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Electron traps and luminescent properties in ZnS:Ag,Al phosphors

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ABSTRACT

We measured the thermal-glow curves of ZnS:Ag,Al phosphors because ZnS phosphors are one of the most important types of phosphors for electron-irradiated types of displays such as Braun tubes, projection tubes, field emission displays, and transmission electron microscope. To investigate traps in the thermal-glow curves of ZnS:Ag,Al, we measured the thermal-glow curves of ZnS:Al and ZnS:Ag phosphors. The trap peaks were observed at 144 K and 230 K for ZnS:Al and ZnS:Ag, respectively. The trap peak at 144 K for ZnS:Al is associated with a bimolecular-type-Al trap. Whereas the trap peak at 230 K for ZnS:Ag is associated with a monomolecular-type-Ag trap because the shape of the thermal-glow curve tails off toward the low-temperature side. We synthesized ZnS:Ag,Al phosphors in a flow of H_2S gas at 900-1200 °C and observed an electron trap at 430 K in the thermal-glow curve for these phosphors. We also found that the thermoluminescence (TL) intensity of the electron trap at 430 K decreased with increasing in the gas flow rate of H_2S. Hence, we assigned it to a deep sulfur vacancy. Moreover we analyzed the luminescent properties of phosphors with various sulfur-vacancy concentrations.

KEYWORDS: thermoluminescence, phosphor, ZnS, trap

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INTRODUCTION

In ZnS:Ag,Al phosphors, the impurities Al^{3+} and Ag^{+} substitute at Zn^{2+} sites and act as the donor (D) and acceptor (A), respectively. The blue emission results from electron-hole recombination in D-A pairs. The luminous efficiency of ZnS:Ag,Al phosphors decreases with electron density and, depending on the concentration of Ag, the luminescent intensity goes into saturation as the excitation density is increased. Raue *et al*. have reported on the saturation behavior of ZnS:Ag,Al phosphors for a wide range of concentrations of the Ag activator and Al coactivator [1, 2]. The luminous-saturation behavior appears at Ag concentrations above 200 ppm, and a nonradiative Auger process may be the responsible mechanism. Nonradiative Auger processes involve donor-acceptor pairs and are of three types and the energy of the electron in the donor state is transferred to the electron in a conduction-band state, to the electron in another donor state, or to the electron in a deep trap state [3]. Investigating deep trap states is thus an important part of investigating the saturation mechanism that appears with high Ag concentrations. For ZnS:Ag,Al phosphors, thermal-glow curves were obtained and trap states associated with Al were observed at 0.25 eV [4]. Recently, our group observed deep trap states in ZnS:Ag,Al phosphors prepared by H_2S gas-flow synthesis [5, 6]. Although the deep trap state is an important factor in the nonradiative Auger process of luminous

saturation, there have been very little studies on the deep trap state.

In the present work, ZnS:Ag,Al phosphors were prepared with various H_2S gas-flow rates to investigate the deep trap state. The concentrations of their deep electron traps were estimated from thermal-glow curves and their luminescent properties under cathode-ray excitation were measured.

MATERIALS AND METHODS

ZnS:Ag,Al phosphors were synthesized from $AgNO_3$, $Al(NO_3)_3$, and ZnS (luminescent grade) powders and aqueous solutions of $AgNO_3$ and $Al(NO_3)_3$ were prepared at concentrations of 0.1 mol/l and applied to the ZnS powder at a molar ratio [Al]/[Ag] of 1.5. As shown in fig. 1, the ZnS:Ag,Al phosphors were synthesized at 900-1200 °C in a quartz tube and H_2S gas is at flow rates in the 50-200-ml/min range. ZnS:Ag,Al phosphors prepared at 950 °C with flux was used as our standard samples and ZnS:Al and ZnS:Ag phosphors were used as supplied samples. As shown in fig. 2, thermal-glow curves were obtained as measurements of electron trap [4]. A conventional method of sedimentation was used to make each powder screen on a substrate of Cu. The weight of the powder screen in each sample was about 4-6 mg/cm^2. Each sample was placed in a vacuum chamber and kept at liq.-N_2-range temperatures. To excite the phosphors in preparation for the thermal-glow tests, each sample was irradiated by a Hg lamp (254 nm) for one hour. Each sample was then heated from 90 K to 650 K, with a fixed temperature rise rate of 6 K/min. The thermoluminescence (TL) of the phosphor was detected by a multi-photon amplifier and recorded on a personal computer. The luminescent properties were measured by a demountable cathode-ray excitation apparatus [1]. Each phosphor sample was irradiated, at room temperature, by an electron beam (1-300 μA, 30 kV, 8 × 8 mm raster) and the emission from the irradiated side was measured by a Si photocell with a radiometric filter.

