



## Effect of Sintering Temperature and Time on the Superconducting Properties of $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ and $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$ Compounds

### KEYWORDS

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**ABSTRACT** The solid state reaction technique has been used to prepare homogeneous superconducting samples for  $Tl_2Ba_2Ca_2Cu_3O_{10}$  and  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  systems type 2223,

The effect of sintering temperature and time on the transition temperature ( $T_c$ ) has been studied. The structural properties and electrical resistivity of the  $Tl_2Ba_2Ca_2Cu_3O_{10}$  and  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  systems have been investigated using x-ray diffraction (XRD) and four probe method respectively. The XRD pattern showed a tetragonal structure, with at least two superconducting phases.

It is found for Tl-2223 system, the  $T_c$  increased and decreased with increasing sintering temperature and time respectively.

### Introduction:

Following the discovery of high-Temperature superconductor in Bi-Sr-Ca-Cu oxid system, Sheng et al<sup>[1,2]</sup> have reported a superconducting transition in a Tl-Ca-Ba-Cu oxide composite with onset temperature up to 120K and zero resistance below 107K.

Two superconducting phases,  $Tl_2Ca_2Ba_2Cu_3O_{10+\delta}$  and  $Tl_2Ca_1Ba_2Cu_2O_{8+\delta}$  were identified in their samples by Hazan et al<sup>[3]</sup>. They found that these phases have a pseudo tetragonal until cell  $(5.40 \times 5.40 \times 36.25) \text{ \AA}$ , correspond to a, b and c lattice dimensions, respectively. Dou et al<sup>[4]</sup> studied superconducting properties of Tl-Ba-Ca-Cu-O ceramics prepared by a solid state reaction under optimum conditions (880°C sintering in flowing  $O_2$  for 3h). The resistivity, AC susceptibility, and Meissner effect were measured. The temperature-dependent resistivity of  $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$  showed a degradation in transition temperature ( $T_c$ ) after increasing the sintering time from 3h to 6h and the temperature dependent AC susceptibility showed that at zero applied field the superconducting transition was reasonably sharp with  $T_c = 110K$ .

Kaell et al<sup>[5]</sup> have studied the variation of  $T_c$  due to partial Sr substitution, for Ba in  $Tl_2Ba_{2-x}Sr_xCa_2Cu_3O_9$  (Tl-2212), ( $x=0-0.6$ ), and  $Tl_2Ba_{2-x}Sr_xCu_1O_6$  (Tl-2201) ( $x=0-0.6$ ). They showed that,  $T_c$  decreased rapidly with increasing Sr content for both Tl-2212 and Tl-2201 systems.

Liu et al<sup>[6]</sup> have studied the samples of  $TlSr_2Ca_2Cu_3O_9$  system prepared by a solid state reaction, with replacing part of the Tl by Pb to get pure phase of  $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_9$ , which enhanced the high temperature superconductivity with  $T_{c(\text{onset})} = 130K$ ,  $T_{c(\text{midpoint})} = 124K$  and  $T_{c(\text{zero})} = 122.5K$  as measured by electrical resistance, whereas the diamagnetic onset temperature  $T_{c(\text{mag})} = 124K$  as determined by DC magnetic susceptibility.

Khan et al<sup>[7]</sup> have studied the enhanced Inter-grain Connectivity in  $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_3O_{10-\delta}$  Superconductors. Kareem and Tariq<sup>[8]</sup> have investigated the effect of simultaneous substitution of strontium at the barium site of  $Tl_{0.6}Pb_{0.4}Ba_{2-x}Sr_xCa_2Cu_3O_{9-\delta}$  Superconductors and found that  $T_{c(\text{off})} = 113K$  for  $Tl_{0.6}Pb_{0.4}Ba_{1.5}Sr_{0.5}Ca_2Cu_3O_{9-\delta}$ .

