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Doping of hydroxyapatite with europium ions Eu^{3+} and investigation of the effect of codoping ions Dy^{3+}, Y^{3+}, B^{3+} on its luminescent properties

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Hydroxyapatite (HAP) was doped with europium ions Eu^{3+}, and the effect of codoping ions Dy^{3+}, Y^{3+} and B^{3+} on its luminescent properties was studied in order to obtain hydroxyapatite with a high luminescence yield in the visible spectrum range. The photoluminescence spectra of the following codoped hydroxyapatites were studied: HAP:Eu,Dy, HAP:Eu,B, HAP:Eu,Y. Codoping with the Y^{3+}, B^{3+} ions was found to drastically change the HAP:Eu photoluminescence spectrum. In the HAP:Eu,B and HAP:Eu,Y spectra there appeared a wide intense photoluminescence band with the maxima at wavelengths $\lambda = 515$ and 520 nm, respectively; the band was characteristic of europium ions Eu^{2+}.

Keywords: hydroxyapatite, rare earth elements, annealing, doping, luminescence spectra.

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Hydroxyapatite (HAP) is one of the main inorganic biocompatible materials whose structure is close to human hard tissue. In the context of biology and medicine, hydroxyapatite is the main mineral component of bones, teeth, and many pathological calcifications in humans. It is used in orthopedics and dentistry as a treatment medication, and, hence, is of great practical interest. For instance, apatite coatings are applied to metal and ceramic prostheses in order to improve their biocompatibility [1,2].

The apatite crystal structure and chemical composition allow for numerous substitutions, including substitution with multiple metal cations replacing Ca in the structure and with anionic complexes replacing PO_4 [1,3]. The presence in hydroxyapatite of impurities and defects provides it with luminescent properties. Hydroxyapatite doped with ions of rare earth elements (REE) is widely used in biomedicine as a biological probe used to visualize the processes occurring in biological objects. In this case, doped hydroxyapatite needs to be non-toxic and to exhibit a high yield of photoluminescence weakly absorbable in biological object tissues. To date, hydroxyapatites doped with different REEs have been obtained: Eu^{3+}, Dy^{3+}, Gd^{3+}, La^{3+}, Yb^{3+}, Sm^{3+}, Ce^{3+}, Tb^{3+}, Er^{3+}, Tm^{3+}, etc. [4–6]. The photoluminescence spectrum depends on what REE is used for doping. In the visible spectrum range, europium-doped hydroxyapatite meets well the above requirements, since europium has a ionic radius close to that of calcium and luminesces in the red spectrum range, and europium-doped hydroxyapatite (HAP:Eu) is low-toxic. Due to these properties, it has been successfully used for medical purposes in recent years. For instance, HAP:Eu nanoparticles are used as a fluorescent labeling material, are able to absorb drugs and, being illuminated by external radiation, can visualize the motion and localization in tissues of nanoparticles with drug molecules [7,8]; they also find application in disease therapy [9], testing antimicrobial activity, magnetic resonance imaging, and cellular tomography [10]. To increase the photoluminescence yield, HAP is additionally codoped with an appropriate impurity acting as a sensibilizer (see, e.g. [4,11]).

The goal of this study was to obtain hydroxyapatite doped with Eu^{3+} ions by high-temperature vacuum annealing and to investigate the effect of codopants Dy, B and Y on the hydroxyapatite $Ca_5OH(PO_4)_3$ photoluminescent properties.

The samples for this study were prepared by high-temperature vacuum annealing of a mixture of hydroxyapatite $Ca_5OH(PO_4)_3$ powder with powders of REE oxides (Eu_2O_3, Dy_2O_3, Y_2O_3) and boric acid (H_3BO_3); the molar mass fraction of Eu_2O_3 was 3 %, those of Dy_2O_3 and Y_2O_3 were 2 % each, that of H_3BO_3 was 3 %. In this work, high-purity commercial hydroxyapatite with parameters $Ca/P > 1.5$ and $pH > 5$ was used. The following compositions were prepared:

$$\text{I} — Ca_5OH(PO_4)_3 + 0.03Eu_2O_3 \rightarrow$$

$$Ca_5OH(PO_4)_3 : Eu^{3+}(\text{HAP : Eu}),$$

$$\text{II} - Ca_5OH(PO_4)_3 + 0.03Eu_2O_3 + 0.02Dy_2O_3 \rightarrow$$

$$Ca_5OH(PO_4)_3 : Eu^{3+}, Dy^{3+}(\text{HAP : Eu,Dy}),$$

$$\text{III} - Ca_5OH(PO_4)_3 + 0.03Eu_2O_3 + 0.03H_3BO_3 \rightarrow$$

$$Ca_5OH(PO_4)_3 : Eu^{3+}(\text{HAP : Eu,B}),$$

$$\text{IV}-Ca_5OH(PO_4)_3 + 0.03Eu_2O_3 + 0.02Y_2O_3 \rightarrow$$

$$Ca_5OH(PO_4)_3 : Eu^{3+}, Y^{3+}(\text{HAP : Eu,Y}).$$

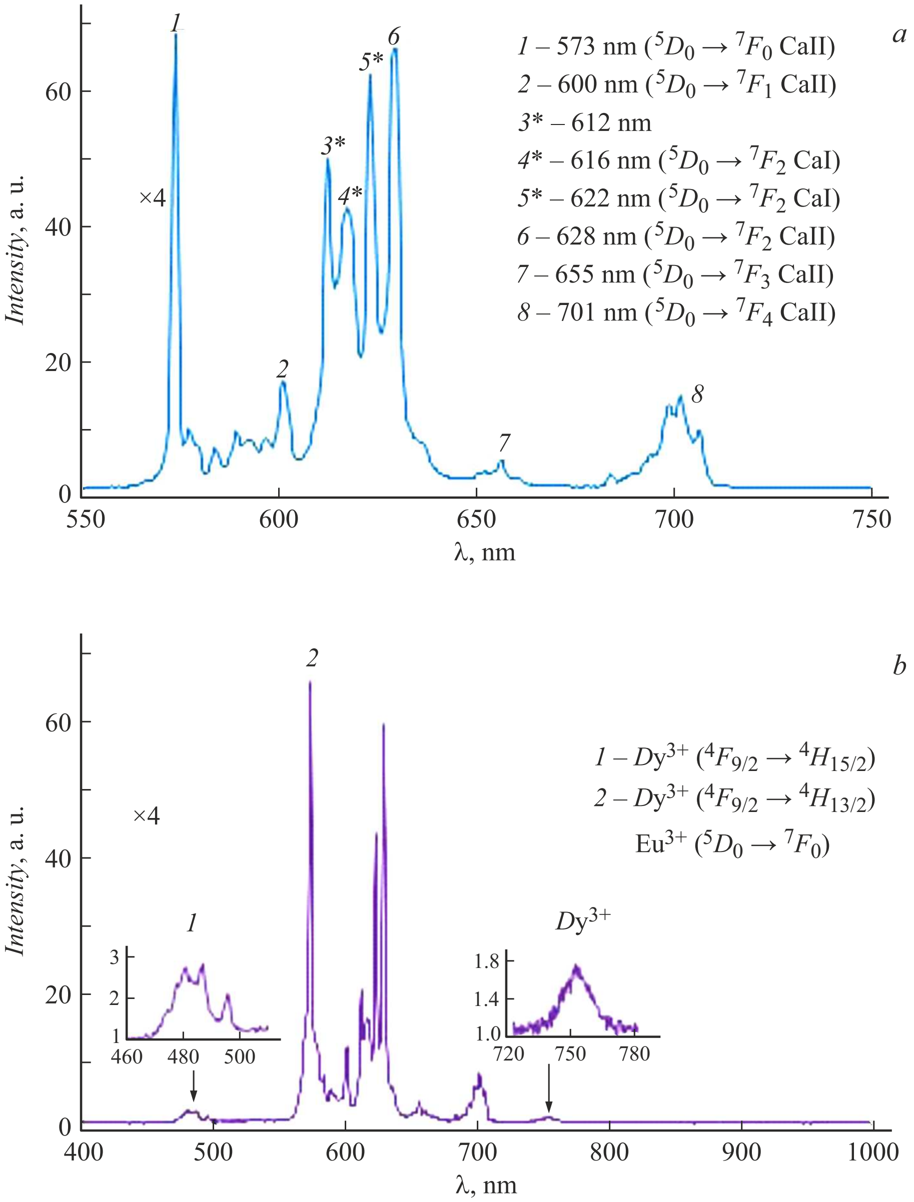

Figure 1. *a* — HAP:Eu photoluminescence excited by a cw laser with $\lambda = 405$ nm (the spectrum is magnified 4 times). *b* — HAP:Eu,Dy photoluminescence excited by a cw laser with $\lambda = 405$ nm (the spectrum is magnified 4 times). Maximum *2* (573 nm) is a superposition of maxima at 573 nm (Eu^{3+}) and 572 nm (Dy^{3+}). *c* — HAP:Eu,B photoluminescence excited by a cw laser with $\lambda = 405$ nm. *d* — HAP:Eu,Y photoluminescence excited by a cw laser with $\lambda = 405$ nm.