RESULTS AND DISCUSSION

1. Thermal-glow curves of ZnS:Ag,Al, ZnS:Al and ZnS:Ag

Figure 3 shows the thermal-glow curve of ZnS:Ag,Al phosphor. The concentrations of

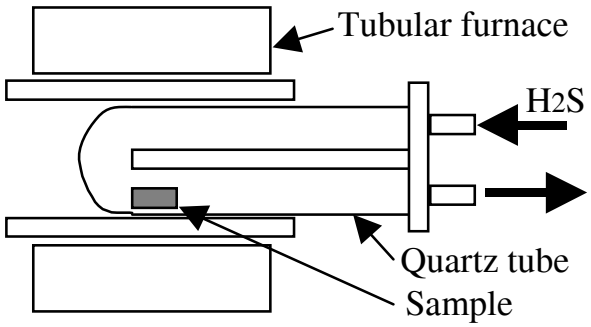

Fig. 1. Apparatus for ZnS:Ag,Al synthesis.

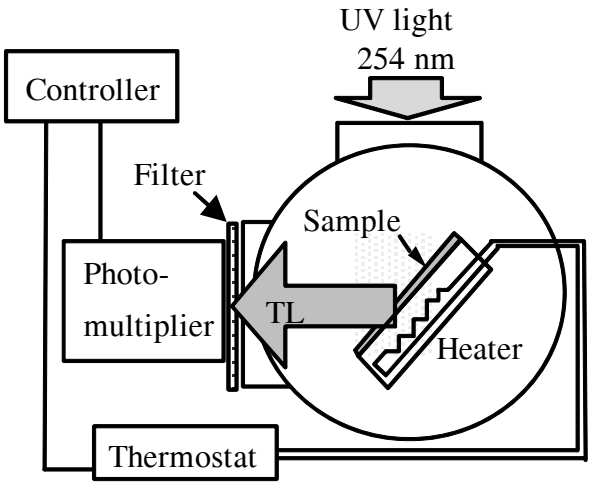

Fig. 2. Apparatus for obtaining thermal-glow curves.

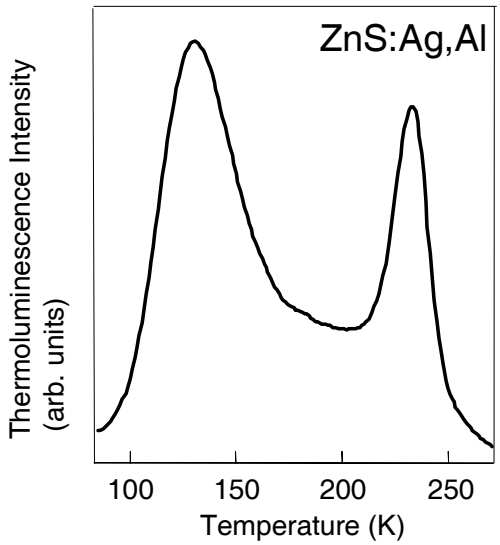

Fig. 3. Thermal-glow curve of ZnS:Ag,Al.

