Thermal Conductivity, Thermal Diffusivity and Thermoelectric Power of Sm-Based Bulk Superconductors

Hiroyuki Fujishiro and Shuichi Kohayashi

***Abstract*—The ab-plane thermal conductivity $\kappa_{ab}(T)$, thermal diffusivity $\alpha_{ab}(T)$ and thermoelectric power $S_{ab}(T)$ were measured for the highly-oriented Ag-doped superconducting materials $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.1 \sim 0.4$) prepared by a melt process. The absolute value of κ_{ab} and its characteristic enhancement below T_c were suppressed with increasing content X of the Sm_2BaCuO_5 (Sm211) secondary phase, while they were enhanced with increasing content of doped-Ag. The application of the magnetic field up to 10 T clarified that the phonon scattering by vortex was most enhanced with the applied field perpendicular to the ab-plane. The trapped magnetic also seriously suppressed the $\kappa_{ab}(T)$ enhancement.**

***Index Terms*—Phonon scattering, Sm-based superconductors, thermal conductivity, thermal diffusivity.**

I. INTRODUCTION

VARIOUS kinds of practical applications using the melt-processed REBaCuO-system superconductors (RE: rare earth ions), such as magnetic bearings, levitation systems, flywheels, bulk magnets, current leads and so on have been recently proposed and developed [1], [2]. The critical current density J_c of REBaCuO-system in high magnetic fields has been improved by employing smaller RE ions such as Sm and Nd, exceeding those of the YBaCuO-system. The melt-processed REBaCuO-crystals consist of both the $REBa_2Cu_3O_{7-\delta}$ (RE123) superconducting phase and the RE_2BaCuO_5 (RE211) impurity phase. Silver (Ag) metal is added in order to improve the mechanical strength and to increase J_c. A small amount of platinum (Pt) metal is also added to disperse finely and uniformly the RE211 particles, which act as pinning centers. For practical applications, thermal properties of superconducting materials such as the thermal conductivity κ, thermal diffusivity α, thermoelectric power S, specific heat C are very important. The low thermal conductivity, for example, is essential for the application of bulk superconducting materials as power current leads. We have reported and analyzed the κ anisotropy for the bulk Y123 and Y211 composite system [3].

Manuscript received September 24, 2001. This work was supported in part by Japan Science and Technology Corporation under the Joint-Research Project for Regional Intensive in the Iwate Prefecture on "Development of practical applications of magnetic field technology for use in the region and in everyday living."

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Publisher Item Identifier S 1051-8223(02)04138-6.

In the present paper, we report $\kappa_{ab}(T)$, $\alpha_{ab}(T)$ and $S_{ab}(T)$ of the highly-oriented Ag-doped $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.1 \sim 0.4$) in the temperature range of 10∼300 K and in the magnetic field of 0∼10 T. We analyze the effect of additions of Sm_2BaCuO_5 (Sm211) and Ag metal, on the thermal properties. The magnetic field dependence of $\kappa_{ab}(T)$ is also investigated and the phonon scattering by the vortex is discussed.

II. EXPERIMENTAL

The preparation of Ag-doped $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.1, 0.2, 0.3, 0.4$) bulk superconductors was described elsewhere [4]. The content of the added Ag was 10 or 15 wt.% and that of the Pt was 0.42 wt.% to the $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ weight. The sizes of the Sm211 and Ag particles were 2∼5 and 20∼30 μm, respectively. From the X-ray diffraction analyses, the grown crystals were crystallographycally highly oriented, where the bulk surface is parallel to the ab-plane of Sm123. The slender-shaped samples (4.0 mm × 4.0 mm × 25.0 mm) were cut parallel to the ab-plane for the measurement. The Sm211 polycrystal was also fabricated by the solid state reaction at 1150 °C in air in order to compare the thermal properties with those of the bulk crystals.

The ab-plane thermal conductivity $\kappa_{ab}(T)$ and the thermoelectric power $S_{ab}(T)$ were automatically measured by a steady-state heat flow method between 10 and 300 K and the thermal diffusivity $\alpha_{ab}(T)$ measurement was performed by an arbitrary heating method under an identical experimental setup with the κ and S measurements [5]. A Gifford–McMahon (GM) cycle helium refrigerator was used as a cryostat. The chromel-constantan thermocouples with ϕ 76 μm in diameter were used as thermometers for the κ, α and S measurements. The magnetic field of up to 10 T was applied using a cryocooler-cooled superconducting magnet.

