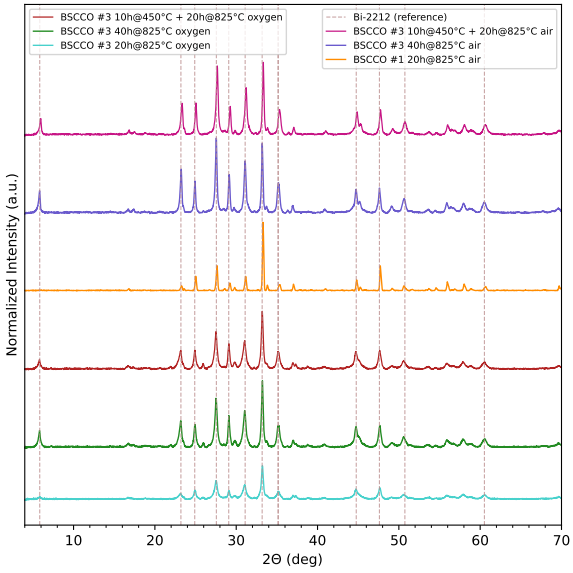


Figure 4: XRD patterns of BSCCO glass-ceramics, annealed at 825°C for different time duration and in different atmosphere.

Fig. 5a and 5b show the microstructure of the sample #3 annealed at 825°C for 40 hrs. A microstructure typical of glass-ceramics is observed, with well-distinguishable crystalline grains (Fig. 5a). The average size of grains is on the order of 1 µm (Fig. 5b).

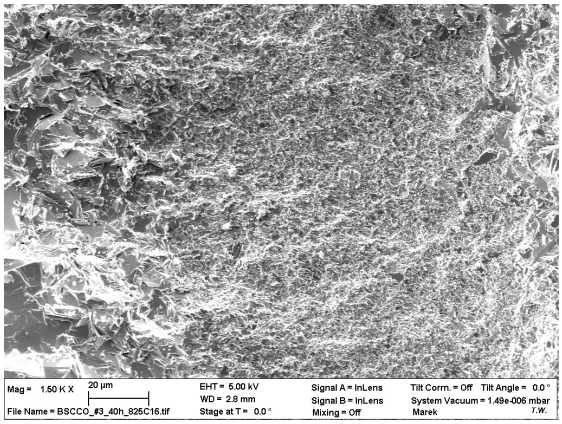


Figure 5a: SEM photo taken with a magnification of 1.50 K X. A microstructure typical of glass-ceramics is observed.

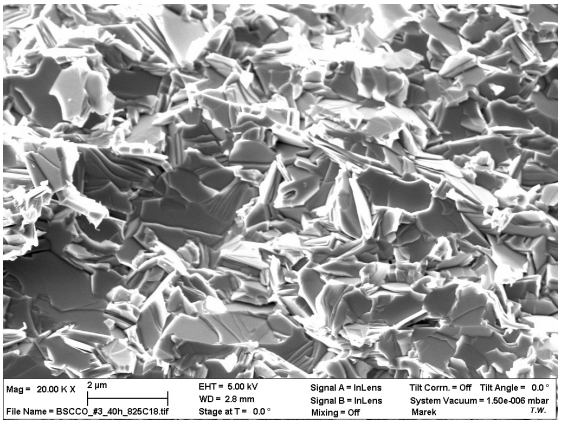


Figure 5b: SEM photo taken with a magnification of 20.00 K X. The average size of grains is on the order of 1 µm.

Preliminary magnetic characterisation of sample #1 annealed at 825°C for 20 hrs is shown in Fig. 6. Below T_c = 82.38 K, the magnetic susceptibility (χ) is lower than zero, which means that the magnetic field is expelled. When $\chi \approx 0$, the normal state is observed.