Al and Ag are 3 ppm and 100 ppm, respectively. As shown in fig. 3, two peaks are observed at 131 K and 233 K for ZnS:Ag,Al phosphor. To investigate the traps of ZnS:Ag,Al phosphor, we observed the thermal-glow curves of ZnS:Al and ZnS:Ag phosphors. Fig. 4 and 5 shows the thermal-glow curves of ZnS:Al and ZnS:Ag phosphors, respectively. The concentration of Al for ZnS:Al phosphor is 1000 ppm and that of Ag for ZnS:Ag phosphor is 700 ppm. As shown in fig. 4 and 5, the Al trap appears at 144 K and the Ag trap appears at 230 K. We also calculated the fitting curves of the observed thermal-glow curves [4]. The Al-trap curve fits with a bimolecular theoretical curve that tails off toward the high-temperature side. Also the thermal-glow curve of ZnS:Al is separated into three peaks; <120 K, 144 K and 205 K peaks. The <120 K peak is the sum of the traps below the starting temperature and it may be assigned to S-vacancy. The 144 K peak is assigned to the Al trap because it is the main peak of ZnS:Al. The 205 K peak is assigned to two S-vacancy from its trap depth [4]. On the other hand, the Ag-trap curve fits with a monomolecular theoretical curve that tails off toward the low-temperature side and fits with a single curve. Fig. 6 shows the dependence of the thermal-glow curves of ZnS:Al and ZnS:Ag phosphors on the rate of temperature rise. The rate of temperature rise changed at 1.0, 1.5, 3.0, 6.0, and 12 K/min. In fig. 6, it is shown that the intensity of the thermal-glow curves of ZnS:Al and ZnS:Ag phosphors increased and its peak position shifted to the high-temperature side as the temperature rise rate increased from 1.0 to 12 K/min.

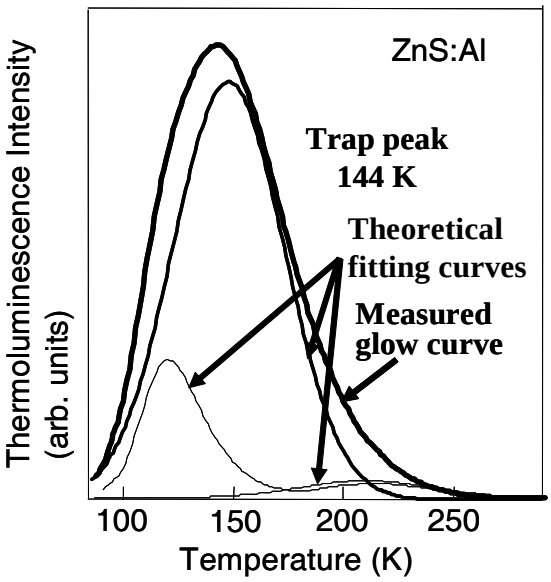

Fig. 4. Thermal-glow curve of ZnS:Al.

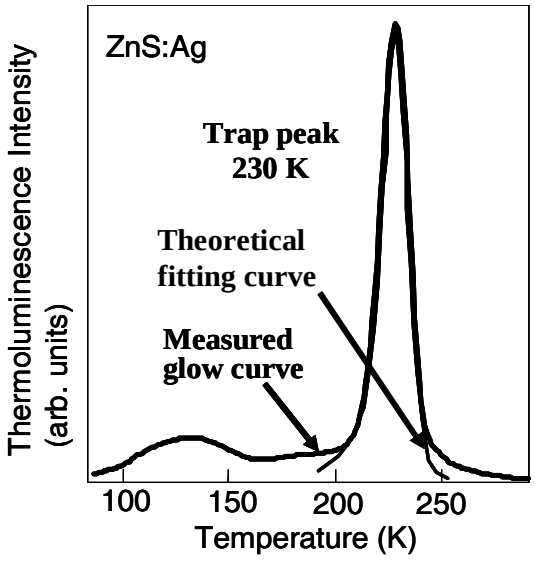

Fig. 5. Thermal-glow curve for ZnS:Ag.

To estimate the trap depth of these traps, we used the Hoogenstraaten plots [4]. Fig. 7 shows the Hoogenstraaten plot for the trap of ZnS:Ag phosphor. The equation used in this plot is given below:

$$\ln(T_{mi}^2/\beta_i) = (E/k)(1/T_{mi}) + C \quad (1)$$

where T_{mi} is the peak temperature in the thermal-glow curve, β_i is the temperature rise, E is the trap depth, and k is the Boltzmann constant. Thus, the slope in fig. 7 shows E/k, and the trap depth (E) was calculated as 0.62 eV for the ZnS:Ag phosphor. The Ag trap at 0.62 eV is newly observed in this study. As the same way, the Hoogenstraaten plot for the trap of ZnS:Al was obtained from the peak temperature (T_{mi}) and the temperature rise (β_i). From the slope of the Hoogenstraaten plot for the trap of ZnS:Al, the trap depth (E) was obtained as 0.28 eV. This trap depth for Al is in good agreement with the previously reported one of 0.25 eV [4].