Each of the compositions was thoroughly mixed in ethyl alcohol, dried at room temperature, and, after drying, mixed again in a mill. Next, the powders were compressed into tablets 15 mm in diameter and 4 mm in thickness. After air evacuation, the furnace pressure was $P \approx 13.3$ Pa. The samples were heated at the rate of 8 K/min to the temperature of 1573 K, after which they were annealed at the same temperature for an hour. Then the furnace was turned off, and crucibles with samples were spontaneously cooled in the furnace to room temperature. The obtained samples looked white in daylight. Next, photoluminescence spectra of the HAP:Eu, HAP:Eu,Dy, HAP:Eu,B, and HAP:Eu,Y samples obtained after annealing were measured with spectrometer BWSpec4. To excite the photoluminescence spectra, the 405-nm diode-laser continuous wave (cw) radiation (up to 70 mW in power) was used. Taken separately, HAP, H_3BO_3, Dy_2O_3, Y_2O_3, and HAP:Y are almost non-photoluminescent under the $\lambda = 405$ nm laser radiation. Adding to hydroxyapatite europium oxide Eu_2O_3 (composition I) and subsequent annealing result in formation of doped HAP:Eu; this is evidenced by arising in the photoluminescence spectrum of peaks corresponding to ions Eu^{3+} in the HAP matrix; the most intense of them are peaks with maxima at $\lambda = 573$,