III. RESULTS AND DISCUSSION

A. Volume Fraction of the Constituent Phases

The present Ag-doped SmBaCuO superconductors consist of the Sm123 superconducting phase, the Sm211 insulating phase, and Ag and Pt particles. The constituent phases and particles contribute the thermal properties of this system. Fig. 1 shows the calculated volume fraction of each component for $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.1 \sim 0.4$). The measured density and the ideal densities of the Sm123, Sm211, Ag and Pt (6.87, 7.46, 10.25 and 21.37 g/cm^3, respectively) were used

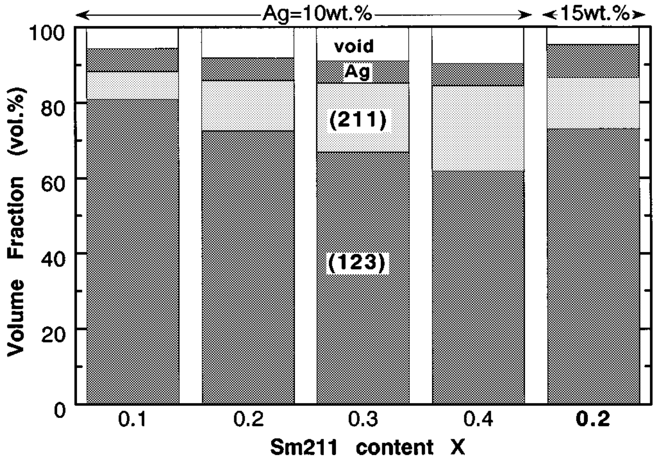

Fig. 1. The volume fraction of each component for $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.1 \sim 0.4$) for Ag = 10 wt.% and 15 wt.% ($X = 0.2$) samples.

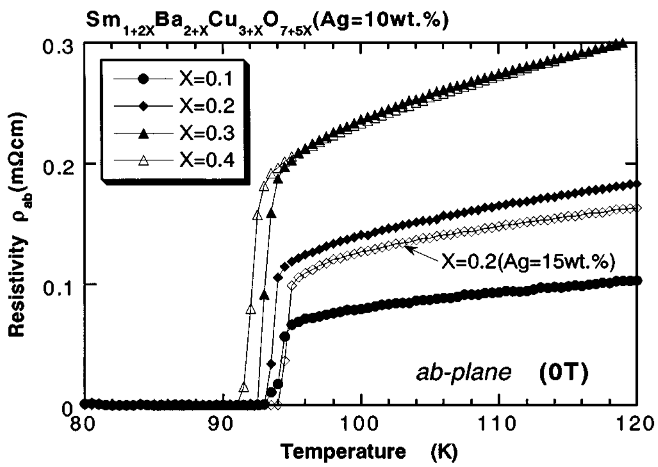

Fig. 2. The temperature dependence of the ab-plane resistivity $\rho_{ab}(T)$.

for the calculation. The volume fraction of Pt was omitted in the figure because it is very small (<0.12 vol.%). The volume fraction of Sm123 decreases and that of Sm211 increases with increasing X. It should be noticed that the fraction of void also increases with increasing X. In Fig. 1, the volume fractions are also shown for the Ag = 15 wt.% ($X = 0.2$) sample. The increase of the Ag content to 15 wt.% markedly reduces voids possibly through the intrusion of Ag particles into the grain boundaries.

Fig. 2 shows the temperature dependence of the ab-plane electrical resistivity $\rho_{ab}(T)$. The ρ_{ab} values for the Ag = 10 wt.% samples increase with increasing X, which may result from the increase of the insulating Sm211 fraction. The superconducting transition temperature T_c slightly decreases with increasing X. As can be seen for the $X = 0.2$ sample, the $\rho_{ab}(T)$ decreases by increasing the Ag content from 10 to 15 wt.%. For the $X = 0.2$ and Ag = 15 wt.% sample, T_c recovers to 94 K, the maximum value of the present samples. The X dependence and the Ag content dependence of T_c cannot be interpreted by only the changes of the volume fraction of the Sm123 phase. It is suggested that the superconductivity of the Sm123 phase is improved by the increase of Ag content up to 15 wt.%.

