The Effect of Processing Parameters on HTS Tube Characteristics

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High-temperature Superconductor(HTS) tubes were fabricated in terms of different chemical compositions and various $SrSO_4$ additions by centrifugal forming method. For powder melting by induction the optimum range of melting temperatures and preheating temperature were 1050 ℃, 1100 ℃ and 550 ℃ for 30 min, respectively. The mould rotating speed was 1000 rpm. A tube was annealed at 840 ℃ for 72 hours in oxygen atmosphere. The plates like grains more than 20 μm were well developed along the rotating direction of mould regardless of initial chemical compositions and the amounts of $SrSO_4$ in Bi2212. The specimen with Bi2212 composition exhibited T_c of 83 K, while the specimens fabricated with other compositions are lower than 60 K. The measured I_c and J_c at 77 K(B = 0 T) in Bi2212 with 7 % $SrSO_4$ composition were about 680 A and 380 A/㎠.

Keywords : Centrifugal forming process, HTS tube, I-V characteristics, I_c, J_c

1. INTRODUCTION

$Bi_2Sr_2CaCu_2O_y$(Bi2212) superconductor is one of the most promising and very attractive materials as a conductor for energy applications among other superconductors because of its easy c-axis alignment, which reduces a weak-link behaviour and maintains high critical current density(J_c) of a-b plane orientation. From a practical point of views these features are very important in bulk HTS applications, such as wires, current leads(CL) and fault current limiters(FCL). So far a number of processing techniques, such as the doctor blade method[1], the dip-coating method[2], the organometallic method[3] and the powder-in-tube method[4] have been proposed in order to fabricate conductors with a high critical current density. All of these methods employ a slow solidification process from a partially molten state in order to enhance texturing of c-axis grain alignment, Which results in a significant improvement of intergrain coupling.

Among them, melt casting process(MCP) is well known as one of novel techniques to manufacture the 3 dimensional compact bodies[5]. MCP Bi2212 rods and the tubes have been successfully tested in a variety of current lead design[6]. The typical advantage of MCP is the fact that any geometry of superconductor with excellent current carrying properties can be easily fabricated. Additionally the temperature and field dependence of the critical current of the material is superior to that of the sintered HTS bulk parts. The HTS MCP bulk is characterized by the absence of weak links. The J_c(77 K, B = 0 T) of the melt casted Bi2212 tubes fabricated by Aventis & Technologies was 600 ℃ 4000 A/cm^2, depending on the tube dimensions[7,8].

The Bi2212 phase is stable in a wide range of compositions and processing temperatures in a form in which T_c is influenced by the composition. It is well known that the highest T_c(93 K) can be obtained in Sr rich samples(Sr:Ca = 2.2:0.8) in Bi2212 state[9]. However there are not many reports and results of Bi HTS on the solidification process after complete melting.

In this study, Bi based tubes with 4 different chemical compositions were fabricated by a complete melting. Also as a separate work, the tube characteristics were systematically evaluated in terms of various $SrSO_4$ amount in Bi2212. Our preliminary results indicate that electrical characteristics and microstructure were quite dependent on the processing parameters, especially initial compositions and the amounts of $SrSO_4$. This paper will discuss about tube fabrication process and compare the tube characteristics including superconducting properties depending on compositions and amount of $SrSO_4$ addition.

2. EXPERIMENTAL

As an initial composition, 4 different chemicals in Bi:Sr:Ca:Cu = 2.0:2.0:1.0:2.0, 2.1:2.0:1.0:2.0, 2.2:1.8:1.0:2.0 and 2.2:1.8:1.0:2.2 cation ratios were designed and prepared by a routine solid state reaction. Typical powders with different composition were charged into a platinum crucible for the complete melting, which is one of important processes in Centrifugal Forming Process(CFP). The melting was done by inductive heating at 1,050 ℃ and 1,100 ℃ within 5 min in platinum crucible in order to maintain initial composition from excessive Bi evaporation and any possible contamination. Following that, the solution of the melted powder was poured into the mould rotating at 1,000 rpm, which was preheated at 550 ℃ for 30 min. The purpose of preheating is to prevent mechanical damage during transportation from melt to mould and solidification. For the electrical contact, 0.5 mm thickness of silver tape was inserted into the top and bottom of mould. Normally the specimen was mechanically stable when the melting temperature was over 1,035 ℃ and mould was preheated over 400 ℃ for 30 min. The tube was annealed at 840 ℃ for 72hours in oxygen atmosphere. Following that, the temperature was slowly cooled down to 740 ℃ at a rate of 1.5 ℃/min and then left to room temperature. As a separate work, tube characteristics were systematically studied with different weight % of $SrSO_4$ from 0 to 15 % in Bi2212. The fabrication stages are exactly the same as described above. For the tube fabrication, normally CFP process are mainly divided into 3 parts depending on its role and functions; the meting part by high inductive frequency, the centrifugal forming part for the tube shape and efficient microstructure control of Bi2212 phase and finally, the moulding part for tube detachment after heat treatment.