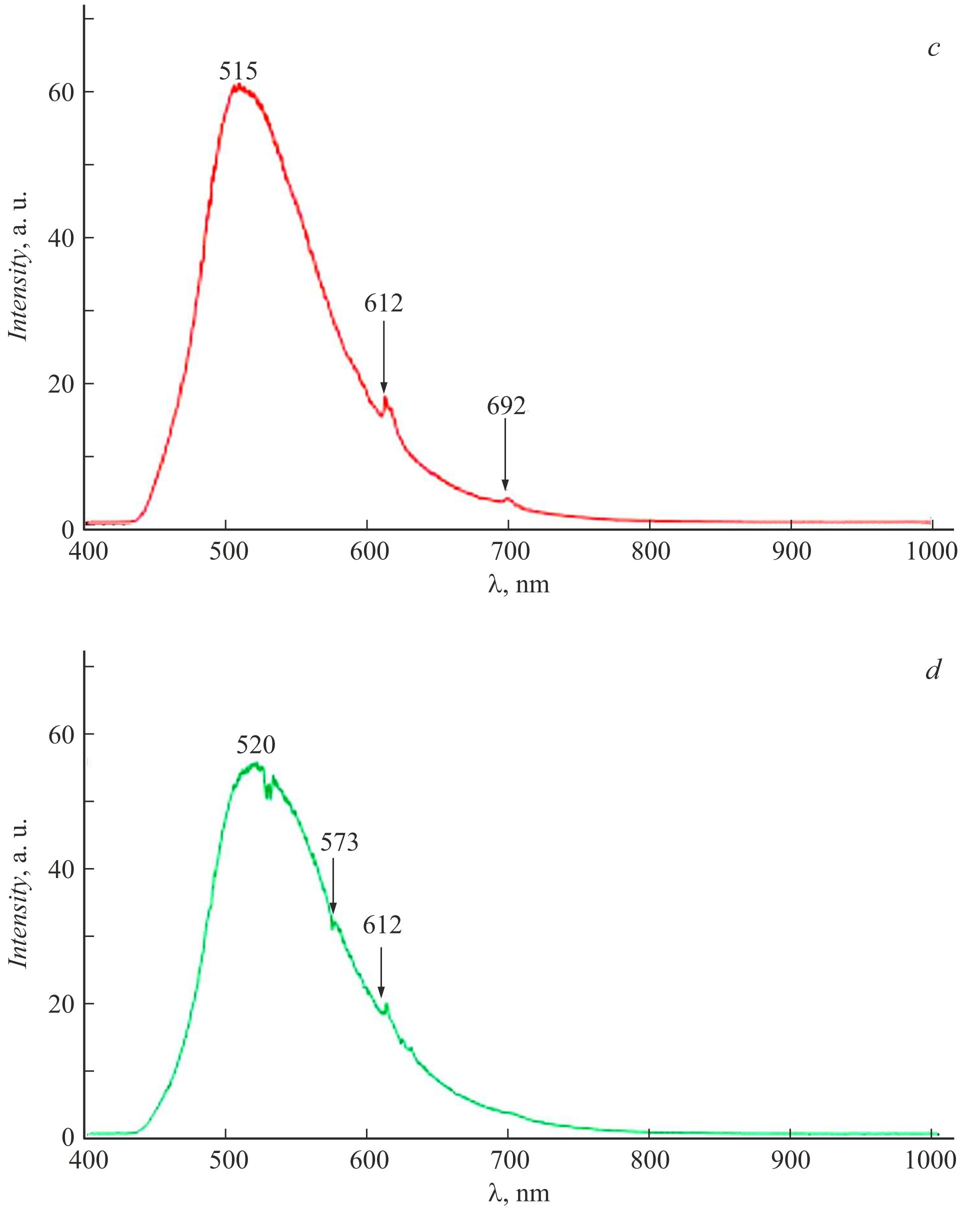

Fig. 1 (*continued*).

628 nm (Fig. 1, *a*). Fig. 1, *b* presents the photoluminescence spectrum of HAP:Eu,Dy after annealing composition II. The spectrum begins exhibiting photoluminescence peaks related to ions Dy^{3+} in the HAP matrix. Fig. 1, *c* shows the photoluminescence spectrum of HA : Eu,B obtained after annealing composition III. As shown in the figure, adding boric acid to composition I radically changes the photoluminescence spectrum: a broad and intense spectral band with the maximum at $\lambda \approx 515$ nm arises in the HAP:Eu,B spectrum. A similar situation is observed in case yttrium oxide Y_2O_3 is added to composition I. Fig. 1, *b* presents the photoluminescence spectrum of HAP:Eu,Y after annealing composition III. Evidently, the HAP:Eu,Y photoluminescence spectrum also differs drastically from the HA : Eu spectrum. Adding yttrium oxide Y_2O_3 to composition I gives rise to a broad photoluminescence band in the HAP:Eu,Y spectrum with the maximum at $\lambda \approx 520$ nm. Against this broad band, one can see small narrow peaks at 573 and 612 nm which coincide with photoluminescence peaks of Eu^{3+} in the HAP:Eu spectrum.

It is known [1–3] that calcium ions can occupy two positions in the HAP structure (positions CaI and CaII), which differ in the symmetry of environment. The ratio between components in the hydroxyapatite under study ($Ca/P = 1.5$) evidences the presence of calcium vacancies (stoichiometry $Ca/P = 1.67$). It is also known that europium ions Eu^{3+} may replace calcium ions in the HAP structure. Positions CaII were found to have lower symmetry. Transition of europium ions to a position with a lower environment symmetry may result in removing

