Original Paper

Use of Ga_2O_3 and In_2O_3 in forming superconducting glass-ceramics in the Bi–Sr–Ca–Cu–O system

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Glass-ceramic processing of Bi–Sr–Ca–Cu–O superconductors was improved through the addition of the intermediate glass formers gallium and indium. The gallium and gallium/indium additions produced $Bi_2Sr_2Cu_1O_6$ and $Bi_2Sr_2CaCu_2O_8$. The $\vartheta_x - T_g$ difference for the gallium and gallium/indium glasses was increased to 73 and 89 K, respectively, with optimum molar ratios for $Bi_2Sr_2Ca_2Cu_3O_{10}$ (stoichiometric batch): gallium = 1.0 : 1.0 and for $Bi_2Sr_2Ca_2Cu_3O_{10}$ (stoichiometric batch): gallium : indium = 1.0 : 0.9 : 0.1, respectively.

Verwendung von Ga_2O_3 und In_2O_3 zur Bildung supraleitender Glaskeramiken im System Bi–Sr–Ca–Cu–O

Durch den Zusatz der Zwischenglasbildner Gallium und Indium wurde die Herstellung von Bi–Sr–Ca–Cu–O-Supraleitern auf dem glaskeramischen Weg verbessert. Die Bildung von $Bi_2Sr_2Cu_1O_6$ und $Bi_2Sr_2CaCu_2O_8$ konnte durch die Additive Gallium und ein Gallium/Indiumgemisch erleichtert werden. Die Temperaturdifferenz $\vartheta_x - T_g$ wurde in den Gallium- und Gallium/Indium-Gläsern auf 73 bzw. 89 K erhöht. Als optimale Molverhältnisse hierfür stellten sich heraus: für $Bi_2Sr_2Ca_2Cu_3O_{10}$ (stöchiometrisches Gemenge): Gallium = 1,0 : 1,0 und für $Bi_2Sr_2Ca_2Cu_3O_{10}$ (stöchiometrisches Gemenge): Gallium : Indium = 1,0 : 0,9 : 0,1.

1. Introduction

The application of mature glass forming technology to the manufacturing of practical high ϑ_c superconductors is a highly desirable goal. Glass-ceramics offer many advantages over typical solid state reactions. They can produce a material which is 99.9 % dense, has superior strength, could have connectivity of the superconducting phases, and offers chemical control of both principal and grain boundary compositions. All of these advantages could increase mechanical strength and critical current density.

Glass-ceramics are materials formed using typical glass forming techniques and then heat-treated to devitrify the desired ceramic phase throughout the glass matrix. A goal in making a useful glass-ceramic is to first produce a glass with a large enough difference between the glass transition temperature (T_g) and the first onset crystallization temperature (ϑ_x) to allow for good formability. The glass must then be heat-treated to allow for nucleation and complete devitrification. The heat treatments must be sufficient to fully crystallize the desired phase but must not induce slumping and flowing of the product.

A number of problems stand in the way of using the glass-ceramic route to produce practical high ϑ_c superconductors. The most serious is the requirement of making a glass: Compositions which permit vitrification may not permit the crystallization of the desired phase. In the case of the $YBa_2Cu_3O_{7-\delta}$ (123)[1]) phase, the addition of a glass former is required to induce glass formation. The first glass-ceramic studies [1] showed that B_2O_3 will permit glass formation and further allow the crystallization of the 123 phase [2 to 4]. On the other hand, some glasses can be made in the bismuth superconducting system (Bi–Sr–Ca–Cu–O) with no modifications to the superconducting phase's stoichiometry. Bismuth is an intermediate glass former [5] and will support a glassy network in the presence of ions of copper, calcium, and strontium for example. Glasses made from various ratios of bismuth, strontium, calcium, and copper have been devitrified to form superconducting crystals of $Bi_2Sr_2CuO_6$ (2201 compound) [6], $Bi_2Sr_2CaCu_2O_8$ (2212 compound) [7 and 8], and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223 compound) [9 to 12].

Another problem is that the actual high-temperature reactions which occur in the glass may not be those required to permit the formation of a desired superconducting phase. For example, in the Bi–Sr–Ca–Cu–O (BSCCO) system, the first phase to crystallize is $Bi_2Sr_2Cu_1O_6$ [6]. However, the formation of the desired $Bi_2Sr_2CaCu_2O_8$ phase is the product of a diffusion reaction into the $Bi_2Sr_2Cu_1O_6$

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[1]) In the following code numbers will be used which refer to the systems Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O. The abbreviations for the formed phases are:
123 : $YBa_2Cu_3O_{7-\delta}$, 2212: $Bi_2Sr_2CaCu_2O_8$,
2201: $Bi_2Sr_2Cu_1O_6$, 2223: $Bi_2Sr_2Ca_2Cu_3O_{10}$.

