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Cation-Size-Mismatch Tuning of Photoluminescence in Oxynitride Phosphors

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Supporting Information

ABSTRACT: Red or yellow phosphors excited by a blue light-emitting diode are an efficient source of white light for everyday applications. Many solid oxides and nitrides, particularly silicon nitride-based materials such as $M_2Si_5N_8$ and $MSi_2O_2N_2$ (M = Ca, Sr, Ba), $CaAlSiN_3$, and SiAlON, are useful phosphor hosts with good thermal stabilities. Both oxide/nitride and various cation substitutions are commonly used to shift the emission spectrum and optimize luminescent properties, but the underlying mechanisms are not always clear. Here we show that size-mismatch between host and dopant cations tunes photoluminescence shifts systematically in $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ lattices, leading to a red shift when the M = Ba and Sr host cations are larger than the Eu^{2+} dopant, but a blue shift when the M = Ca host is smaller. Size-mismatch tuning of thermal quenching is also observed. A local anion clustering mechanism in which Eu^{2+} gains excess nitride coordination in the M = Ba and Sr structures, but excess oxide in the Ca analogues, is proposed for these mismatch effects. This mechanism is predicted to be general to oxynitride materials and will be useful in tuning optical and other properties that are sensitive to local coordination environments.

The (oxo)nitridosilicates $M_2Si_5N_8$ and $MSi_2O_2N_2$ (M = Ca, Sr, Ba) doped with Eu^{2+} are widely used as red phosphors to provide warm white light-emitting diode (LED) devices.[1−9] Intermediate materials made by substituting AlO^+ for SiN^+ in the $M_2Si_5N_8$ family to create $M_2Si_{5-x}Al_xN_{8-x}O_x$ SiAlONs (silicon aluminum oxide nitrides) are mentioned briefly in an early paper, but systematic substitutional effects on the photoluminescence were not reported.[10] We have prepared and characterized ceramic $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials with a constant 2.5% doping of Eu^{2+} at the M^{2+} sites for M = Ca, Sr, and Ba up to the approximate solid solution limit of x = 1.

Smooth changes of lattice parameters with x in Figure 1a demonstrate that $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ solid solutions are formed. The lattice expands with x for all three M cations, as expected for the replacement of SiN^+ (sum of ionic radii $^{[4]}r(Si^{4+})$ + $^{[4]}r(N^{3-})$ = 0.26 + 1.46 = 1.72 Å; the leading bracketed superscript shows the coordination number throughout) by the slightly larger AlO^+ combination ($^{[4]}r(Al^{3+})$ + $^{[4]}r(O^{2-})$ = 0.39 + 1.38 = 1.77 Å).[11] The parent structures contain equal numbers of nitrides bonded to two or three silicon neighbors, as represented in the formula