Discoveries of Tl-based system have not only set new  $T_c$  records with zero resistance up to 125K, but also have provided a new insight into the mechanism of high- $T_c$  oxide superconductivity<sup>[11]</sup>.

In this paper we investigated the effect of sintering tempera-

ture and time on the transition temperature for  $Tl_2Ba_2Ca_2Cu_3O_{10}$  and  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  systems type 2223. Also we studied the effect of these parameters on the structural and electrical resistivity of both prepared systems.

### Experimental

Two types of superconducting systems according to their nominal composition  $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ ,  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  were prepared by a two step solid state reaction method. Precursors  $Sr_2Ca_2Cu_3O_{10+\delta}$  and  $Ba_2Ca_2Cu_3O_{10+\delta}$  were first prepared using high purity powders of  $Sr(NO_3)_2$ ,  $BaCO_3$ ,  $CaO$  and  $CuO$  as starting materials, then,  $Tl_2O_3$  was added to the mixture and grinding them in agate mortar for about 30 min to obtain a very fine and optimum homogenous powder. The mixtures were pressed into a pellet of (0.2-0.3) cm in thickness and 1.3cm in diameter, under a pressure of about 3 ton/cm<sup>2</sup>. The samples were sintered in air atmosphere of (840, 850 and 860°C) for 3h and 6h.

The resistivity measurement were carried out by the four probe method and the formation of the 2223-phase was systematically checked by x-ray diffraction technique using Phillips diffractometer with source  $Cu_{\alpha}$  radiation.

### Results and discussion

In order to clarify the effect of sintering temperature ( $T_s$ ) on the electrical resistivity and the transition temperature ( $T_c$ ), the prepared samples of nominal compositions  $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$  and  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  have been sintered at different temperatures (840, 850 and 860°C) the results were shown in Fig.(1a,b). The outcome of this figure illustrated the values of normal state resistance decreased with increasing the sintering temperature albeit to a certain limit. However, the resistivity of the samples sintered at 840°C increases with decreasing the temperature thus, it showed a semiconducting behavior. When the sintering temperature increased to 850°C, the resistivity decreased slowly with decreasing temperature but did not become zero even at the liquid nitrogen temperature (77K). In Fig.(1a) we observe a second order transition for  $T_s = 860^\circ C$ . This was indeed a very interested result which reflects that the HTSc was of type II which is very important phase for the future industry where the transition to the normal phase required two steps and using wide range of temperature. A similar behavior has been obtained by Sheng et al [1] for  $Tl_1Ba_1Ca_1Cu_3O_x$  system.

When the sintering temperature increased to a higher than 860°C, we obtain a negative result, such as producing melted or bended samples. Oppositely, in such case we can deduce that the low temperature super phase grow on the account of

the HTSc phase, consequently this inferred that the holes in the Cu-O or Cu-O<sub>2</sub> planes had decreased; therefore, the sintering temperature was considered to be critical for the growth of high T<sub>c</sub> phase and the optimum temperature seem to be close to the partial melting point.

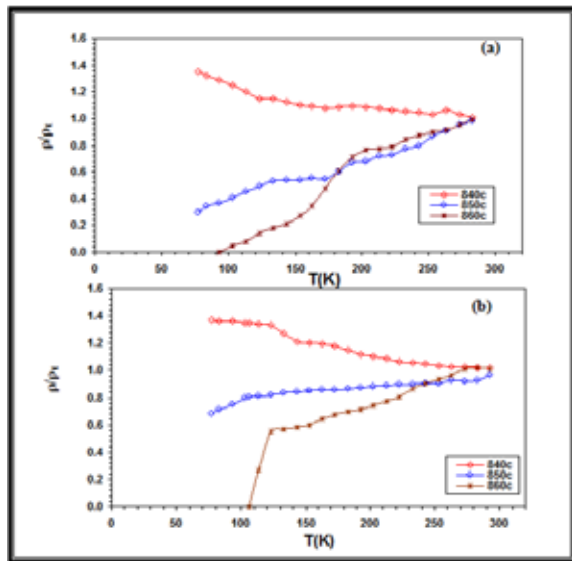


Fig. (1): Temperature dependence of normalized resistivity for (a) Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> system (b) Tl<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> system sintered at different temperature for 3h in air