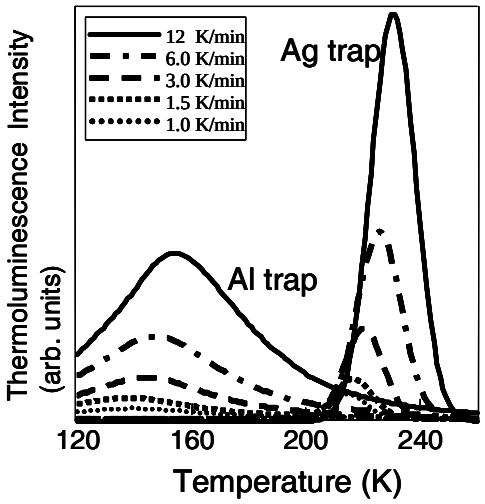

Fig. 6. Temperature-rise dependence for thermal-glow curves of ZnS:Al and ZnS:Ag.

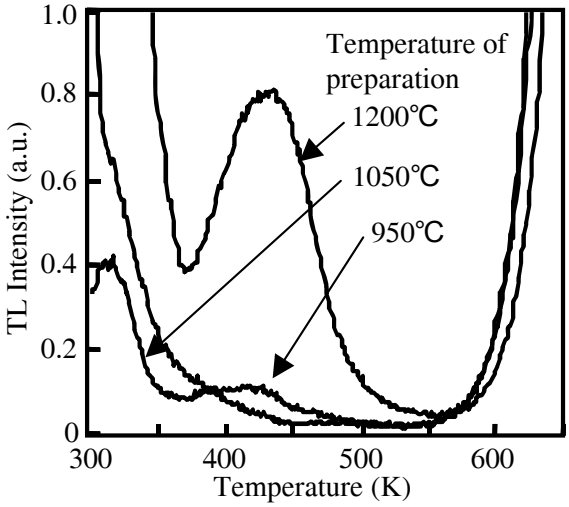

Fig. 8. Thermal-glow curves of Zns:Ag,Al.

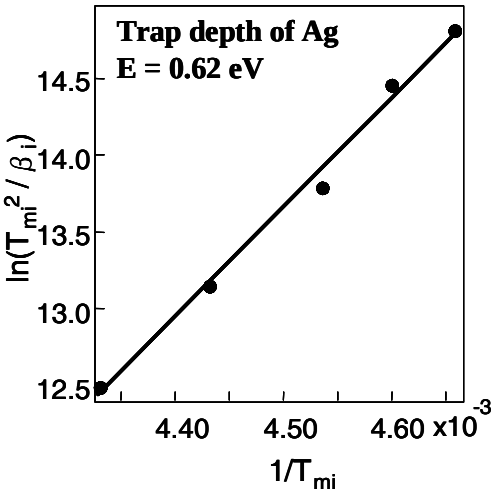

Fig. 7. Hoogenstraaten plot for the trap of ZnS:Ag.

2. Thermal-glow curves of deep electron traps

Next, we investigated the deep trap state for ZnS:Ag,Al phosphors. Fig. 8 shows the thermal-glow curves of ZnS:Ag,Al phosphors prepared at 950 °C, 1050 °C and 1200 °C. The rate of H_2S gas flow was controlled at 100 ml/min while preparing the phosphors at 1050 °C and 1200 °C. The results given for preparation at 950 °C are for the ready-made phosphor. In fig. 8, we see a trap state at 430 K in the phosphors prepared at 950 °C and 1200 °C. The TL intensity of the trap in the 1200 °C sample is greater than that of the trap in the 950 °C sample. This trap has no visible effect on the curve for the sample prepared at 1050 °C. In ZnS:Ag,Al phosphors, thermal quenching is strong and a deep trap has been recently observed in thermal-glow curves above 400 K. Our group analyzed the energy of this state and it was found to be 1.15 eV [5, 6]. Table 1 shows the trap peaks observed in thermal-glow curves of ZnS:Ag,Al, ZnS:Al and ZnS:Ag phosphors along with the corresponding energy levels and fig. 9 shows the energy diagram for each states.