For the structural analysis and phase identification X-ray diffraction method was employed. Microstructure observation was performed by a scanning electron microscopy(SEM) on both the surface and the inner side of the tube. The critical temperature(T_c) was measured by four-probe resistive method and the transport critical current(I_c) and current density(J_c) were determined from the current/voltage curve using a 1 μV/cm criterion respectively.

3. RESULTS AND DISCUSSIONS

Figure 1 shows Bi2212 based tubes with a silver electrode fabricated by Centrifugal Forming Process. Typical tube dimension was 30/27 mm in outside/inside diameter and 150 mm in length. The tube surface was quite smooth and looks homogeneous.

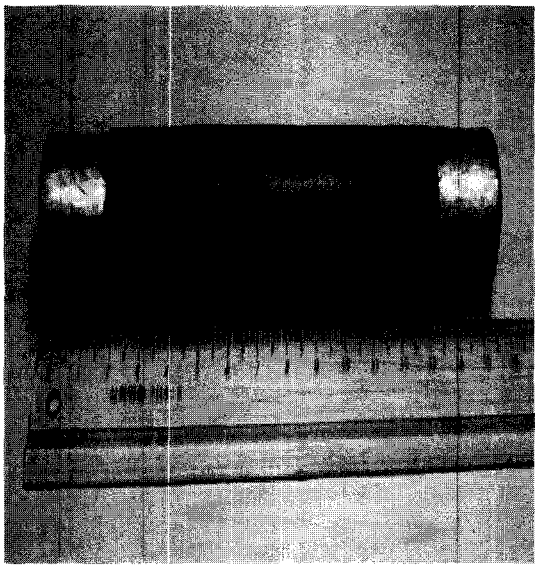
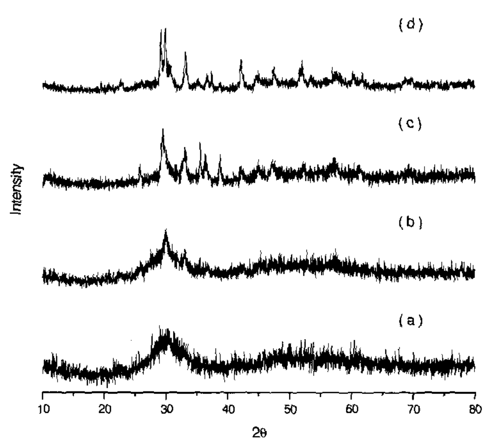


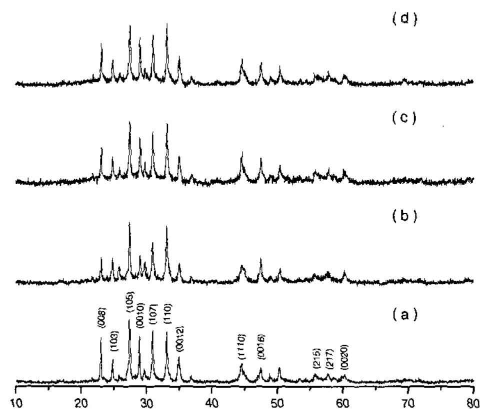
Fig. 1. Bi 2212 based tubes with a silver electrode fabricated by centrifugal forming process (dimension: 30 mm x 150 mm x 23 mm).