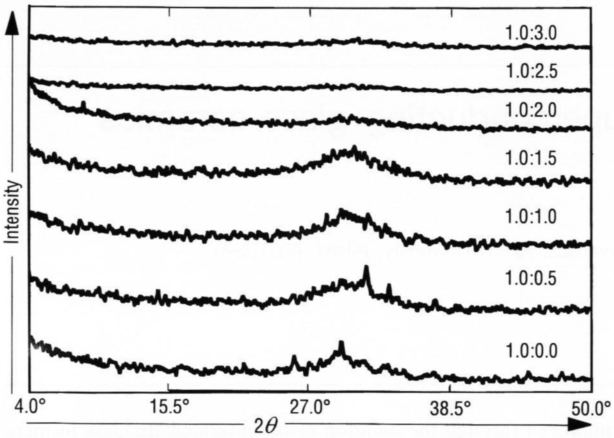

Figure 1. XRD patterns of gallium glasses with a 2223 stoichiometric batch in increasing molar ratios of gallium.

phase [8]. As a result, glass-ceramic like technology is still applicable. Despite such problems, progress has already been made towards making practical superconductors using this technology [13 and 14]. The principal remaining problem is the limited extent of the glass-forming range. The goal of this study is to find a glass that has an acceptable $\vartheta_x - T_g$ difference, can maintain its form after long heat treatments, and will promote the formation of the desired ceramic phase. As a starting point the authors [15] chose to pursue the suggestion of Aßmann et al. [16] and look at additions of Ga_2O_3 as a glass former.

2. Experimental procedure

2.1. Sample preparation with gallium

The gallium study involved adding gallium to a 2223 cation stoichiometric batch composition to help increase the $\vartheta_x - T_g$ difference. This method was first attempted by Aßmann et al. [16]. The basic starting materials (Bi_2O_3, CuO, CaO, $Sr(NO_3)_2$, Pb_2O_4, and Ga_2O_3) were weighed out in the stoichiometric proportions (in mol%) of 1.0 : 0.0 (1.0 mole 2223 compound : 0.0 mole gallium), 1.0 : 0.5, 1.0 : 1.0, 1.0 : 1.5, 1.0 : 2.0, 1.0 : 2.5, and 1.0 : 3.0. The 2223 compound refers to 1.6 mole bismuth, 0.4 lead, 2.0 strontium, 2.0 calcium, and 3.0 copper. These 10 g batches were mixed by hand in a mortar and pestle for 40 min. Melting was carried out at 1100 °C in a resistance furnace in a platinum or MgO crucible for 7 min. All samples were quenched to room temperature between two steel plates. The glasses produced underwent X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Differential Thermal Analysis (DTA). The glasses were then heat-treated in a resistance furnace on platinum foil in air to determine the phases associated with the peaks found in the DTA and DSC runs.

Table 1. T_g values of stoichiometric batch compositions with increasing gallium addition (2223 phase : gallium) and ϑ_x values of formed 2201 and 2212 phases after heat treatment

2223 phase : gallium		ϑ_x (in °C) of the formed phases	
composition	T_g in °C	2201 phase	2212 phase
1.0 : 0.0	369	436	750
1.0 : 0.5	405	474	775
1.0 : 1.0	433	506	766
1.0 : 1.5	425	536	750
1.0 : 2.0	430	559	743
1.0 : 2.5	475	609	750
1.0 : 3.0	450	609	738

2.2. Sample preparation with gallium/indium mixture

The gallium/indium study involves taking the best 2223/gallium glass and partially replacing the gallium with indium. This method was chosen because of the trend displayed in the work by Aßmann et al. [16]. Generally speaking Aßmann's group found that as the ion size increased the $\vartheta_x - T_g$ difference also increased. Aßmann et al. did not study the effects of indium. Since indium is too ionic to be an intermediate glass former it can not be used alone. Therefore it was used to partially replace gallium in the 1.0 : 1.0 batch. The methods of study used in this experiment are exactly the same as that used in the gallium study. The stoichiometric ratio of the base composition used was 1.0 : 1.0 (gallium : indium) where the 1.0 gallium was broken down into 0.9 : 0.1, 0.8 : 0.2, 0.7 : 0.3, 0.6 : 0.4, 0.5 : 0.5. In other words, the total batch compositions were: 1.0 : 0.9 : 0.1, 1.0 : 0.8 : 0.2, etc. The indium was obtained in the form of In_2O_3.