Indeed different cuprate compound systems had different T<sub>c</sub>'s depending on the main elements in the system. This was one of the merits of HTSc research. It was well known now that the system, which had a Ba-based, displays a higher T<sub>c</sub>'s than it's Sr-containing counter part<sup>[9]</sup>. It had been pointed out that a Ba-containing ferroelectric perovskite compound usually has a higher Curie temperature than its Sr containing counter part which is due to the greater polarizability of the Ba-ion<sup>[10]</sup>. We suggest a similar reason holding for superconductivity in other cuprates, since we believed that the polarizability played a serious role in the HTSc process due to oxygen stoichiometric deviation.

Table (1): Variation of T<sub>c</sub> values, lattice parameters and oxygen content with different T<sub>s</sub> and t<sub>s</sub>.

Samples	T <sub>s</sub> (°C)	t <sub>s</sub> (h)	a (Å)	c (Å)	T <sub>c</sub> (K)	δ
Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10+δ</sub>	840	3	—	—	semi	—
	850	3	3.850	35.472	77>	-0.081
	860	3	3.849	35.500	120	0.229
	860	6	3.852	35.420	113	0.204
Tl <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10+δ</sub>	840	3	—	—	semi	—
	850	3	4.321	33.652	77>	0.125
	860	3	4.350	33.780	110	0.189
	860	6	4.580	33.258	100	0.126

The XRD patterns of the nominal composition of Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> and Tl<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> prepared with different sintering temperature were shown in Figs. (2 and 3). It was seen from Fig.(2a) that the main peaks were at (107), (1110) and (208) for the HTSc phase<sup>[4]</sup>, implying that the sample were mainly of the phases Tl-2223 and Tl-2212. Interestingly the same peaks of Fig.(2b) for the sample sintered at 860°C were much sharper. In the same time, one can infer

from the latter figure that the size of the crystallites had increased. This was attributed to the sharpness of the peaks 2223-phase. The lattice parameters of Tl-2223 were reported in Table (1) which showed that as the sintering temperature increased the a lattice parameter changed a little, but the c lattice parameter increased with increasing T<sub>s</sub>. The larger Ba atoms also contribute to the increase of c-parameter. Hence, the super electrons will move more freely in the Cu-O planes. Thus, we attribute that the c-parameter play influential role in the HTSc process.

We should point out that the crystal structure of Tl-2223 prepared at 860°C always had a tetragonal phase<sup>[10]</sup>.

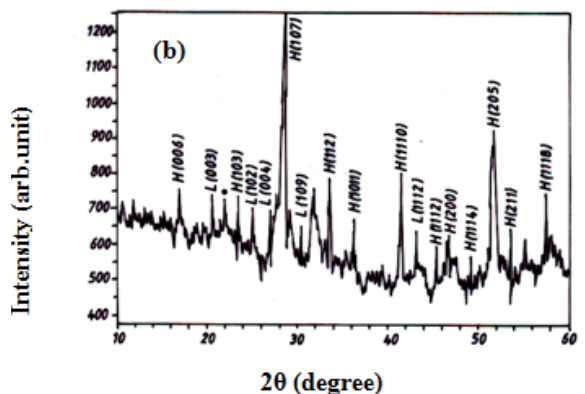
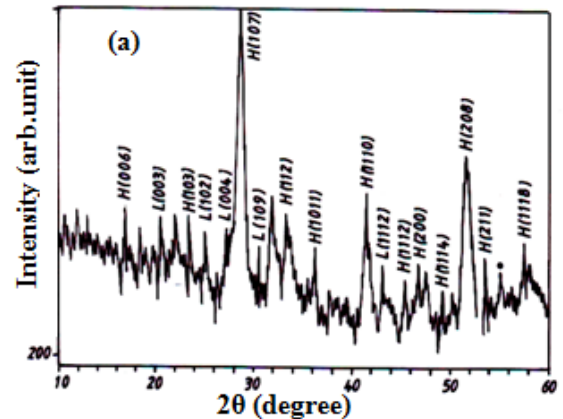