For the process, the optimum range of melt and preheating temperatures and time for mould were 1050 ℃,1100 ℃ and 550 ℃ for 30 min respectively. The applied mould rotating speed was 1000 rpm. Final tube density and shape were quite dependent on many processing parameters such as melting temperature, melting time, mould rotation speed and heat treatment schedule. Especially proper adjustment in viscosity of melted powder is important to control the uniform thickness and length. It was confirmed the melted solution was solidified within 20 sec when it contacted with a mould, which was preheated at 550 ℃. Therefore it seems the mould rotation speed more than 500 rpm does not much affect texture formation.

Figure 2 represents XRD diffraction patterns taken from the surface of tube with 4 different chemical compositions. The XRD data suggests that the phase formed after direct solidification from melt is identified as amorphous phase. After heat treatment at 840 ℃ for 72 hours in oxygen atmosphere diffraction patterns indicate the existence of multiphase mixture consisting of prominent Bi2212 with some additional peaks from some other phases of Bi2201, Cu-free and (Sr,Ca)-Cu-O phases. It was known that Bi2212 phase decomposes into a liquid phase plus the solid phase of Bi-(Sr,Ca)-O(Cu free phase) and (Sr,Ca)-Cu-O at the partial melting temperature, about 870 ℃ during the heating process [10]. However Bi2212 phase was predominant regardless of compositions while the peak intensity was somewhat varied in terms of initial chemical composition.



(a) before heat treatment



(b) after heat treatment

Fig. 2. XRD diffraction patterns taken from the surface of tube with 4 different chemical compositions:
(a) $Bi_2Sr_2Ca_1Cu_2O_x$, (b) $Bi_{2.1}Sr_2Ca_1Cu_2O_x$,
(c) $Bi_{2.2}Sr_{1.8}Ca_1Cu_2O_x$ and (d) Bi $_{2.2}Sr_{1.8}Ca$ $_{1.2}Cu_2O_x$

Figure 3 shows diffraction patterns in terms of different $SrSO_4$ addition in Bi2212 compounds after heat treatment
at 840 ℃ for 72 hours in oxygen atmosphere. As can be seen in Fig. 4, most of main peaks are relatively well matched with Bi2212 diffraction ones even though there are some variations of peak intensity and some minor phases as indicated above. Therefore, the XRD results suggest that the electrical properties will be hindered or influenced by the existence of some other non-superconducting phases.

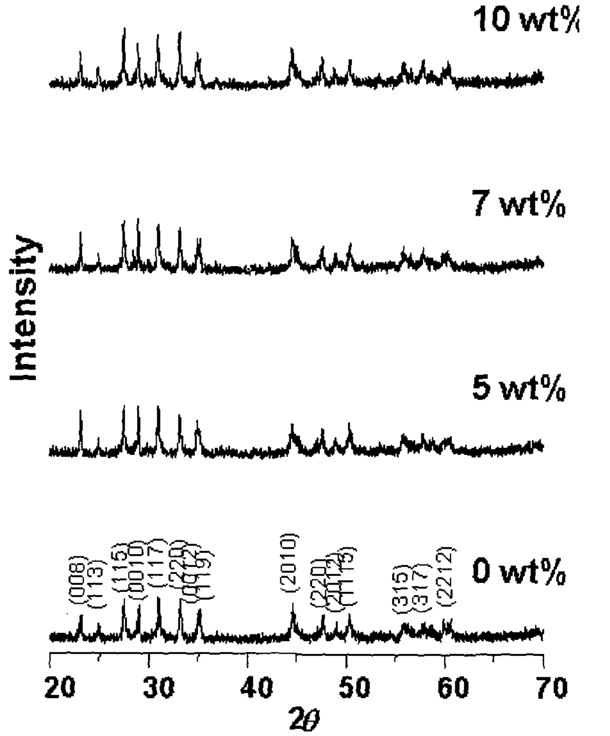
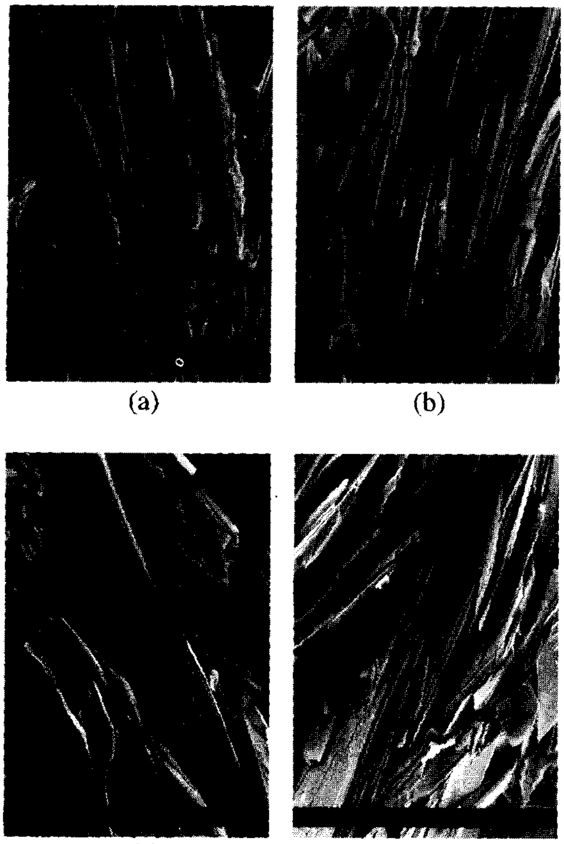