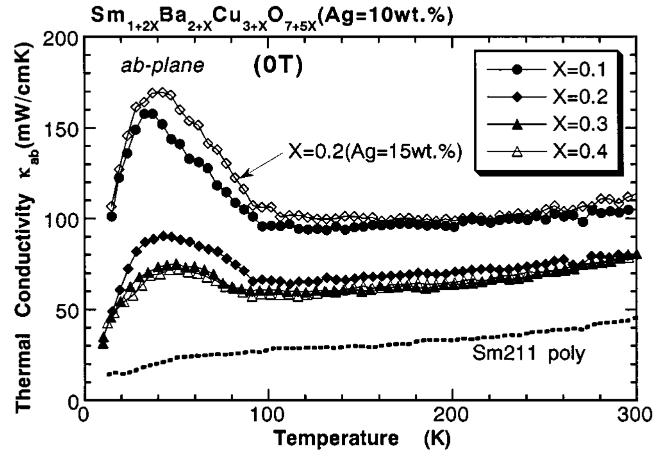

Fig. 3. The temperature dependence of the ab-plane thermal conductivity $\kappa_{ab}(T)$ for various X under the zero magnetic field.

B. Thermal Conduction in Zero Magnetic Field

Fig. 3 shows the temperature dependence of $\kappa_{ab}(T)$ for various X with Ag = 10 wt.%. For the $X = 0.1$ sample which consists of the maximum amount of Sm123 superconducting phase, the absolute κ_{ab} value above T_c (=93 K) is large and the $\kappa_{ab}(T)$ enhancement below T_c is prominent. For the $X = 0.2$ sample, the $\kappa_{ab}(T)$ enhancement becomes less prominent and it is further reduced with further increase of X. At the same time, $\kappa_{ab}(T)$ in the normal state decreases. However, it is to be noticed that $\kappa_{ab}(T)$ values of $X = 0.3$ and $X = 0.4$ samples almost coincide each other over the entire temperature range. $\kappa(T)$ of the Sm211 polycrystals is also presented in Fig. 3, which decreases with decreasing temperature and is very small, making a contrast with that of the Y211 polycrystal [3]. $\kappa(T)$ of Y211 was somewhat larger, took a faint maximum at $T \sim 50$ K and decreased with further increase of T. The electronic thermal conductivity $\kappa_e(T)$, estimated by the Wiedemann–Franz law using the ρ_{ab} values, decreases with increasing X. The ratio of κ_e to the total κ at 300 K is 31% and 16% for $X = 0.1$ and 0.4, respectively. The decrease of $\kappa_{ab}(T)$ with increasing X above T_c may come mainly from the reduction of κ_e, the increase of low thermal conductive Sm211 phase and the enhanced phonon scattering in the Sm123 phase.

It has been found that in REBaCuO-systems with the light RE (LRE) element such as Sm and Nd, a part of the LRE ions is substituted for the Ba site, thus forming the $LRE_{1+y}Ba_{2-y}Cu_3O_z$-type solid solution [1]. Then T_c should decrease with increasing RE ion substitution. T_c actually decreases with increasing X as shown in Fig. 2, which suggests increased substitution of Sm for Ba site with increasing X. The increased migration of Sm and Ba enhances the phonon scattering in the Sm123 phase, working as a kind of point defect type phonon scattering centers.