Fig.(2): XRD patterns of Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> samples sintered at (a) T<sub>s</sub>=850°C, (b) T<sub>s</sub>=860°C for 3h in air, where (H) High T<sub>c</sub> phase, (L) low T<sub>c</sub> phase, (.) impurity phase BaCuO<sub>2</sub>, (#) impurity phase CaCuO<sub>3</sub>

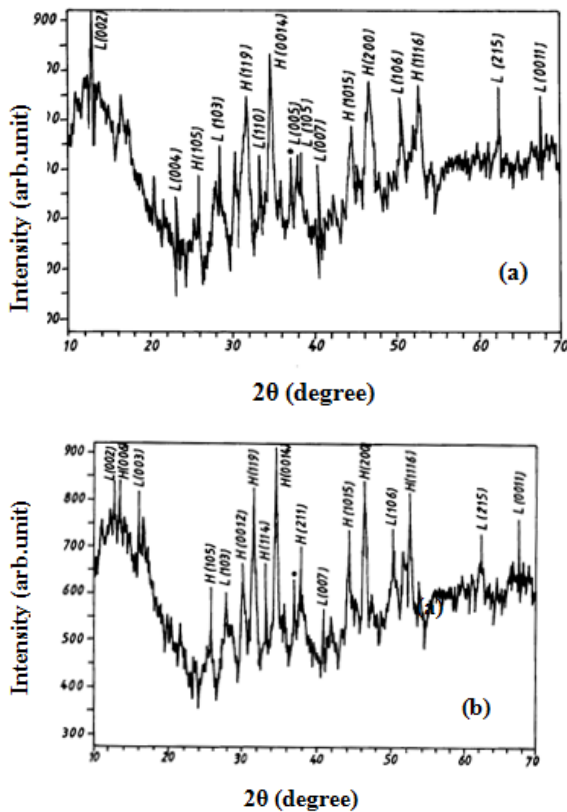


Fig.(3): XRD patterns of  $Ti_2Sr_2Ca_2Cu_3O_{10+\delta}$  samples sintered at (a)  $T_s=850^\circ C$ , (b)  $T_s=860^\circ C$  for 3h in air, where (H)High  $T_c$  phase, (L)low  $T_c$  phase, (.)impurity phase( $Sr_2Ca_2Cu_3O$ ).

Figure (4a,b) showed the effect of prolonged sintering times on the electrical resistivity of  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  and  $Ti_2Sr_2Ca_2Cu_3O_{10+\delta}$  specimens. Initially the specimens sintered at  $860^\circ C$  for 3h had a low resistivity and  $T_c$  of about 120K and 110K for  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  and  $Ti_2Sr_2Ca_2Cu_3O_{10+\delta}$  respectively. When the specimens were heat treated for an additional 3h, the superconducting properties degrade. Similar results had been reported by Dou et al<sup>[4]</sup> for  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  system sintered at  $880^\circ C$  with flow  $O_2$ . The  $\rho-T$  data indicated that the higher  $T_c$  phase (TI-2223) dissociated giving rise to a second phase of composition (TI-1223) with  $T_c=113K$  for  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  and 100K for  $Ti_2Sr_2Ca_2Cu_3O_{10+\delta}$ . X-ray diffraction data given below confirm this finding.