To investigate the deep trap state, we synthesized ZnS:Ag,Al phosphors with various trap concentrations. If the concentration of the deep trap states decreases, the luminous efficiency will increase. Fig. 10 shows thermal-glow curves of ZnS:Ag,Al phosphors prepared at 1200 °C with H_2S gas-flow rates of 50, 100 and 200 ml/min. The trap state at 430 K is visible in all of the thermal-glow curves and its TL intensity decreases slightly with the increase in the H_2S gas-flow rate from 50 to 100 ml/min. It almost vanishes with the increase in the H_2S gas-flow rate from 100 to 200 ml/min. The TL intensity of the trap state thus tends to decrease with increase in H_2S gas-flow rate. We thus assumed that the peak at 430 K represented a state associated with a deep sulfur vacancy. As was mentioned above, the TL intensity of the deep trap is strong for the high preparation temperature of 1200 °C.

Table 1. Trap peaks and the corresponding energy levels of ZnS:Ag,Al phosphors.

	Heating rate (K/min)	Al	Ag	S-vacancy	Two S-vacancy	Deep S-vacancy
Hoogenstraaten	120-180	183 K (0.25 eV)	—	148 K (0.27 eV)	238 K (0.44 eV)	—
This study	6	144 K (0.28 eV)	230 K (0.62 eV)	<120 K (0.08 eV)	205 K (0.42 eV)	430 K (1.15 eV)
Investigated phosphors		ZnS:Al	ZnS:Ag	ZnS:Al	ZnS:Al	ZnS:Ag,Al

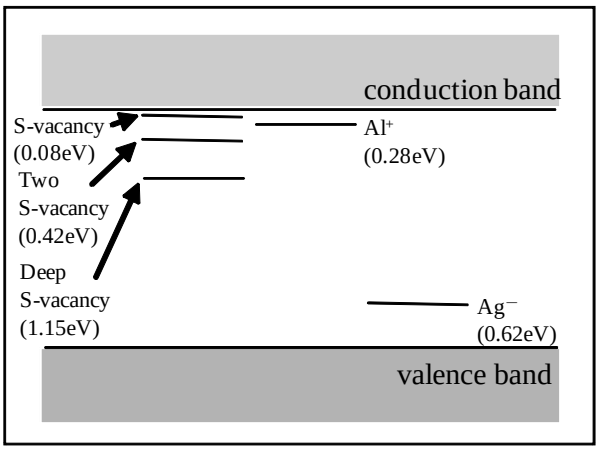

Fig. 9. Energy diagram for the states of ZnS:Ag,Al.

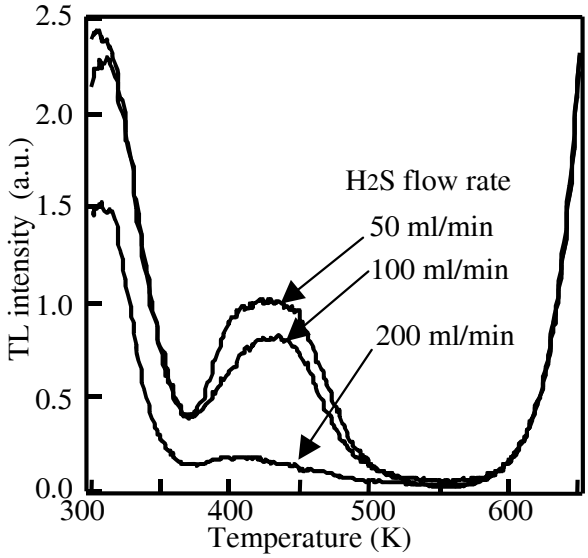

Fig. 10. Thermal-glow curves of ZnS:Ag,Al produced with various H_2S gas-flow rates.

The transition temperature of ZnS is 1020 °C, at which the crystal formation changes from cubic-ZnS to hexagonal-ZnS. The transition in crystal structure from cubic-ZnS to hexagonal-ZnS will thus be a factor in the increased concentration of this deep trap state with the higher temperatures of preparation.