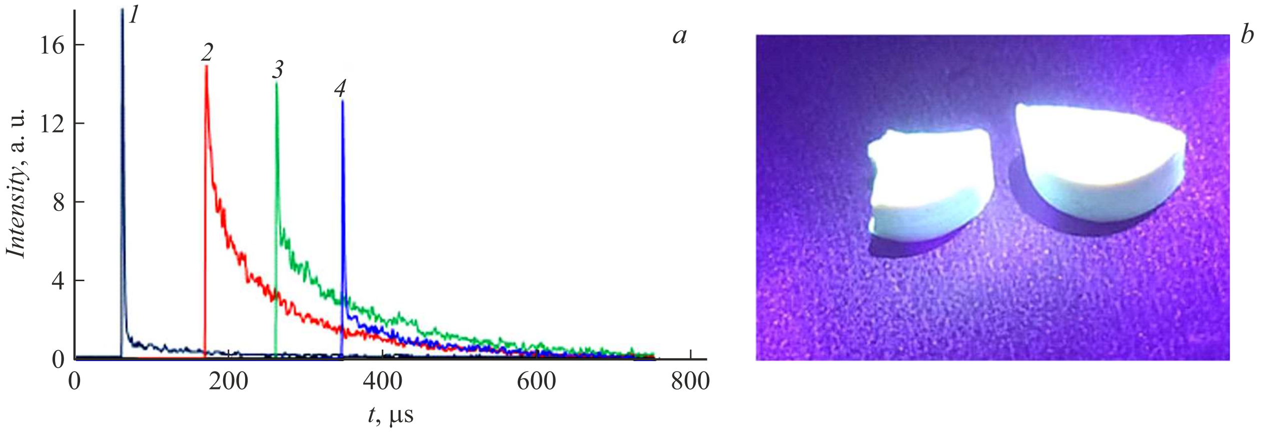

Figure 2. *a* — kinetics of attenuation in different spectral regions of the broad band of HAP:Eu,Y photoluminescence excited by laser radiation with wavelength $\lambda = 355$ nm and pulse duration $\tau = 8$ ns. *1* — 520 nm (the band maximum associated with radiative transitions of Eu^{2+} ions), attenuation constant $\alpha \approx 1.6 \cdot 10^{-1}\,\mu\mathrm{s}^{-1}$; *2* — 573 nm (coincides with the maximum of the Eu^{3+}radiative transition ($^5D_0 \to {}^7F_0$), attenuation constant $\alpha \approx 1.4 \cdot 10^{-2}\,\mu\mathrm{s}^{-1}$. Curves *3*, *4* correspond to the vicinity of the Eu^{3+} transition (573 nm) and contain sections of rapid and slow decay related to contributions of the Eu^{2+} and Eu^{3+} ions. *b* — image of the HAP:Eu,Y sample (tablet) illuminated by weak radiation with $\lambda = 405$ nm.

(splitting) of degenerate energy levels and in emergence of additional photoluminescence spectrum lines. In [11–14], luminescent properties of doped HAP:Eu, HAP:Eu,Dy were studied; the observed photoluminescence spectrum peaks were related to relevant HAP-matrix radiative transitions between spectral terms $^5D_0 \to {}^7F_j$ of europium ions Eu^{3+} and $^4F \to {}^6H_j$ of dysprosium ions. It is known that at low annealing temperatures (up to 723 K) ions Eu^{3+} occupy predominantly the CaI positions; as the temperature increases, more and more intense transitions to the CaII positions are observed. At $T \geqslant 1173$ K, almost all europium ions Eu^{3+} transit to the CaII positions.