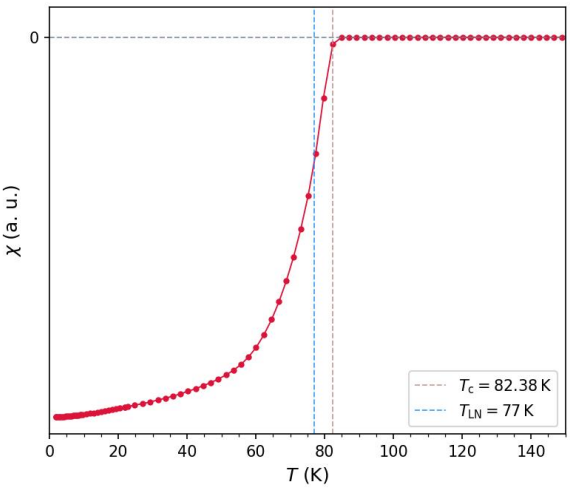


Figure 6: Temperature-dependent magnetic suscpeptibility (χ) of sample #1 annealed at 825°C for 20 hrs. T_N is the temperature of liquid nitrogen.

3. Methodology

Five glass samples were synthesised using the melt-quenching method, according to the approach described in detail in Ref. [6]. Two compositions were prepared: i) Bi_2O_3, $SrCO_3$, $Ca(NO_3)_2{\cdot}4H_2O$ and CuO for sample #1 and #3, ii) Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO for the remaining samples. The high-purity starting materials were mixed in a Bi:Sr:Ca:Cu molar ratio of 4:3:3:4. The mixtures were melted in a furnace at 1250°C for 15 minutes in an air atmosphere using a platinum crucible. Afterwards, the melts were quenched between copper plates, obtaining glassy materials. XRD studies confirmed the amorphousness.

DTA measurement was conducted on the first glass sample using a Thermal Analysis Q600 calorimeter. It was carried out in an air atmosphere with a heating rate of 10°C min^{-1}.

Then, the batches were nanocrystallised with a heating rate of 10°C min^{-1}. The batches were annealed at 825°C for: i) 20 hrs, ii) 40 hrs. Also, one sample was subjected to nucleation at 450°C for 10 hrs, followed by annealing at 825°C for 20 hrs. The same temperature and time conditions were employed during the investigation of the influence of an oxygen atmosphere on nanocrystallisation of the Bi-2212 superconducting phase, according to Ming Xu's study [9] (as cited by Wong, 1994 [10]).

Thereafter, XRD data were collected using Cu-Kα radiation (λ = 1.54 Å), filtered by a focusing X-ray mirror using a Panalytical Empyrean Series 2 diffractometer, and equipped with a PIXcel3D detector in the angle range of 2.60° to 100°. Afterwards, SEM observations were conducted for the sample #1 annealed at 825°C for 40 hrs in an air atmosphere, using a Carl Zeiss Auriga - CrossBeam Workstation device. The photos were taken with an electron imaging resolution of 1 nm at 5 kV. Finally, magnetic properties were carried out on the SQUID magnetometer Quantum Design MPMS XL for the sample #1 annealed at 825°C for 20 hrs. The measurement was conducted over a temperature range of 1.9 - 300 K, up to 20 Oe, in DC, and RSO modes.

4. Conclusions

This work confirmed that it is possible to synthesise BSCCO glasses and obtain glass-ceramics via nanocrystallisation within the technological park available at the Faculty of Physics. It is noticeable that temperature and annealing time influence the containment of the Bi-2212 phase. By now, the Bi-2212 phase (with T_c reported in the literature to be approx. 85 K) was obtained after annealing at 825°C for more than 20 hrs. Prolonged heat-treatment leads to micrometer-sized grains with a size of approx. 1 µm. Preliminary magnetic measurements demonstrated that a glass-ceramic sample obtained within this work exhibited superconductivity below T_c = 82.38 K. The behaviour of the studied sample was typical for a high-temperature superconductor.

Further work includes low-temperature measurements of electrical conductivity and magnetisation. Also, the influence of annealing in an oxygen atmosphere is necessary to be conducted in order to obtain the Bi-2223 superconducting phase.

Acknowledgements

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