The thermal conductivity of high T_c oxide superconductors (HTSC) is enhanced below T_c by both the electronic contribution κ_e and the phonon contribution κ_{ph}. In not ideally pure HTSC with sizable residual electron scattering by impurities, the enhancement mainly comes from the phonon component κ_{ph} [6]. The κ_{ph} enhancement below T_c is caused by the reduction in the phonon scattering by quasiparticles with the

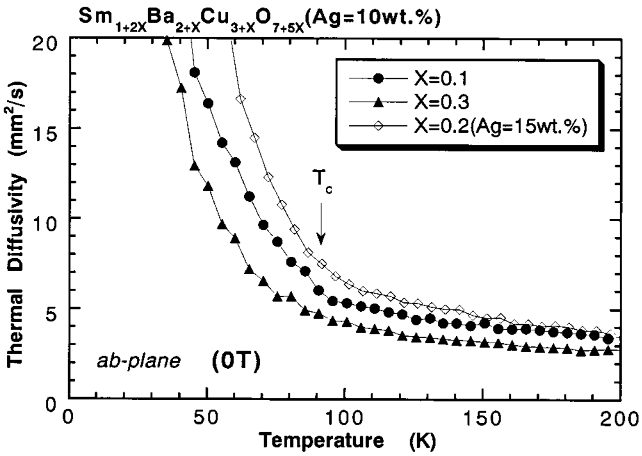

Fig. 4. The temperature dependence of the ab-plane thermal diffusivity $\alpha_{ab}(T)$ for typical samples.

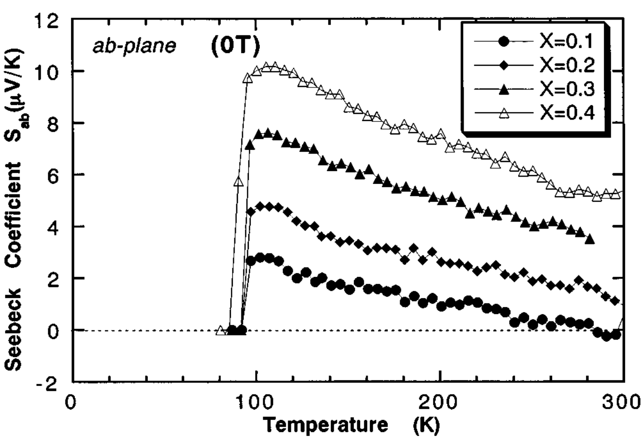

Fig. 5. The temperature dependence of the thermoelectric power $S_{ab}(T)$ in the ab-plane.

progress of their condensation into cooper pairs [5]. Because the present $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ samples belong to the impure HTSC material containing a considerable amount of the Sm and Ba migration and the impurity Sm211 phase, the κ enhancement is due to the κ_{ph} contribution. The κ_{ph} enhancement is masked out if the phonon scattering strength by other mechanisms becomes stronger. The suppression of the κ enhancement with increasing X may reflect the enhanced phonon scattering due to increased Sm and Ba migration. For the $X = 0.2$ sample with Ag $=$ 15 wt.%, T_c recovers to 94 K and then the absolute value and the $\kappa_{ab}(T)$ enhancement also recover as shown in Fig. 3. This may result from the suppression of the migration and/or from the improved crystallinity in the Sm123 phase.

Fig. 4 shows the temperature dependence of $\alpha_{ab}(T)$. In the normal state, $\alpha_{ab}(T)$ of all the samples increases slightly with decreasing temperature. Below T_c, $\alpha_{ab}(T)$ increases more and more rapidly with decreasing temperature. The absolute value of α decreases with the increase of X and increases with increasing content of the doped-Ag, in accord with the behavior of κ_{ab}.

Fig. 5 shows the temperature dependence of $S_{ab}(T)$. For the Ag $=$ 10 wt.% samples, $S_{ab}(T)$ above T_c positively increases