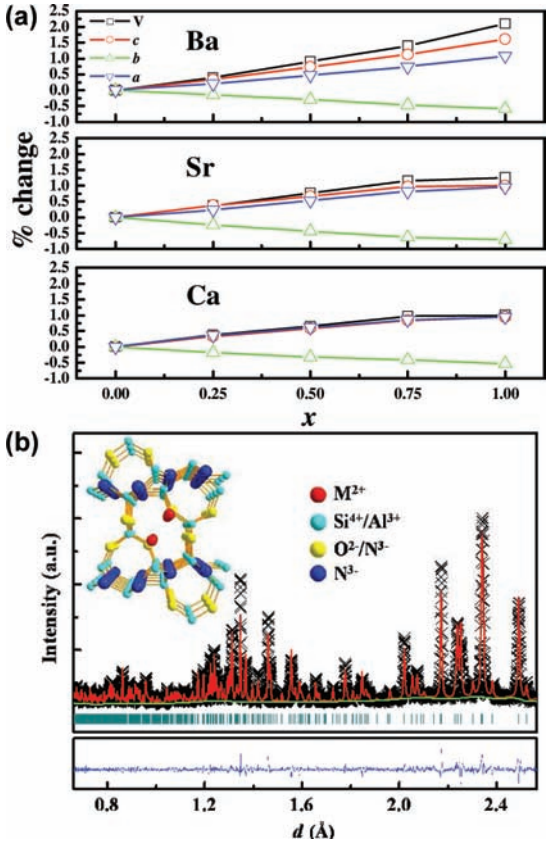

Figure 1. Structural results for $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ (M = Ca, Sr, Ba) materials. (a) Relative shifts in the lattice parameters with x. We use pseudo-orthorhombic parameters $a = b_m$, $b = a_m/2$, $c = c_m$ for the monoclinic Ca series cells (m subscripts) for direct comparison with the orthorhombic M = Sr and Ba series. (b) Fit to time-of-flight neutron diffraction data for $Ba_{1.95}Eu_{0.05}Si_4AlN_7O$. Structure refinement shows that the oxygen atoms substitute only for $^{[2Si]}N$ (nitrides bonded to two silicons), and not at $^{[3Si]}N$ sites, as illustrated in the inset view of the crystal structure.

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$M_2Si_5{}^{[3Si]}N_4{}^{[2Si]}N_4$. The anion distribution in a $Ba_{1.95}Eu_{0.05}Si_4AlN_7O$ sample, determined from a neutron diffraction study (Figure 1b), shows that the oxygen atoms substitute only at $^{[2Si]}$N sites. This is consistent with oxosilicate chemistry, where $^{[3Si]}$O coordination is not observed, and illustrates the "Pauling's second rule" model for anion distributions,[12] as the lower valent oxide anion is less coordinated by high-valent silicon. This partial anion order is important to the optical properties below, as the M cation sites are coordinated principally by the $^{[2Si]}$N/O anions.

Photoluminescence spectra of the $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials are shown in Figure 2a. The peak emission wavelengths for the $x = 0$ nitride materials are similar to those reported previously[8,13−15] and are in the order Sr > Ca > Ba. This irregular sequence reflects a complex balance of lattice and local coordination effects, notably a change in crystal structure type between the M = Sr and Ca materials. A surprising observation is that the photoluminescence maximum shifts to longer wavelengths (a red shift) with increasing AlO^+ substitution, x, in the M = Ba and Sr series, but a pronounced blue shift to shorter wavelengths is observed in the Ca analogues. This variation and switching of energy shift was not reported in studies of $M_{2-y}Eu_ySi_5N_8$ and $M_{1-y}Eu_ySi_2O_2N_2$, where the emission wavelength shows a red shift with y reflecting typical Stokes and reabsorption effects in both series.[8,9] Our observed energy shifts for M = Ba, Sr, and Ca samples display a size-mismatch variation. The host M = Ba, Sr, and Ca cations show a significant dispersion of sizes ($^{[8]}r(M^{2+})$ = 1.42, 1.26, and 1.12 Å respectively), and the europium dopant ($^{[8]}r(Eu^{2+})$ = 1.25 Å) is slightly smaller than Sr^{2+}. A red shift is observed for M = Ba and Sr hosts larger than the emitting dopant Eu^{2+} ions, but for smaller Ca^{2+} cations this switches to a blue shift. Plotting the energy shifts against the size difference $\Delta r = r(M^{2+}) - r(Eu^{2+})$ for each set of three samples with the same x gives a series of lines that cross near $\Delta r = 0$ (Figure 2b), showing that the shifts have an approximately linear dependence on size-mismatch.