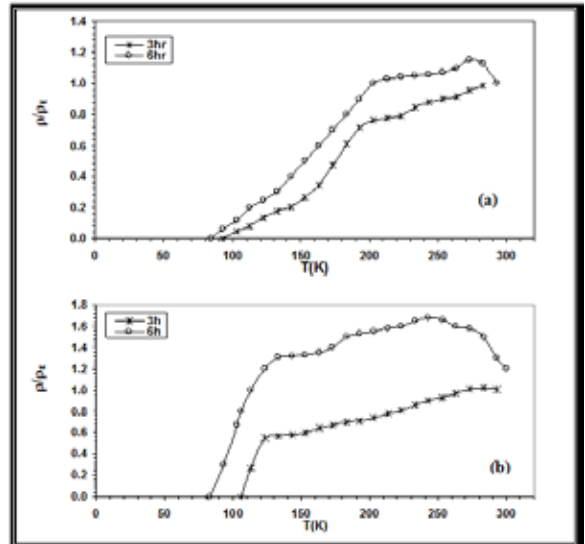


Fig. (4): Temperature dependence of normalized resistivity for (a)  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  system (b)  $Ti_2Sr_2Ca_2Cu_3O_{10+\delta}$  system sintered at  $860^\circ C$  for two periods of time in air

However  $T_c$  was observed to decrease after a longer thermal treatment. It has been claimed that such a decrease can be attributed to crack formation a result of excessive mechanical deformation<sup>[4]</sup>. In our view higher time could not lead to crack process but it come nearer to a melting state as we mentioned before It was more probably the low temperature phase grow and was preferable at a state near the melting point as it is almost always the case. We should point out also if any deformation acceptable would have taken place, it would rather enhance the polarization which helped for a better  $T_c$ . On the other hand drastic deformation leads to negative results, a thing which we believe would not happen.

The significant point which can be deduced from our data to explain why  $T_c$  decreased for longer period was that data of  $\delta$  given in Table (1). It has been shown from other researchers and our work that the decreasing  $\delta$  blow a certain limit,  $T_c$  degrades. Dou et al.<sup>[4]</sup> found that  $T_c$  for  $Ti_2Ba_2Ca_2Cu_3O_{10+\delta}$  decreased as the sintering time increased. They attributed the decrease of  $T_c$  to the loss of thallium during the prolonged sintering treatment.

It was well accepted that the phonon coupling interaction(Cooper pairs) was necessary for  $T_c$  to take place .In case of degradation ,we can think of such reaction became weaker and resonant tunneling through localized centers along the c-axes between the  $CuO_2$  planes across TIO plane or it's dopant partner decreased. The reason was that for tunneling to take place some conditions should be satisfied first the transport across the 2D in the  $CuO_2$  plane should be high enough to produce high electron density at Fermi level second small energy gap should be formed third Cu-O bond stretching phonon- coupling fluctuation should be low and the transport in the 2D should not be suppressed, fourth the Cu-O bonds must be ordered.

Moreover, x-ray diffraction patterns of these samples are shown in Figs.(5 and 6), we found that during the first sintering time (3h) the main peaks observed were corresponding to the TI-2223 phase, with the prolongation of sintering time (6h); the intensity of the peaks attributable to the low- $T_c$  phase became stronger. This result indicated that the low- $T_c$  phase had increased in these samples. The values of critical temperature and lattice parameter for these samples were listed in Table (1).

From the above result, it was obvious that the optimum condition for preparing pure composition of HTSc behavior with higher  $T_c$  value was to be held at 860°C for 3h, and the process was carried out in air.