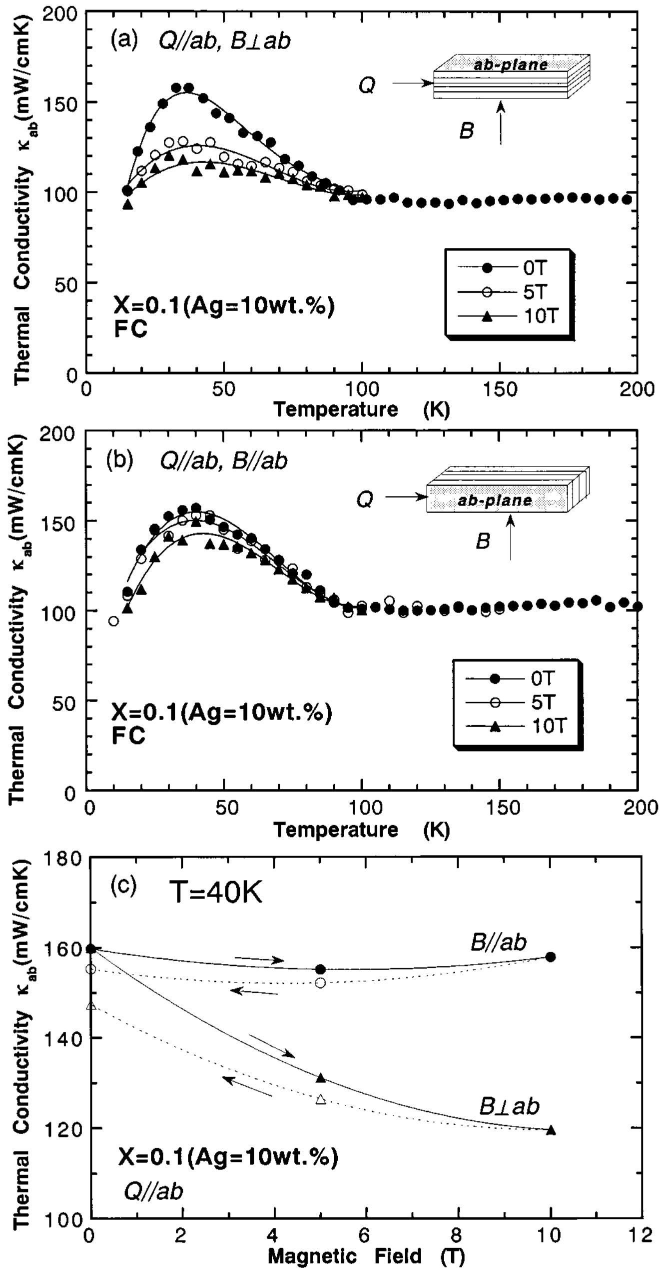

Fig. 6. The ab-plane thermal diffusivities $\kappa_{ab}(T)$ with the applied field B (a) perpendicular and (b) parallel to the ab-plane, respectively, for the $X = 0.1$ (Ag $=$ 10 wt.%) sample. (c) The magnetic field dependence of κ_{ab} at 40 K where B in both parallel and perpendicular directions to the ab-plane.

with increasing X. The thermoelectric power S of a metal is given by

$$S = \frac{\pi^2}{3}\left(\frac{k}{e}\right) kT\rho \frac{\partial}{\partial E}\left(\frac{1}{\rho(E)}\right), \tag{1}$$

where E the electron energy. Quantitatively, S is expected to increase in impure metals because of increasing ρ values. Accordingly, the observed increasing S_{ab} with X may partly be attributable to the $\rho_{ab}(T)$ increase in the Sm123 phase caused by the migration effect. Since the present Ag-doped Sm-based material is a composite system composing of Ag particle, Sm123 and Sm211, it is difficult to analyze S_{ab}. However, it is worth while to note that S_{ab} of the $X = 0.4$ sample is clearly larger than that of the $X = 0.3$ sample in spite of almost indistinguishable ρ_{ab}. This fact indicates that the Sm211 phase also intrinsically, i.e., not only through the increase of ρ_{ab}, enhances S_{ab} of this composite system.

C. Thermal Conduction Under the Magnetic Field

In this subsection, we present κ_{ab} of the $X = 0.1$ (Ag $=$ 10 wt.%) sample under the magnetic fields. Fig. 6(a) and (b) shows κ_{ab} for field cooling runs with the applied field B perpendicular and parallel to the ab-plane, respectively. The solid lines are to guide the reader's eyes. In both figures, κ_{ab} above T_c is independent of the applied magnetic fields. In Fig. 6(a), the κ_{ab} enhancement below T_c is drastically suppressed with increasing B perpendicular to the ab-plane. This reduction can be understood as caused by the enhanced phonon scattering by the quasiparticles in the vortex cores. For the application of B parallel to the ab-plane, however, the reduction of the κ_{ab} enhancement is barely discernible as shown in Fig. 6(b). In this case, the vortices parallel to the ab-plane hardly hinders the heat flow. The similar anisotropic effect of the magnetic field on $\kappa_{ab}(T)$ was observed for YBCO and Bi-2212 single crystals.