The observed spectrum variations resulting from annealing compositions I–IV are associated with crystallization and rearrangement of the HAP matrix crystalline structure and with thermally activated diffusion (hereinafter referred to as diffusion) of the Eu^{3+}, Dy^{3+}, Y^{3+} and B^{3+} ions from respective oxides and boric acid into the HAP matrix in the process of high-temperature annealing. An increase in peak intensity with increasing annealing temperature and duration also evidences the ion diffusion during annealing. Broad luminescence bands are typically characteristic of luminescent impurities in glasslike and amorphous media where the impurity is distributed randomly throughout the bulk and have no certain crystalline environment, which results in „nonuniform“ broadening, shifts of levels, and merging of luminescence peaks. However, in this case it is noteworthy that adding to HAP:Eu either boric acid or yttrium oxide almost identically results in formation of a broad and intense luminescence band (Figs. 1, *c*, *d*). As Figs. 1, *a*, *b* show, the Eu^{3+} ions do not exhibit radiative transitions in the wavelength range of 500–525 nm. The europium impurity is known to take, in a number of compounds, oxidation states of both the Eu^{3+} and Eu^{2+} forms, and just on them the luminescence spectrum depends. As a rule, ions Eu^{2+} have luminescence maxima in the range of 500–525 nm in different compounds, e. g., in the SrAl$_2$O$_4$:Eu^{2+} ceramics which also exhibits intense broad luminescence bands with the maxima at $\lambda \approx 520$ nm [15,16]. Therefore, the observed spectrum variations may be explained by assuming that, in annealing compositions III and IV, diffusing europium ions exhibit oxidation state Eu^{2+}, and their radiative transitions induce photoluminescence with the maxima at $\lambda \approx 515$ and 520 nm. Changes in the oxidation state are associated with the influence of H$_3$BO$_3$ and Y$_2$O$_3$ on the europium ions diffusion from Eu$_2$O$_3$ into HAP. The significant photoluminescence width of $\Delta\lambda \approx 95$ nm is caused by that, probably, the B^{3+} and Y^{3+} ions diffusing into HAP also occupy vacant positions CaI and CaII. Since they are smaller in mass and size, they diffuse into HAP faster and occupy a significant portion of the CaI and CaII vacant positions. As a result, a lower number of the CaI and CaII vacant positions remains to be occupied by diffusing ions Eu^{2+} which, therefore, get randomly distributed throughout the HAP bulk; this results in broadening of the photoluminescence spectrum. The presence of narrow peaks at 573 and 612 nm against the broad photoluminescence band (indicated by arrows in Fig. 1) evidences that some of the diffusing europium ions do occupy CaII positions and has oxidation state Eu^{3+}. Fig. 2, *a* illustrates the decay kinetics for different regions of the broad HAP:Eu,Y photoluminescence band: curve *1* ($\lambda \approx 520$ nm) corresponds to the maximum of the broad photoluminescence band, curve *2* ($\lambda \approx 573$ nm) corresponds to the maximum of the photoluminescence peak of Eu^{3+} in HAP:Eu,Y (Eu^{3+} in the CaII position), curves *3*, *4* ($\lambda \approx 574$, 575 nm) correspond to the vicinity of the $\lambda \approx 573$ nm peak's maximum. One can see that the attenuation curves have rather complex shapes. This shows that the broad photoluminescence band is contributed by different-lifetime electronic transitions. Curve *1* decays rapidly and is, probably, associated with short-lifetime transitions of the Eu^{2+} ions (decay constant $\alpha \approx 1.6 \cdot 10^{-1}\,\mu s^{-1}$). Curve *2* decreases significantly slower and characterizes the decay of Eu^{3+}-ion radiative transitions having a longer lifetime (decay constant $\alpha \approx 1.4 \cdot 10^{-2}\,\mu s^{-1}$). Curves *3, 4* have more complex shapes: they consist of rapidly and slowly decreasing sections associated with contributions of the Eu^{2+} and Eu^{3+} ions; with distance from the maximum, the Eu^{3+} ions' contribution rapidly decreases. Fig. 2, *b* demonstrates an HAP:Eu,Y tablet on a black substrate in a dark room illuminated by weak short-wave radiation ($\lambda = 405$ nm). One can see that the sample is almost white with a slight green tint. In the absence of illumination (in the dark), the tablets are invisible.

Thus, hydroxyl-apatite $Ca_5OH(PO_4)_3:Eu$ doped with europium ions has been obtained. The influence of codopants Dy^{3+}, B^{3+} and Y^{3+} on the $Ca_5OH(PO_4)_3:Eu$ photoluminescence has been studied. The study has revealed that codoping hydroxyapatite $Ca_5OH(PO_4)_3:Eu$ with the B^{3+} and Y^{3+} ions gives rise to an intense broad photoluminescence band for $Ca_5OH(PO_4)_3:Eu,B$ and $Ca_5OH(PO_4)_3:Eu,Y$ with the maxima at 515 and 520 nm, respectively. When $Ca_5OH(PO_4)_3:Eu$ is codoped with the Dy^{3+} ions, such a phenomenon is not observed; the $Ca_5OH(PO_4)_3:Eu,Dy$ spectrum consists of narrow spectral peaks corresponding to radiative transitions of the Eu^{3+} and Dy^{3+} ions in the $Ca_5OH(PO_4)_3$ matrix. The doped biocompatible hydroxyapatites $Ca_5OH(PO_4)_3:Eu,B$ and $Ca_5OH(PO_4)_3:Eu,Y$ characterized by high photoluminescence yield may be used in medicine as visualizers and markers.

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Conflict of interests

The author declares that he has no conflict of interests.

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