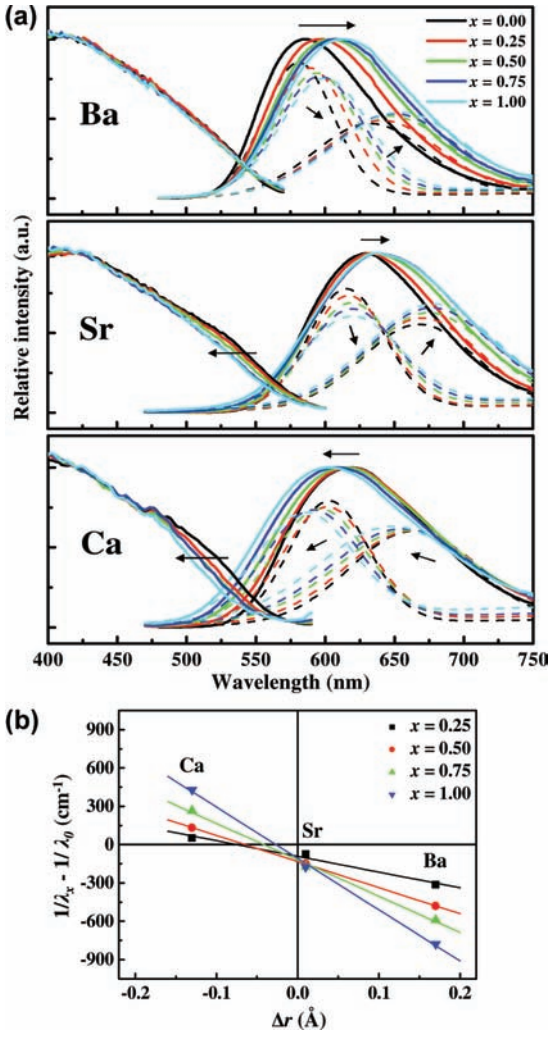

Figure 2. Photoluminescence of $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials (M = Ca, Sr, Ba). (a) Normalized excitation (lower wavelength contribution) and photoluminescence spectra from excitation by a Xe lamp at room temperature. The photoluminescence spectra are decomposed into Gaussian contributions from the two M cation sites in the $M_2Si_5N_8$ type structures. The arrows illustrate the energy shift and change in relative intensity of the spectra with increasing x. (b) Graph showing the energy shift (in wavenumbers) for the peak photoluminescence of $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials (M = Ca, Sr, Ba) vs $\Delta r = r(M^{2+}) - r(Eu^{2+})$, the difference between ionic radii of the host (M) and dopant (Eu) cations, for several compositions x. The crossover of the constant composition lines near $\Delta r = 0$ demonstrates the size-mismatch effect.

A strong size-mismatch influence on thermal quenching of photoluminescence, which is important to the performance of white-LED devices, is also observed in the $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials, as shown in Figure 3. The onset temperature for thermal quenching remains at ∼300 K for the M = Sr and Ba series as the level of AlO^+ substitution increases up to $x = 1$, but decreases to ∼150 K for M = Ca materials. The undoped $x = 0$ materials all have quenching activation energies ∼0.28 eV, but the values for the three series diverge with increasing x (Figure 3b). The activation energy rises slightly in the Ba series but is suppressed to 0.10 eV at x = 1 for M = Ca.

Systematic changes in Eu^{2+} populations at the two distinctive M^{2+} sites with different coordination environments in the $M_2Si_5N_8$ crystal structures were investigated as a possible origin of the above size-mismatch effects.[16] Figure 2a shows that photoluminescence intensity is transferred from the shorter wavelength (higher coordination M-site) component to the longer wavelength (less coordinated site) peak with increasing x in all three $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series. This increase in nonradiative crossing is supported by time-resolved photoluminescence spectra shown in Supporting Information, but the time-dependent energy shifts and the crossing rates do not correlate with Δr, so the size-mismatch variations in Figures 2 and 3 are not attributable to changes of relative Eu^{2+} site populations.