Fig. 3. XRD diffraction patterns in terms of different $SrSO_4$ addition in Bi2212 compounds after heat treatment at 850 ℃ for 72 hours in oxygen atmosphere.

Figure 4 shows SEM micrographs of fractured tube surface with different compositions. The plate shaped structure more than 20 μm was well developed and densified along the rotating direction of mould regardless of initial chemical compositions. Theses kinds of orientations were significant for the fractured surface close to mould as compared with one near the inner part of the tube.



(a) (b)

(c) (d)

Fig. 4. SEM micrographs of fractured tube surface with different compositions:
(a) $Bi_2Sr_2Ca_1Cu_2O_x$ (b) $Bi_{2.1}Sr_2Ca_1Cu_2O_x$
(c) $Bi_{2.2}Sr_{1.8}Ca_1Cu_2O_x$ and (d) $Bi_{2.2}Sr_{1.8}Ca_{1.2}Cu_2O_x$

Figure 5 represents the SEM image and EDAX results taken on the fractured surface of Bi2212 tube with 7 weight % of $SrSO_4$. Sulfur element was strongly detected, especially near the grain boundary; even XRD data does not reveal the exact existence of Sulfur compound as a second phase

Figure 6 shows temperature-resistance of the tube fabricated with 4 different compositions. After heat treatment at 840 ℃ for 72 hours in oxygen atmosphere the specimen with 2212 composition exhibited T_c of 83 K while the specimens with other composition are as low as 60 K or much lower than 60 K with a broad transition width and long tail, which is lower than what we expected. This can be explained by the poor grain boundary connectivity related with the phase decomposition of Bi2212, oxygen deficient phases, porosity and other impurities near the grain boundary area.