3. Results

3.1. Influence of the addition of gallium

Figure 1 shows the amorphous XRD patterns of the glasses produced with gallium. Upon heat treatment at various temperatures as specified by the peaks in the DSC and DTA scans it was found that the first phase to devitrify after T_g was the 2201 phase. CuO also crystallizes just above the 2201 crystallization temperature. Table 1 presents the values of T_g and ϑ_x of the 2201, and 2212 compounds in the samples. Heat treatments at 850 °C in air were not successful in producing the 2223 compound. The largest $\vartheta_x - T_g$ difference (159 K) occurred with the 1.0 : 3.0 sample. The 1.0 : 1.0 sample (the sample predominantly studied by Aßmann et al.) displayed a $\vartheta_x - T_g$ difference of 73 K.

The samples were then heat-treated for 1 and 24 h to help to identify the crystallization peaks. Table 2 shows the phases present at various temperatures.

Table 2. Survey of the formed phases after a heat treatment of stoichiometric batch compositions with increasing gallium addition as determined by XRD

Composition of 2223 phase : gallium	formed phases after DSC and at various temperatures (in °C)				
	DSC	400 to 500	530	775	850
1.0 : 0.0	2201, –	2201, –	–, –	2212, –, –	2212
1.0 : 0.5	2201, CuO	2201, CuO	2201, CuO	2212, –, –	2212
1.0 : 1.0	2201, CuO	–, –	2201, CuO	2212, –, –	2212
1.0 : 1.5	2201, CuO	–, –	2201, CuO	2212, 2201, CuO	melted
1.0 : 2.0	2201, CuO	2201, CuO	2201, CuO	2201, CuO, –	melted
1.0 : 2.5	2201, CuO	–, –	2201, CuO	2201, CuO, –	melted
1.0 : 3.0	2201, CuO	–, –	2201, CuO	2201, CuO, –	melted

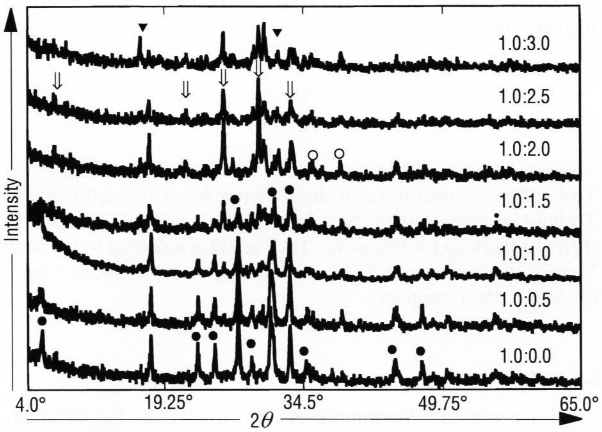

Figure 2. XRD patterns of heat-treated gallium glasses with a 2223 stoichiometric batch in increasing molar ratios of gallium at 775 °C for 24 h. ●: 2212 phase, ↓: 2201 phase, ○: CuO, ▼: $(Ca, Sr)_2PbO_4$.

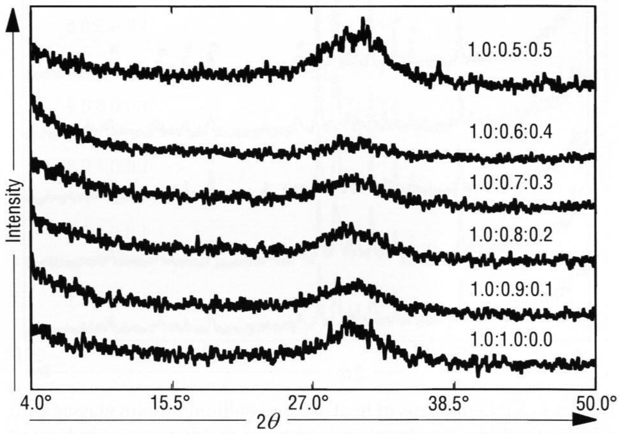

Figure 3. XRD patterns of gallium/indium glasses with a 2223 stoichiometric batch in increasing molar ratios of indium.

The 2212 phases were not present until the samples were heat-treated at 775 °C. The 0.0 to 1.5 mole compositions of gallium displayed the 2212 phase but, as the amount of gallium increased, so did the concentration of the 2201 phase and CuO. This trend can be seen in figure 2. Though the 1.0 : 1.5 composition had higher $\vartheta_x - T_g$ differences it also contained the 2201 phase. Therefore the 1.0 : 1.0 composition, which only formed the 2212 phase, is the best composition for obtaining the 2212 phase in a glass-ceramic. It should be noted that none of the samples slumped while being heat-treated.