To explain the size-mismatch variations of energy shift and thermal quenching with x in $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ phosphors, we propose a model based on changes in the local numbers of nitride and oxide anions coordinated to Eu^{2+}. These changes tune the photoluminescence energy by altering the balance between two competing effects. The lattice and the Eu^{2+} coordination environments expand with x, as AlO^+ is slightly larger than SiN^+, resulting in a red shift. However, the partial substitution of oxide for nitride coordinated to Eu^{2+} leads to a blue shift with x through changes in crystal field and nephalauxetic effects. The net outcome in an ideal, cation-size-matched $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series turns out to be a small red shift, as evidenced by the energy offsets of the lines in

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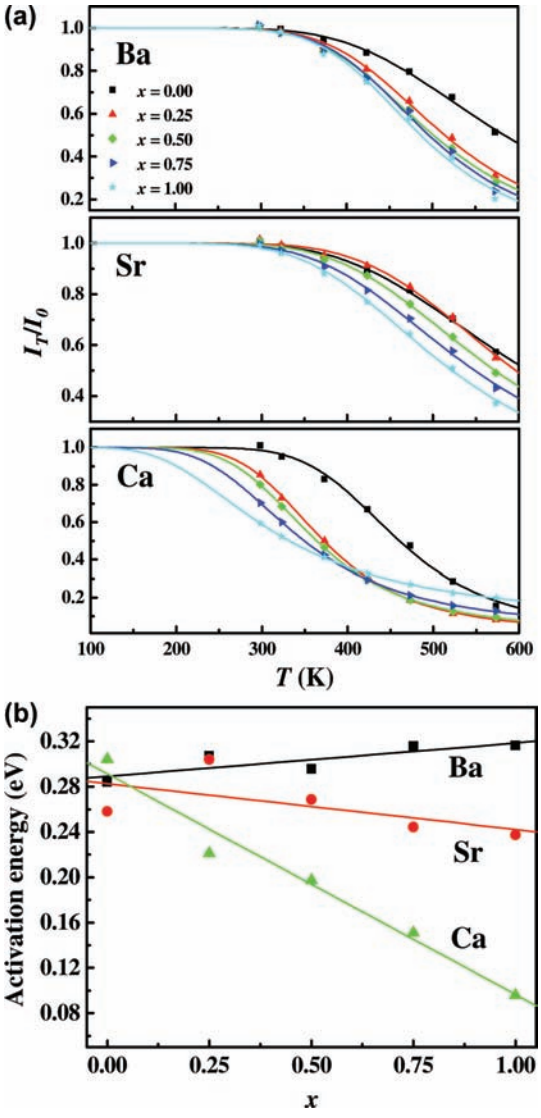

Figure 3. Thermal quenching of photoluminescence for $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials (M = Ca, Sr, Ba). (a) Photoluminescence intensity ratios I_T/I_0 measured at temperatures T = 298 − 573 K. The curves show fits of the equation $I_T/I_0 = [1 + D\exp(-E_a/kT)]^{-1}$, where I_0 (the intensity at T = 0), D, and the activation energy E_a were refined variables. (b) Plot of the activation energies against composition variable x for the M = Ca, Sr, and Ba series showing a size-mismatch variation of the slopes.

Figure 2b at Δr = 0 (and the M = Sr series data where the size-mismatch is small). In this ideal structure, the average numbers of oxide and nitride anions coordinated to Eu^{2+} would be the same as the overall structural average for the M^{2+} cations. However, the local Eu^{2+} coordination changes when a large mismatch is present through a simple size-compensation mechanism as the difference between anion radii ($^{[4]}r(N^{3-}) - {}^{[4]}r(O^{2-})$ = 0.08 Å) is comparable to the cation size-mismatches between large Ba^{2+} or small Ca^{2+} and the dopant Eu^{2+}. Local anion clustering provides an effective way of reducing lattice strains by equalizing the mean cation−anion distances, as illustrated in Figure 4.