3. Luminescent properties under cathode-ray excitation

To investigate the nonradiative Auger process with the deep trap states, we measured the energy efficiency of ZnS:Ag,Al phosphors. Fig. 11 shows log-log plots of energy efficiency versus current density for ZnS:Ag,Al phosphors produced with H_2S gas-flow rates of 50 and 200 ml/min. The energy efficiency and its slope increase with the H_2S gas-flow rate. The luminous saturation appears in the slope of the current coefficient γ in the log-log plot of energy efficiency versus the current density of an electron beam.

$$L \propto I_k^{\gamma}, \qquad (2)$$

where L is the energy efficiency and I_k is the current density [7]. When there is no luminous saturation, the value of γ is 1.0. When the luminescence goes into saturation, the value of γ falls below 1.0. In the phosphors prepared at 1200 °C, the value of γ was 0.63 for a H_2S gas-flow rate of 50 ml/min and increased with the higher flow rate of 200 ml/min (γ = 0.77). Increasing the H_2S gas-flow rate thus improved the energy efficiency and luminous saturation of the ZnS:Ag,Al phosphors.

The concentration of a trap is reflected in the area under its peak in the thermal-glow curve. Fig. 12 shows the concentration of deep traps

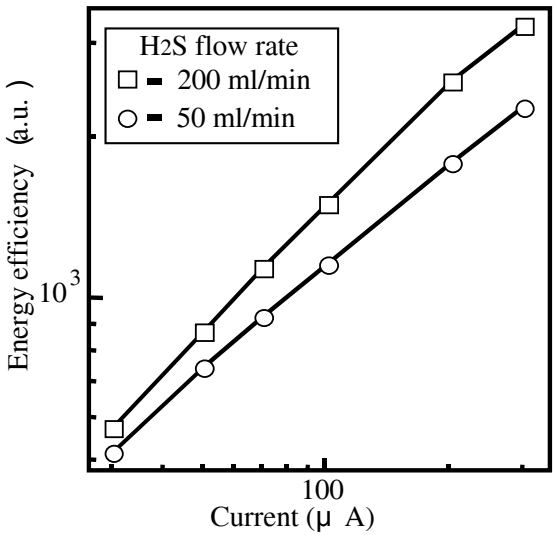

Fig. 11. Energy efficiency of ZnS:Ag,Al.

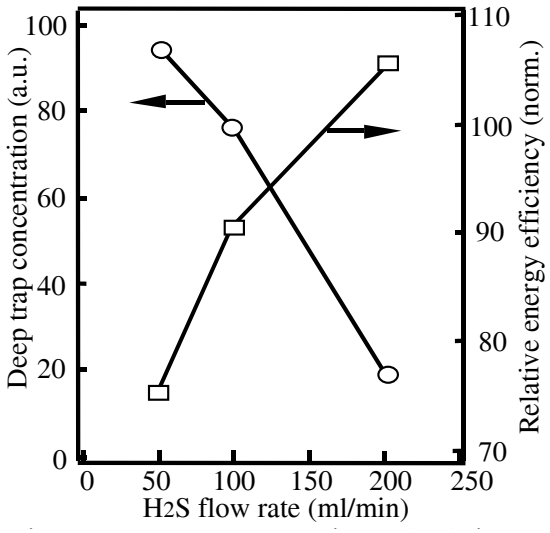

Fig. 12. Deep trap concentration and relative energy efficiency for ZnS:Ag,Al.

at 430 K and the relative energy efficiency of ZnS:Ag,Al phosphors. The deep trap concentration decreases as the flow rate of H_2S gas is increased. The relative energy efficiency increases as the deep trap concentration decreases. Hence, the deep trap concentration is an important factor in the increase in the energy efficiency with H_2S flow rate. In this case, the deep trap forms a nonradiative Auger center with a donor-acceptor pair, with luminescent energy in the donor-acceptor pair being transferred to an electron occupying the deep trap state.

SUMMARY

We prepared ZnS:Ag,Al phosphors with various flow rates of H_2S and obtained thermal-glow curves for the phosphors thus produced. We also measured their luminescent properties under cathode-ray excitation. We located a deep electron trap in the thermal-glow curves.

- This deep trap appears in the thermal glow curve at 430 K and its concentration decreases as the flow rate of H_2S gas is increased.
- The trap peak was assigned at 430 K to a state associated with a deep sulfur vacancy.
- The energy efficiency and luminous saturation improve as the deep trap concentration is decreased.

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CONFLICT OF INTEREST STATEMENT

The authors indicate that there are no conflicts of interest.

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