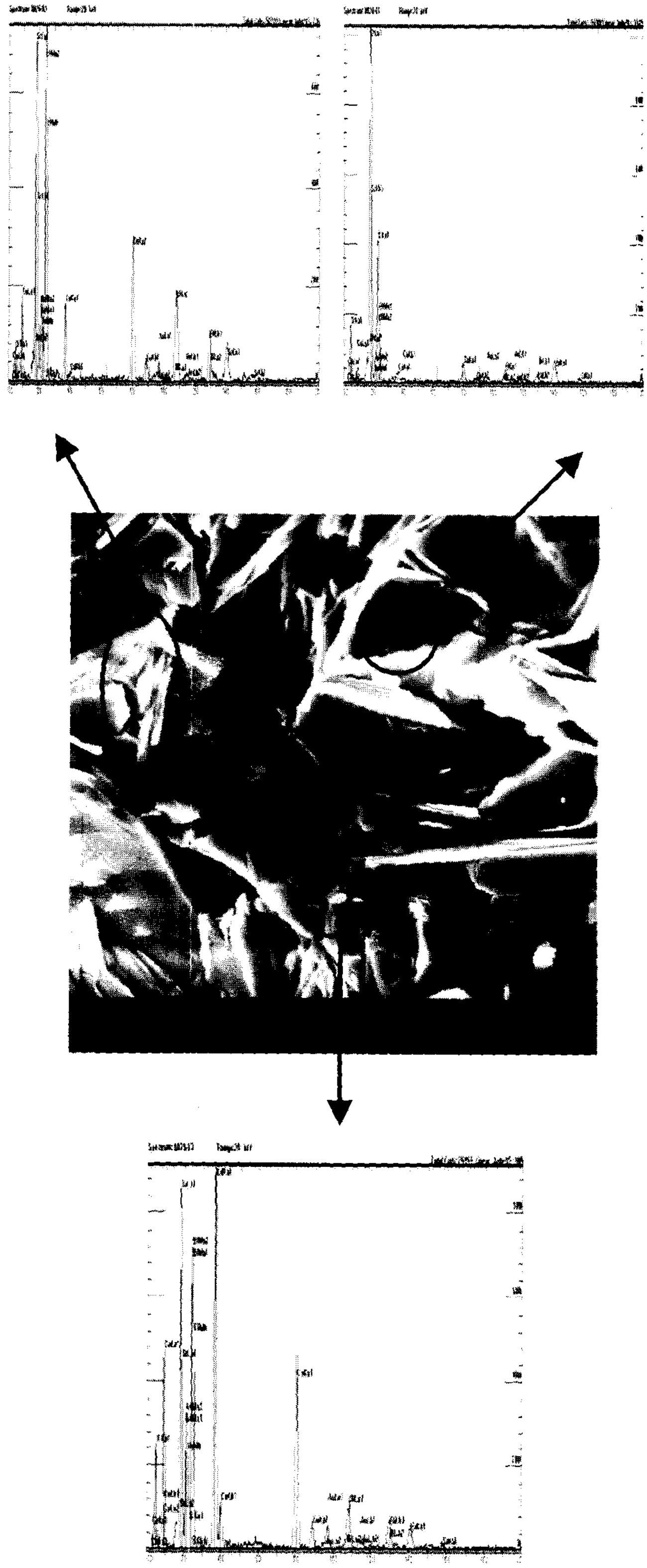


Fig. 5. SEM image and EDAX results taken on the fractured surface of Bi2212 tube with 7 weight % of $SrSO_4$.

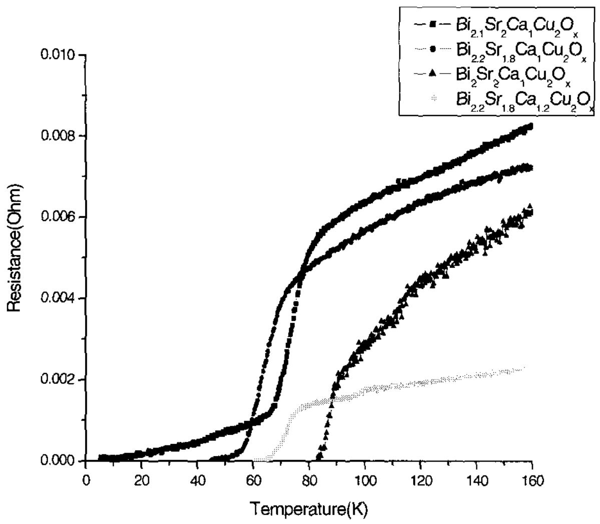
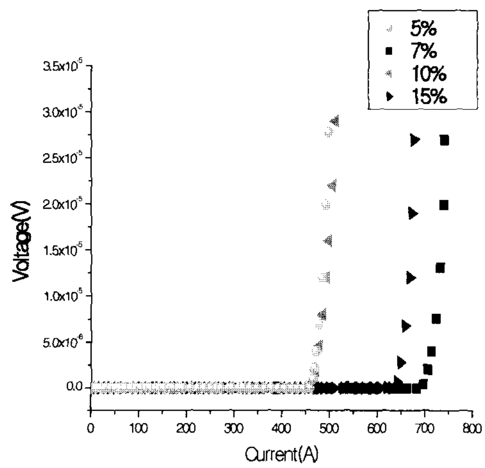
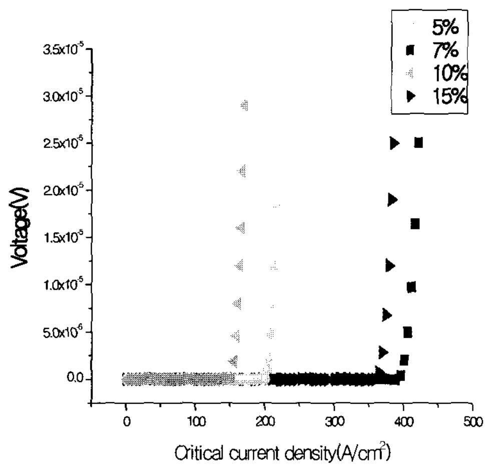


Fig. 6. Temperature-resistance characteristics of the tube fabricated with 4different compositions.