The Eu^{2+} dopants are larger than the host cations in the $Ca_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series, so lattice strain is minimized by clustering above-average numbers of oxide anions around Eu^{2+} cations (and hence more nitrides around Ca^{2+}), as in

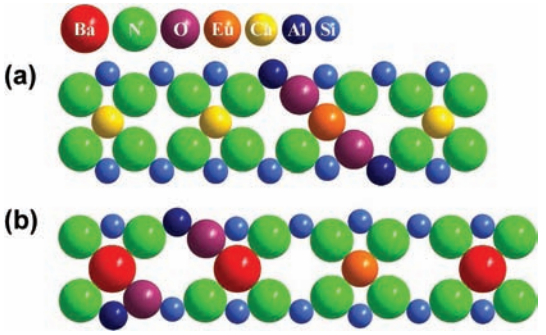

Figure 4. Schematic local anion distributions driven by cation size-mismatch in $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ phosphors. (a) Local structure for $Ca_{1.95}Eu_{0.05}Si_4AlN_7O$, where Eu^{2+} is bigger than the host Ca^{2+} cations and lattice strain is minimized by clustering oxide anions around Eu^{2+} cations (and hence more nitrides around Ca^{2+}), resulting in a blue shift of the photoluminescence. (b) $Ba_{1.95}Eu_{0.05}Si_4AlN_7O$, where Eu^{2+} is smaller than the host Ba^{2+} cations and so tends to be coordinated by nitride, while the introduced oxide anions preferentially coordinate Ba^{2+}. Al^{3+} is shown as preferentially coordinating oxide, consistent with the solid-state NMR spectra in Supporting Information.

Figure 4a. The increased oxide coordination around Eu^{2+} results in a large blue shift of the photoluminescence energy (Figure 2), from which the approximate coordination change may be estimated as follows. The anion coordination to each Ca^{2+} in the $Ca_2Si_5{}^{[3Si]}N_4{}^{[2Si]}N_4$ parent structure is $^{[2Si]}N_5{}^{[3Si]}N_2$, illustrating the predominant coordination by nitrides bonded to two Si sites. Oxide substitutes only at $^{[2Si]}N$ sites in the SiAlON derivatives, as demonstrated above by neutron diffraction (Figure 1b), so in $Ca_{1.95}Eu_{0.05}Si_4AlN_7O$ the average Ca^{2+} and Eu^{2+} coordination is $(^{[2Si]}N_{0.75}{}^{[2Si]}O_{0.25})_5{}^{[3Si]}N_2 = O_{1.25}N_{5.75}$, in the absence of any anion clustering. The change from this average is estimated by assuming that the observed blue shift of 1700 cm^{-1} between the reported peak photoluminescences of $Ca_{1.96}Eu_{0.04}Si_5N_8$[16] and $Ca_{1.98}Eu_{0.02}Si_2N_2O_2$[9] results mainly from the change of Ca^{2+}/Eu^{2+} cation coordination from N_7 in the former material to O_6N in the latter. Hence, by interpolation, the 520 cm^{-1} blue shift of $Ca_{1.95}Eu_{0.05}Si_4AlN_7O$ relative to the ideal Δr = 0 analogue (see Figure 2b) corresponds to an estimated change of $O_{+1.85}N_{-1.85}$ in the average Eu^{2+} coordination, so although the average cation coordination in $Ca_{1.95}Eu_{0.05}Si_4AlN_7O$ is $O_{1.25}N_{5.75}$, the local Eu^{2+} environment is approximately $O_{3.1}N_{3.9}$ and the balancing Ca^{2+} coordination is $O_{1.2}N_{5.8}$. The change around the majority host Ca^{2+} cations is very slight, but a substantial size-driven clustering of oxides around the Eu^{2+} dopants drives the blue shift in the photoluminescence.