Fig. 6(c) shows the magnetic field dependence of κ_{ab} at 40 K where B was swept up and down up to 10 T. For the $B \perp ab$-plane setting, κ_{ab} (40 K) promptly decreases with increasing magnetic field and partly recovers with decreasing field; very clear hysteretic behavior of κ_{ab} is noticed. The κ_{ab} (40 K) value at 0 T after applying field is 8% smaller than the initial one. This suggests that the trapped magnetic field scatters the phonon transport even after removing the field. The trapped magnetic field for the $B \perp ab$-plane setting is estimated to be about 2 T from the data for the increasing virgin run. On the other hand, for the $B // ab$-plane setting, the field dependence of κ_{ab} (40 K) are quite small up to the applied field of 10 T.

Lastly, we comment on the effect of the added-Ag particles on the thermal transport. In the previous paper, we reported the thermal conductivity of the Ag+YBCO mixed crystals for various Ag contents and determined the purity of Ag particles in these crystals [7]. Using the previous data, the residual resistivity ratio (RRR) of the doped-Ag particles is estimated to be $\sim$15 in the present case. The measured thermal conductivity of Ag+0.22 at.% Au alloy with RRR$\sim$15 does not show the $\kappa(T)$ enhancement around 40 K. The addition of 10 and 15 wt% Ag enhances the absolute value of $\kappa(T)$ over the entire temperature range, but it cannot directly cause the $\kappa_{ab}(T)$ enhancement below T_c.

IV. Summary

The ab-plane thermal conductivity $\kappa_{ab}(T)$, diffusivity $\alpha_{ab}(T)$ and thermoelectric power $S_{ab}(T)$ were measured for highly oriented Ag-doped $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ materials, which consisted of superconducting $Sm_1Ba_2Cu_3O_7$ (Sm123) and semiconductive $Sm_2Ba_1Cu_1O_5$ (Sm211) phases by the ratio $1:X$. The obtained results are summarized as follows.

i) For the Ag $=$ 10 wt.%-doped series, the $\kappa_{ab}(T)$ values and the κ_{ab} enhancement below T_c, characteristic of high-T_c superconductors, are largest for $X = 0.1$, which are rapidly reduced with increasing X up to $X = 0.3$. $\kappa_{ab}(T)$ values became almost identical for the $X = 0.3$ and $X = 0.4$ samples. An important origin for the reduction was suggested to come from increasing migration of Sm and Ba ions. The quality of the Sm123 crystal was deteriorated with decreasing X, as suggested also by the T_c dependence on X. The increasing Ag-doping from 10 wt.% to 15 wt.% for the $X = 0.2$ crystal enhanced the $\kappa_{ab}(T)$ values, accompanying the T_c increase to 94 K. These results indicate that the deteriorated crystallinity of Sm123 is recovered or improved by the increased Ag-doping. The diffusivity $\alpha_{ab}(T)$ behaved consistently to κ_{ab}.

ii) Under the magnetic field up to 10 T, the κ_{ab} enhancement was markedly reduced for the applied field configuration, $B \perp ab$-plane. In contrast, very weak suppression was observed for the $B // ab$-plane configuration. These results are consistent with the explanation that the κ_{ab} enhancement below T_c originates from the reduction in the phonon scattering by quasiparticles. The anisotropic suppression with respect to the field direction can be understood to come from the appearance of anisotropic vortex scattering for phonons which originates from the layer structure of Sm123 lattice. From the hysteretic behavior of $\kappa_{ab}(B)$ under the applied fields, we could estimate the trapped magnetic flux B_{res} to be about 2 T after the 10 T field scan in the $B \perp ab$-plane configuration.

iii) The ab-plane thermoelectric power S_{ab} was positive and increased with increasing X, precisely reflecting the Sm211 content X up to $X = 0.4$. It is worthwhile to notice that both $\rho_{ab}(T)$ and $\kappa_{ab}(T)$ behaved almost identically for $X = 0.3$ and 0.4 samples, making a sharp contrast with the behavior of S_{ab}.

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