Figure 7 shows the I-V characteristics of Bi2212 tubes, which has 30 mm in diameter and 60 mm in length, depending on $SrSO_4$ additions from 5 to 15wight %. The critical current(I_c) and critical current density(J_c) increased as the $SrSO_4$ weight % increased up to 7 % and then decreased beyond. It seems that increasing weight % of $SrSO_4$, however, did not have any significant negative effects on I_c and J_c. This can be concluded $SrSO_4$ addition into Bi2212 might be helpful for texture formation. Our preliminary results indicate that the measured I_c and J_c at 77 K(B = 0 T) in Bi2212 with 7 weight % of $SrSO_4$ composition were about 680 A and 380 A/㎠ and showed the highest as compared with other compositions.



a) I_c



b) J_c

Fig. 7. I-V characteristics of Bi2212 tubes depending on $SrSO_4$ additions from 5 to 15 weight % : a) I_C and b) J_C.

Figure 8 show I-V measurement on tube with 7 weight % of $SrSO_4$ at 35 K. The measured Ic value at 35 K was about 1,500 Amp. Based on I-V results, the obtained data especially in terms of n value is still lower than the data taken by Hobl group even this Ic value shows somewhat promising[8]. Tc results already suggest that there are poor grain connectivity indicating phase unstability and inhomogenity. Now further detailed works to optimize the process to increase the n value are still undergoing.

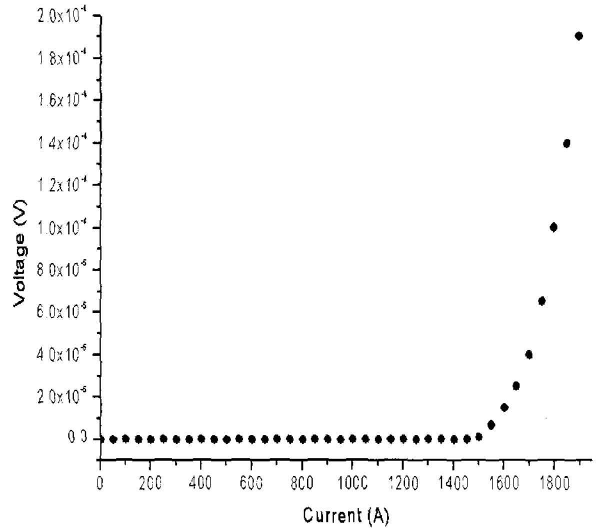


Fig. 8. I-V characteristics of Bi2212 tubes with 7 weight % of $SrSO_4$ additions at 35 K.

4. CONCLUSION

The tubes with 4 different chemical compositions were fabricated by CFP. Also the tube characteristics were systematically evaluated in terms of various $SrSO_4$ amount in Bi2212. For tube fabrication the optimum range of melt temperatures and preheating temperature and time for mould were 1050 ℃, 1100 ℃ and 550 ℃ for 30 min respectively. The applied mould rotating speed was 1000 rpm. Normally the specimen was mechanically stable when the melting temperature was over 1035 ℃ and steel mould was preheated over 400 ℃ for 30 min. A tube was annealed at 840 ℃ in oxygen atmosphere for 72 hours.

XRD data suggest that the phase formed after direct solidification from melt was identified as amorphous phase and this phase was transformed into Bi based structure after heat treatment at 840 ℃ for 72 hours in oxygen atmosphere. The highly oriented plate-like grains were well developed along the rotating direction of mould regardless of initial chemical composition. Typical grain size was more than 20 ㎛. The specimen with 2212 composition exhibited T_c of 83 K while the specimens with other composition are as low as 60 K or much lower than 60 K with a broad transition width and long tail, which is lower than what we expected. The measured I_c and J_c at 77 K(B = 0 T) in Bi2212 with 7 weight % of $SrSO_4$ composition were about 680 A and 380 A/㎠ and showed the highest as compared with other compositions.

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