A reverse argument applies to predicted anion clustering in the $Ba_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series. Here Eu^{2+} is smaller than the host Ba^{2+} cations and so tends to be coordinated by nitride, while the introduced oxide anions preferentially coordinate Ba^{2+} as shown in Figure 4b. An estimate based on the photoluminescence shift of 3200 cm^{-1} between $Ba_{1.96}Eu_{0.04}Si_5N_8$[16] and $Ba_{1.98}Eu_{0.02}Si_2N_2O_2$[9] phosphors shows that the number of oxides coordinated to Eu^{2+} is approximately zero. Hence, for $Ba_{1.95}Eu_{0.05}Si_4AlN_7O$, the mean cation coordination (averaged over 8- and 10-fold sites) is $O_{1.5}N_{7.5}$, but the approximate local coordinations are N_9 for Eu^{2+} and $O_{1.55}N_{7.45}$ for the Ba^{2+} hosts. The red shift observed in the $Ba_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series thus reflects only the lattice-

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expanding effect from AlO^+ substitution, as the Eu^{2+} dopants are not significantly coordinated by oxide anions.

The above anion clustering model also accounts for the size-mismatch control of thermal quenching (Figure 3). Oxide phosphors are known to have lower quenching activation energies than comparable nitrides.[17,18] In an ideal, size-matched $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ series this leads to a slight decrease in activation energy with x, illustrated by the M = Sr materials in Figure 3b, as the local Eu^{2+} coordination reflects the average anion composition. However, in the M = Ca series, Eu^{2+} ions are coordinated by substantially above-average numbers of oxides (Figure 4a), leading to a rapid decline in quenching activation energy with x. Conversely, Eu^{2+} is in a virtually pure nitride coordination environment in the M = Ba materials, despite the presence of oxides within the lattice (Figure. 4b), and the quenching activation energy increases slightly with x.

The above results show that lattice strains resulting from size-mismatch between host and dopant cations can drive large changes in the dopant coordination relative to the average in SiAlONs, even in materials synthesized at high temperatures (1600 °C for our ceramic $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ samples), where entropically favored randomization might be expected to dominate the anion distributions. Minimization of local lattice strains created by cation size-mismatch results in local coordination numbers that may be far from averages based on the chemical composition or even on anion distributions from neutron diffraction. The expected number of coordinating oxides per Eu^{2+} dopant in $M_{1.95}Eu_{0.05}Si_4AlN_7O$ lattices would be 0.9−1.1 from the chemical formula, and 1.25−1.5 based on the average anion distributions within the crystal structure. However, the coordination can increase up to ∼3 oxides per Eu^{2+} for small M = Ca host cations or decrease to ∼0 in the Ba analogue. This clustering effect provides a useful tuning of the photoluminescence wavelength by up to 700 cm^{-1} relative to a size-matched reference material (here approximated by M = Sr) and also controls the thermal quenching behavior.

The size-mismatch effect discovered in $M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x$ materials could be used to tune photoluminescence in related phosphors such as α- and β-SiAlONs and the $MSi_2O_2N_2$ (M = Ca, Sr, Ba) family, and to help understand the results of combinatorial studies. Furthermore, we note that this effect should be general to cation-doped oxynitrides, including those not based on (oxo)nitridosilicate frameworks. For example, size-mismatch-driven clustering of anions may be significant in perovskite-type solid solutions in $BaTaO_2N$−$SrTaO_2N$ photocatalysts[19] and $CaTaO_2N$−$LaTaON_2$ red-yellow pigments,[20] where disordered zigzag TaN chains[21] may be pinned by the local cation-mismatch strains. The same effect is also expected to operate in other mixed-anion systems such as oxyfluoride ceramics and glasses, which are also important optical materials, where the anion size difference ($^{[4]}r(F^-)$ = 1.31 Å; $^{[4]}r(O^{2-}) - {}^{[4]}r(F^-)$ = 0.07 Å) is comparable to the 0.08 Å difference responsible for the clustering that we have observed here in oxynitride phosphors.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; supporting figures and tables showing further crystallographic, photoluminescence, and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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