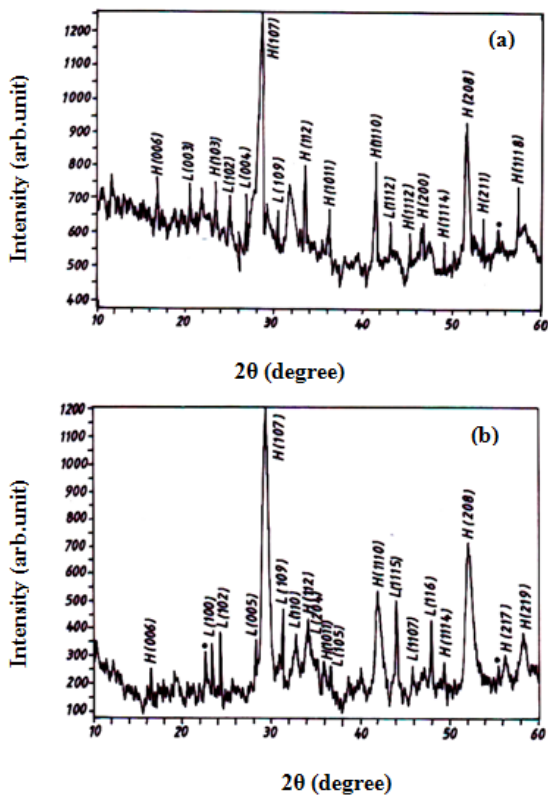


Fig.(5): XRD patterns of  $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$  samples sintered at 860°C for two periods of time in air (a)  $t_s=3h$ , (b)  $t_s=6h$ , where (H) High  $T_c$  phase, (L) low  $T_c$  phase, (.) impurity phase  $BaCuO_2$ .

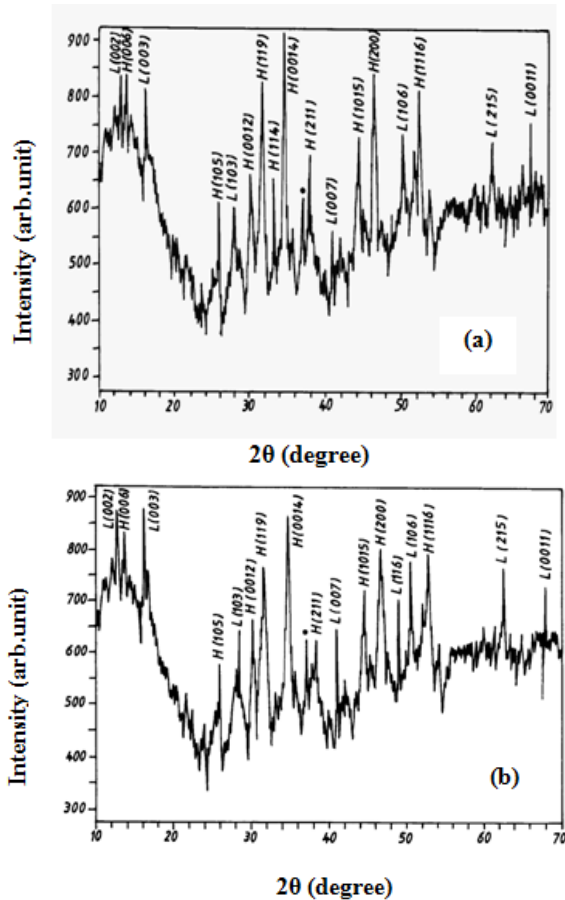


Fig.(6): XRD patterns of  $Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$  samples sintered at 860°C for two periods of time in air (a)  $t_s=3h$ , (b)  $t_s=6h$  where (H) High  $T_c$  phase, (L) low  $T_c$  phase, (.) impurity phase ( $Sr_2Ca_2Cu_2O$ ).

**Conclusions:**

The outcome foundation of above data is the following:

1. The optimum sintering temperature which was characteristic for the growth of high- $T_c$  phase equal to 860°C.
2. Cuprates with a Ba-containing have a higher  $T_c$  than those Sr containing.
3. Prolonging the sintering time to 6h lead to decrease the transition temperature.
4. XRD pattern analyses have shown a tetragonal structure, and there were at least two superconducting phases.
5. The  $T_c$  increased and decreased with increasing  $T_s$  and  $t_s$  respectively.

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