3.2. Influence of the addition of the gallium/indium mixture

The amorphous XRD patterns of the glasses formed from the addition of gallium/indium are presented in figure 3. Heat treatments for 1 and 24 h at various temperatures to ascertain the phases present at each DTA and DSC peak were carried out. Table 3 shows the results of the heat treatments. The 1.0 : 0.9 : 0.1 composition had a $\vartheta_x - T_g$ difference of 89 K. This is larger than that of the original composition of

Table 3. T_g values of stoichiometric batch compositions with increasing gallium/indium addition (2223 phase : gallium : indium) and ϑ_x values of formed 2201 and 2212 phases after heat treatment

2223 phase : gallium : indium		ϑ_x (in °C) of the formed phases	
composition	T_g in °C	2201 phase	2212 phase
1.0 : 0.9 : 0.1	420	509	775
1.0 : 0.8 : 0.2	420	491	775
1.0 : 0.7 : 0.3	410	478	737
1.0 : 0.6 : 0.4	400	475	750
1.0 : 0.5 : 0.5	405	469	775

1.0 : 1.0 : 0.0 which was 73 K. XRD analysis of the samples shows that the 2201 phase and CuO always crystallize first at low temperatures. Table 4 shows the results of XRD analysis data. At 775 °C, the 2212 phase formed. Figure 4 shows the XRD patterns of the heat-treated samples at 775 °C. All of these samples remained stable during heat treatment at 775 °C. It should be noted that the formation of the 2212 phase is associated with an endothermic DTA peak rather than the exothermic peak expected from a crystallization. The ϑ_x values quoted here are

Table 4. Survey of the formed phases after a heat treatment of stoichiometric batch compositions with increasing gallium addition as determined by XRD

composition of 2223 phase : gallium : indium	formed phases after DSC and at various temperatures (in °C)					
	DSC	400 to 500	500 to 550	600	775	850
1.0 : 0.9 : 0.1	2201, CuO	2201, CuO	2201, CuO	–, –	2212	melted
1.0 : 0.8 : 0.2	2201, CuO	2201, CuO	2201, CuO	–, –	2212	melted
1.0 : 0.7 : 0.3	2201, CuO	2201, CuO	–, –	–, –	2212	melted
1.0 : 0.6 : 0.4	2201, CuO	2201, CuO	2201, CuO	–, –	2212	2212
1.0 : 0.5 : 0.5	2201, CuO	2201, CuO	–, –	2201, CuO	2212	2212

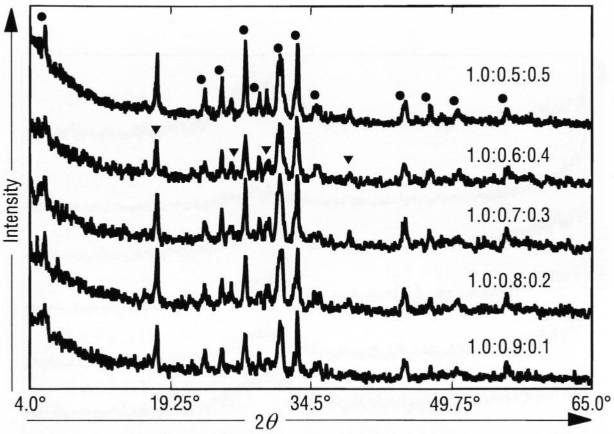

Figure 4. XRD patterns of heat-treated gallium/indium glasses with a 2223 stoichiometric batch in increasing molar ratios of indium at 775 °C for 24 h. ●: 2212 phase, ▼: $(Ca, Sr)_2PbO_4$.

obtained from the location of this endothermic peak and should not be viewed as a conventional value for ϑ_x. Matheis et al. [7] have shown that the formation of the 2212 phase occurs as a diffusion reaction of CuO into the 2201 phase thus accounting for the presence of an endothermic peak in this region of the DTA curve.

4. Conclusions

As table 1 shows, adding 1.0 mole of gallium to 1.0 mole of a $Bi_2Sr_2Ca_2Cu_3O_{10}$ stoichiometric batch does significantly improve the $\vartheta_x - T_g$ difference. As the concentration of gallium increases the $\vartheta_x - T_g$ difference also increases. However, the position of T_g is sometimes ambiguous and therefore not highly reliable. Furthermore, at higher concentrations of gallium it becomes more difficult to crystallize a superconductive phase.

The gallium/indium addition (1.0 : 0.9 : 0.1) resulted in a $\vartheta_x - T_g$ difference, as seen in table 3, that was higher than that of the gallium sample (1.0 : 1.0). As the indium concentration increased the $\vartheta_x - T_g$ difference decreased because of the indium's inadequate glass-forming abilities. The $Bi_2Sr_2Ca_2Cu_3O_{10}$: gallium : indium composition of 1.0: 0.9: 0.1 produced a good glass with a working range of approximately 90 K.

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